Stellingen behorende bij het proefschrift

Dynamic Compaction of Ceramics

Paul Boogerd

1. De bewering, dat hechting tussen korrels bij dynamisch verdichten verklaard wordt door smelten aan het oppervlak van de korrels\(^1\), is alleen verdedigbaar indien onder de term "smelten" tenminste ook plastische vervorming met verbreking van chemische bindingen verstaan wordt.

2. De afwezigheid van thermisch evenwicht in een schokgolffront\(^1\) maakt de interpretatie van pyrometrische schoktemperatuur-bepalingen\(^2\) zeer riskant.

3. Voor berekeningen aan het breken van chemische bindingen door een schokgolf, zal de energie van de schokgolf berekend moeten worden uit de schoksnelheid en niet uit de deeltjes- of massaverplaatsingssnelheid, waaruit in de evenwichtstoestand de interne energietoename door een schokgolf wordt berekend.

4. Het effect van het anisotrope karakter van een schokgolf in combinatie met ordening op korte afstand is al merkbaar bij schokgolf-geinduceerde reacties van aromaten. Het is daarom te verwachten dat het anisotrope karakter van een schokgolf in een kristallijne vaste stof belangrijke gevolgen zal hebben voor schok-geinduceerde excitatie in vaste stoffen.

5. Het effect, dat de elektronen met een groter impulsmoment zich terugtrekken binnen de elektronenwolk, die gevormd wordt door de elektronen met een kleiner impulsmoment\(^1\), is sterker in een vaste stof dan in een twee-atomig gasmolecuul, omdat de elektronenwolken in het laatste geval veel sterker asymmetrisch kunnen vervormen. Dit verschil wordt sterker met toenemend aantal schillen, hetgeen verklaart waarom de berekeningen voor vast Be, met behulp van infrarood-spectroscopische gegevens van gasvormig Be\(_2\), succesvoller zijn dan analoge berekeningen voor Mg, Ca en Sr\(^2\).
   2. Dit proefschrift.
6. De vervanging van een ruimtelijk lichaam door een massapunt, een door Newton geïntroduceerd principe, maakt het onmogelijk evenwichtseigenschappen toe te kennen aan het verschil in positie van de massakrachten en de aan de buitenzijde van het lichaam aangrijpende reactiekrachten. Op het massapunt gebaseerde analyses van wetenschappelijke gegevens, waarbij geen rekening gehouden wordt met de achterliggende verwaarlozingen, kunnen aanleiding geven tot foutieve interpretaties.


7. Tijd is een gevolg van afstand tussen substantie.

8. Het woord "Wetenschap" moet met voorzichtigheid worden betracht, want zodra men iets weet is onderzoek niet meer nodig.

9. De mededeling van de Nederlandse Spoorwegen; "Vertraging ± 5 min." wekt ten onrechte de hoop, dat de trein in kwestie 5 minuten te vroeg zou kunnen komen.

10. Schaken is een spel, dat beperkt is tot de bewoners van deze wereld, maar Go heeft iets buitenaards. Als er op enige planeet denkende wezens zijn, dan kennen zij Go.

   Emmanuel Lasker, Wereldkampioen Schaken (tot 1921).

11. Er wordt regelmatig opgemerkt dat nieuwe fundamentele theoretische denkbeelden voornamelijk ontwikkeld worden in kleine stoffige kamertjes. Alhoewel hier veel voor te zeggen valt, moet men niet uit het oog verliezen, dat het uitmaakt wie in deze stoffige kamertjes aanwezig is.

12. Een van de aspecten, die de mens onderscheiden van de dieren, is dat de mens steeds vertelt, dat hij zich onderscheidt van de dieren.
Theses belonging to the dissertation

Dynamic Compaction of Ceramics

Paul Boogerd

1. The claim, that interparticle 'fusion' during dynamic compaction can be explained by melting, which occurs at the surface of the particles, is defendable only if "melting" also includes plastic deformation with chemical bond cleavage.

2. The absence of thermal equilibrium in a shock wave front renders the interpretation of pyrometrical shock wave temperature measurements very ambiguous.

3. For calculations on the cleavage of chemical bonds by a shock wave, the energy of a shock wave should be calculated from the shock wave velocity, and not from the particle or mass displacement velocity, which is used to calculate the internal energy increase due to a shock wave in equilibrium.

4. The effect of the anisotropic nature of a shock wave in combination with short range ordering can already be observed during shock-induced reactions of aromatics. It is, therefore, likely that the anisotropic nature of a shock wave in a crystalline solid will have important consequences for shock-induced excitation in solids.

5. The effect, that electrons of higher angular momentum are withdrawn into the electron cloud established by the low-angular-momentum electrons, is stronger in a solid than in a diatomic gas-molecule, because in the latter the electron clouds can deform much more asymmetrically. This difference increases with the number of orbitals, which explains why the calculations for solid Be, using infrared spectroscopic data of gaseous Be₂, are more successful than analogous calculations for Mg, Ca, and Sr.
   2. This dissertation.
6. The replacement of a body with physical dimensions by a center of mass, a principle introduced by Newton, renders the assignment of equilibrium properties to the difference in position of mass-forces, and the reaction-forces, which act upon the exterior of the body, impossible. Analyses of scientific data, based upon the center of mass, in which the implicit simplifications are not accounted for, can lead to erroneous interpretations.


7. Time is a consequence of distance between substances.

8. The Dutch word "Wetenschap" (i.e., The art of knowing, or science) should be handled with care, because once one knows something research is superfluous.

9. The announcement by the Dutch Railways; "Vertraging ± 5 min." (i.e., Delay ± 5 min.) wrongly creates hope for a 5-minutes-early arrival of the respective train.

10. Chess is a game, which is limited to the inhabitants of this world, but Go has something extraterrestrial. If, on any planet, there are intelligent lifeforms, they know Go.

   Emmanuel Lasker, World Champion Chess (until 1921).

11. It is frequently remarked that new fundamental theoretical views are predominantly developed in small dusty rooms. Although much can be said in favour, it should be borne in mind, that it matters who is present in these dusty rooms.

12. One of the aspects, which differentiate man from the animals, is that man keeps on telling, that he differs from the animals.
Dynamic Compaction of Ceramics
Dynamic Compaction of Ceramics

PROEFSCHRIFT

ter verkrijging van de graad van doctor
aan de Technische Universiteit Delft
op gezag van de Rector Magnificus Prof. ir. K.F. Wakker,
in het openbaar te verdedigen ten overstaan van een commissie,
door het College van Dekanen aangewezen,

op maandag 15 mei 1995 te 13.30 uur

door

Paul BOOGERD

scheikundig ingenieur
geboren te Rotterdam.
Dit proefschrift is goedgekeurd door de promotor
Prof. dr. J. Schoonman

Samenstelling promotiecommissie:

(plv.) Rector Magnificus
Prof. dr. J. Schoonman
Prof. dr. ir. R. Prümmer
Prof. dr. ir. H. Verwey
Prof. dr. R. Metselaar
Prof. dr. J.H.W. de Wit
Prof. dr. ir. E. van der Giessen
Dr. A.C. van der Steen

faculteit STM
Ernst Mach Inst., Freiburg, Dld
TU-Twente
TU-Eindhoven
faculteit STM
faculteit WbMT
TNO-PML

Dit onderzoek is uitgevoerd op het TNO Prins Maurits Laboratorium in het kader van het Innovatief Onderzoek Programma Technische Keramiek (IOP-TK) van het Ministerie van Economische Zaken (IOP-TK 89 A 027).
Aan J.C. Boogerd en

C.M. Boogerd-van Gastel.
Contents

1. Introduction 1
2. Introduction to shock waves 13
3. Experimental techniques 19
4. General shock wave equation of state for solids 29
5. Shock wave equation of state for metals 59
6. Shock wave equation of state for ceramics and boron 89
7. Shock wave mechanics in porous ceramic assemblies 123
8. Shock wave absorption in AlN powder in a cylindrical configuration 149
9. Shock wave absorption in ZrO_2 and Si_3N_4 powders in a cylindrical configuration 187

Summary 219
Samenvatting 223
Nawoord 227
Curriculum Vitae 229
List of Publications 231
CHAPTER 1

Introduction

1.1 COMPACTION OF CERAMICS: FROM POWDER TO PRODUCT

The starting materials for most ceramic products are powders, and hence many methods have been developed to compact these powders to solid products. These methods, from the earliest forms of sintering to the most advanced forms, like hot isostatic pressing (HIP) belong to two basic categories of densification: pressure induced, and temperature induced.

In this thesis a relatively new approach will be discussed, i.e. the dynamic compaction method which is a shock stress induced method. The differences between the compaction mechanisms of dynamic compaction and the conventional methods make it an attractive alternative with particular advantages, as will be discussed in paragraph 1.2 of this chapter.

The main disadvantage of dynamic compaction is the contemporary nature of the process. It is a rather new compaction process as compared to the conventional sintering and pressing techniques. The theoretical background and experimental experience are still in an early stage of development. For this reason the research described in this thesis was aimed on further development of our understanding of the effect of a shock wave on solids and powders, as described in Chapters 4 to 6, and 7, respectively. In addition, the development of an experimental technique, which could with as few experiments as possible determine the optimal conditions for dynamic compaction is described in Chapters 8 and 9. The theoretical knowledge developed in Chapters 4 to 6, and 7 is applied to the development of this experimental technique. Furthermore, this technique provides in situ information of the conditions, which occur during dynamic compaction, like the height of the shock wave velocity in the sample during compaction. This approach enables us to relate the dynamic compaction parameters to the quality of the compact.

An important feature of this experimental technique is that it enables us to treat the two different aspects of dynamic compaction; i.e. the configuration, or setup and the powder properties independently. The powder properties determined with this technique (e.g. shock wave absorption, and the resulting densification) are independent of the experimental setup used, and the results found for the cylindrical configuration should in principle
apply to any configuration. The powder properties thus found are meant to be used in calculations on dynamic compaction of more complex shapes.

1.2 DYNAMIC COMPACTION COMPARED WITH STATIC COMPACTION: THE PRINCIPLES

To illustrate the technological merit of the dynamic compaction process for the production of ceramic components, the two other densification methods will be discussed briefly and then compared with the dynamic approach.

Methods based upon mechanical pressure use an external force to deform the powder particles, while in methods based upon thermal treatment the particles sinter together. A combination of mechanical pressure and thermal treatment is hot isostatic pressing (HIP).

Because of the unusual properties of ceramics, two types of problems arise during these densification, or compaction methods. The first type of problems is related to the high compressive strength which makes most ceramics difficult to press, while due to their extremely high melting points (e.g. ZrO₂ melts at 2677°C) they are also difficult to sinter, because the sinter temperature is usually two-thirds of the melting temperature.

The problem of high compressive strength can only be overcome by increasing the pressure span of the compaction apparatus. The high sintering temperature is often decreased with additives. These additives, however, may decrease the performance of the product at high temperatures.

The second type of problems is related to material properties. The prolonged thermal excursions during sintering can deteriorate mechanical properties, e.g. for some amorphous materials sintering may cause crystallisation, while in composites chemical reactions between the constituents may form a grainboundary layer with poor properties. Similar problems may arise, when sinter additives are used. In addition, the thermal excursions during sintering can also change physical properties. The increase in the crystal size, especially in the small size range, for example, decreases the amount of fluxpinning in superconductors, which lowers their maximum current density. Contrary, dynamic compaction often decreases the crystal size, and increases the amount of defects, which increases the amount of fluxpinning.

Variations in chemical compositions and stoichiometry may result also during sintering. Hydroxy apatite, Ca₅(PO₄)₃OH, which is an important bioceramic material decomposes at sintering temperatures to form compounds
which are rapidly soluble in vivo. The high temperature superconductors like YBa$_2$Cu$_3$O$_{7-x}$, may loose oxygen upon sintering, and this deviation from stoichiometry dramatically reduces the superconducting properties.

The advantages of dynamic compaction compared to processes based on static pressure or high temperatures are a consequence of the differences in the underlying mechanisms. Although comparison is possible it must be remembered that the densification and interparticle bonding mechanisms are extremely complex and difficult to understand.$^1$ However, despite the complexity of the process several aspects of the process are well understood to date. For example, one of the merits of dynamic compaction is that long temperature excursions do not occur.

In the dynamic compaction process the solid material in a porous assembly is set into motion by a shock wave, causing rearrangement, plastic deformation, and fracture of the particles, and this results in densification. Due to shock wave, effects such as the passage of the shock wave through the solid phase, friction between the particles upon collision, fracture, and plastic deformation of the particles, the temperature of the material in the porous assembly is increased. However, because of the localized nature of these effects only relatively small hot spots occur, where the temperature rises above 1000°C (this temperature is an estimate based on traces of melting found in copper after dynamic compaction).$^2$ The temperature rises and drops occur within microseconds,$^3$ because of the short duration of the shock pulse and the thermal conduction to the particle centers. Due to the short duration of the high temperature period and the fact that only a small part of the particles is heated, few temperature activated processes, such as recrystallization or chemical reactions, like decomposition, occur.

Despite the absence of high temperatures it is possible by dynamic compaction to compact ceramics without additives to densities of 99% of the theoretical maximum density (TMD), or even higher. The absence of additives usually improves the performance in high temperature applications, and provides the possibility of obtaining chemically pure ceramic parts.

The difference between dynamic compaction and static compression lies in the distribution and nature of the stresses that cause compaction. In static compression external stresses are applied to a porous assembly. Due to these stresses the particles move to a denser assembly. After this initial compaction the density is further increased by fracture and deformation of the particles at contact areas.

In dynamic compaction stresses are also applied externally, but these
travel into the assembly as an anisotropic shock wave with very large stress gradients. Like in static compaction, the particles are first rearranged, after which they deform and fracture due to anisotropic shock stresses. These anisotropic stresses, however, do not only result in deformation near the contact areas, but also force other particles, which are not in direct contact, towards each other. The amount of deformation and fracture, and the stresses at which they occur, vary strongly depending on the choice of ceramic.

Furthermore, due to the anisotropic nature of a shock wave, and the large stress gradients in the shock wave, the amount of plastic deformation during dynamic compaction is very large, compared to static pressing. In Figs. 1.1 and 1.2 SEM micrographs are shown of AlN before, and after dynamic compaction. In Fig. 1.2 it can be seen that in several areas the grain boundaries are no longer visible due to the strong plastic deformation.

![SEM micrograph of AlN powder.](image)

**Figure 1.1**: SEM micrograph of AlN powder.
1.3 SHORT HISTORY AND STATE OF THE ART
OF DYNAMIC COMPACTION

A. Origin

The first publications on dynamic compaction stem from 1958. In this year La Rocca and Pearson deposited a patent, which described the compaction of a powder with the use of explosives, and Rice, McQueen, and Walsh published a review article on the effect of shocks on materials.

B. Techniques

The different configurations used for dynamic compaction can be distinguished by source and method of application of the shock wave. Two common sources for shock waves are:
(a) Impact of a projectile.
(b) Detonation of an explosive.
Projectiles can be accelerated in a gun either by compressed gas, gun powder, or even by electromagnetic means. Nowadays there are even commercially available high-velocity forges, which use a piston as an impactor. These forges can easily be incorporated in a semi-continuous production process.

In the indirect explosive compaction process the projectile is an explosively accelerated flyer plate. In this case the shock wave is caused by the impact of the flyer plate on the target. In direct explosive compaction processes the shock wave of the detonation in a explosive is applied to a porous assembly.

The main difference between these two processes is the shape of the shock wave (block pulse, or complex shape) which in the indirect processes is determined by the flyer plate (or impactor), and in the direct processes by the detonation properties of the explosive. For instance, in the direct contact processes aluminized explosives are used in order to obtain a gradual decrease of the shock stress after the initial shock wave, thus diminishing the sudden release of the shock stress after passage of the shock wave.

There are two generally applied direct explosive compaction methods: flat and cylindrical. An excellent review of the flat configurations has been reported by Thadhani. In the present thesis only the cylindrical direct explosive compaction method has been explored (Chapter 3, Experimental techniques). This method was chosen for several reasons; the configuration is simple to build, uses few materials, and is more accessible for mathematical analysis than the flat configuration, because the shock wave reflections which occur on the sides of the sample in the flat configuration are absent.

The optimal conditions for cylindrical compaction are found between under- and over-compaction. Under-compaction occurs if the shock pulse from the explosive is too weak to densify the sample to TMD, while the center of the sample remains porous. This occurs when the shock wave is absorbed too strongly in the outer region of the sample. However, when the shock wave is absorbed too weakly the shock stresses at the center of the sample become very high due to the steep decrease in the area through which the shock wave travels, which is proportional to the square of the radius. This effect results in over-compaction. Over-compaction is manifested as cracks in the sample, due to the high stresses in the center, or even as a cylindrical hole along the axis of the sample.

The conditions for optimal homogenous compaction, found between over- and under-compaction for a given explosive and starting powder do not necessarily yield a 100% dense compact. When the shock stress from the explosive is too weak, the optimal conditions could yield e.g. an 80% dense
homogenous compact. The density can be increased using an explosive with a higher shock stress (detonation velocity). Due to the delicate balance between absorption and decrease in area, it is often better to aim at a 99% density.⁸

To determine the optimal conditions for dynamic compaction in the cylindrical configuration, Prümmer introduced the \( E/M \) method,⁹ which is still the most generally used method not based on computer simulations. Computer simulations can only be applied if the material properties are well-known and, therefore, have little predictive value when it comes to new materials.

The \( E/M \) method is an experimental approach (\( E \) is the mass of the explosive and \( M \) the mass of the sample to be densified). It is basically a step-wise adjustment of two parameters, the detonation velocity of the explosive, and the amount of explosive to obtain a sample, which is as dense as possible. The two parameters \( E \) and \( M \) determine the height and duration of the dynamic stress pulse, or shock wave.

A disadvantage of the \( E/M \) method is that its results only apply to one powder size distribution, and one sample size. In general, several steps are necessary in order to obtain the optimal conditions for compaction, and these optimal conditions do not apply when e.g. the powder size distribution, or the solid properties are changed.

In Chapter 8 an experimental technique is introduced that is aimed to find one parameter that can be obtained in one experiment, and which fully characterizes the shock wave behavior of a porous material. If this single parameter is known, the optimal conditions for compaction can be calculated without further experiments. For this purpose a shock wave absorption parameter is introduced, which describes the relative absorption of shock wave energy per unit length. With this absorption parameter it is possible to calculate the parameters which would yield a compact as homogenous as possible. The method is also developed to model up- and downscaling of the process. The absorption parameter is independent of the shape of the configuration, in order to make it possible to predict shock wave 'dead' areas, when more complex shapes than the cylinder are to be compacted.
C. Commercial evaluation of dynamic compaction

1. Technology and possibilities

An excellent commercial evaluation of the dynamic compaction technique is given by Frankhouser. Frankhouser estimates the product price for dynamically compacted TiB₂ tiles at $180 per kilogram. He finds the new technology to be cost effective when compared with commercial prices for hot-pressed TiB₂ tiles of $222 to $889 per kilogram.

Several remarks should be made regarding the calculated product price as an estimate for the price of products made with dynamic compaction process as described in this work.

Firstly, the process described by Frankhouser involves preheating of the ceramic powder prior to the compaction process, which complicates the technology considerably, and increases the processing costs by about 27%.

Secondly, the process described by Frankhouser uses a mass ratio of nine to one of explosive to ceramic powder. In the experiments described in this work this ratio is about five to one. This would result in a 13% decrease in material costs, or an additional 9% reduction of the total costs.

Above-mentioned differences could easily amount up to a cost reduction of 10% or more. Therefore, when differences between prices for labour, land, and equipment in the U.S.A. and Europe are neglected the process described in this work should be even more cost effective than the process studied by Frankhouser.

It should be noted that about 47% of the total costs represent the costs for the starting TiB₂ powder. Frankhouser mentions a added value of 1.3 for the final product. Efforts aimed on decreasing raw material costs are thus as effective as improving the process, which generally indicates that a process is commercially attractive.

2. Safety considerations

Explosives have been employed commercially for a long time in mining, road construction, offshore techniques, and in seismic research. Usually, however, explosives are associated with destructive applications. It should be borne in mind that the impressive destructive power of explosives is not the only measure for potential hazards. Even more important is the sensitivity of the explosives to fire, electricity, impact, and such. Research of the safety of the storage of explosives has resulted in explosives which obey
extreme safety restrictions. This is especially true for blasting agents as used in mining and dynamic compaction. Thus, although safety precautions must be obeyed, the process of dynamic compaction offers no more hazards than other industrial practice.

1.4 ALTERNATIVE APPLICATIONS OF SHOCK WAVES ON CERAMICS

Besides in dynamic compaction, shock waves have also been applied to ceramics for pre-treatments. The most important examples of the use of shock waves are to modify ceramics, e.g. powder conditioning, and shock activated sintering\textsuperscript{11}. In catalysis the effect of shock waves on the defect structure of ceramics has been explored.\textsuperscript{12} The commercial production of c-BN and hexagonal diamond is based on shock-induced phase transitions.

A process that has much in common with the dynamic compaction process is referred to as reactive dynamic compaction. In this process an exothermic reaction is induced in a solid mixture that results in a hot porous ceramic (or mixture in the case of a composite). This hot porous ceramic is densified subsequently with a shock wave as in conventional dynamic compaction.

1.5 SCOPE OF THE THESIS

The aim of this thesis is twofold. The first aim is the improvement of the commercial applicability of dynamic compaction by reducing the number of experiments necessary to obtain an adequate compact. The second aim is to improve the theoretical knowledge of the effect of shock waves on solid and porous ceramics.

Because the field of shock wave physics is an unknown area for most ceramists Chapter 2 aims to introduce this field to the readers.

Chapter 3 discusses the experimental techniques of dynamic compaction as used in this work, and the employed explosives.

The theoretical aspects of shock waves in solids are discussed in Chapters 4, 5 and 6, in which a shock wave equation of state is derived that can be determined without any shock wave data, and, subsequently, is applied to metals and ceramics (Chapters 5 and 6, respectively). The effects
of a shock wave on a porous assembly are discussed in Chapter 7, in which shock wave equation of state is derived based on a spherical powder model.

An experimental technique was developed to rapidly determine optimal conditions for dynamic compaction. This technique is discussed in Chapters 8 and 9, in which the technique is used on AlN (Chapter 8), Si$_3$N$_4$, and ZrO$_2$ (Chapter 9). Several models theoretical underlying this technique were developed. These models also meant to further our the theoretical knowledge of the effects of a shock wave on solid and porous assemblies.

Chapter 8 introduces a model for the absorption of shock wave energy in a porous assembly. This absorption of shock wave energy underlies the densification effect of a shock wave on a porous assembly. This model is developed as part of an experimental technique that is meant to find the optimal conditions for dynamic compaction with the least possible number of experiments. In this chapter the effect of the average particle size of AlN powders on shock wave absorption is discussed. The models derived in Chapters 4 and 7 are practically applied in this technique.

In the final Chapter 9 the effect is discussed of the average particle size and the solid state material properties on the shock wave absorption in Si$_3$N$_4$ and ZrO$_2$. 

10
1.6 REFERENCES


12. Reference 6, p. 120.
CHAPTER 2

Introduction to shock waves

2.1 GENERAL PRINCIPLES

In order to describe shock wave phenomena a number of key properties of the shock wave will be used. These properties will be introduced by describing a planar shock wave.

A shock wave travels with a shock wave velocity, $U$. Due to the unidirectional compressive nature of the shock wave, atoms in a material through which the shock wave travels, start moving in the shock wave direction directly after passage of the shock front. The velocity of the atoms, and hence the material, which is moving directly after passage of the shock front, is called displacement velocity, $u$. This effect is shown schematically in Fig. 2.1.

![Diagram of shock wave propagation](image)

**Figure 2.1:** A shock wave propagating in a linear chain, caused by impact with an impactor. The principles of the mass displacement velocity, $u$, and the shock wave velocity, $U$. 

13
The mass displacement velocity is always lower than the shock velocity, otherwise material would have to pass other material before the shock wave arrives. In the literature of shock physics the displacement velocity, \( u \), is often referred to as the particle velocity. This is confusing, and the term mass displacement velocity will be used instead for reasons which will become clear later.

The shock wave and displacement velocity are both related to the shock stress, \( \sigma \). The shock stress is the stress in the material directly after the shock front. Under equilibrium-shock-wave conditions this stress is related to the specific volume \( V \). Material conditions before arrival of the shock wave are indicated with a subscript \( 0 \) (\( \sigma_0, V_0 \)).

When a shock wave arrives at the interface of a material and a vacuum the surface of the material starts to move with the so-called free-surface velocity, \( u_f \). This free-surface velocity is normally twice the displacement velocity, \( u \), with a maximum equal to the shock wave velocity, \( U \). This can easily be understood. Imagine that the shock wave is travelling through an ideal single crystal in the direction of one of the crystallographic axes, the transmission of shock wave impulse from atom to atom occurs in the shock wave direction. The atoms at the surface do not have a neighboring atom to transfer the shock impulse to. As they can not transfer the impulse, the impulse is used for the motion of the surface layer at twice the displacement velocity. The layer next to the surface layer looses its neighbor, when that neighbor starts moving at twice the displacement velocity. This means that the layer next to the surface layer has a impulse that can not be transferred, hence it also starts moving at twice the displacement velocity. This process continues into the material, resulting in a free surface velocity that is twice the displacement velocity.

2.2 THERMODYNAMICS IN SHOCK WAVES

A. The conservation laws in shock wave physics

The balance equations in shock wave physics are determined over the shock wave front with a coordinate system that moves with the shock wave velocity. The parameters of the shock wave state are shown schematically in Fig. 2.2.
<table>
<thead>
<tr>
<th>After shock front</th>
<th>Before shock front</th>
</tr>
</thead>
<tbody>
<tr>
<td>Stress (GPa)</td>
<td>$\sigma$</td>
</tr>
<tr>
<td>Density (kg/m³)</td>
<td>$\rho$</td>
</tr>
<tr>
<td>Mass displacement velocity (km/s)</td>
<td>$u$</td>
</tr>
<tr>
<td>Shock wave velocity (km/s)</td>
<td>$U$</td>
</tr>
<tr>
<td>Internal energy (J/kg)</td>
<td>$E$</td>
</tr>
</tbody>
</table>

**Planar shock wave front**

**Figure 2.2:** Schematic representation of the shock wave state and relevant parameters.

The mass entering the shock wave front per unit surface, per unit time is the product of the density of the material before arrival of the shock wave $\rho_0$ and the shock wave velocity, $U$, i.e. $\rho_0 U$. The compressed mass per unit surface, per unit time leaving the shock wave front is the product of the density of the material after compression $\rho$ and the velocity at which the material leaves the shock front, which is the shock wave velocity, $U$, minus the velocity of the mass, $u$, i.e. $\rho(U-u)$. The mass preservation law over the shock wave front dictates that these masses per unit surface, per unit time are equal, hence:

$$\rho_0 \ U = \rho \ (U-u) \tag{2.1}$$

The amount of material per unit surface, which is accelerated to the mass displacement velocity, $u$, in a period $\Delta t$ is the product of the mass entering the shock wave front per unit surface, per unit time $\rho_0 U$, and the duration of the period, $\Delta t$, i.e. $\rho_0 U\Delta t$. If the mass is accelerated from standstill ($u_0=0$), the change in momentum is $(\rho_0 U\Delta t)u$. The force per unit surface is the shock
stress \( \sigma \). The conservation of momentum dictates that the product of the force per unit surface, \( \sigma \), and the time, \( \Delta t \), i.e. \( \sigma \Delta t \) equals the change in momentum, hence:

\[
\sigma \Delta t = (\rho_0 \ U \ \Delta t) \ u
\]

(2.2)

This equation is used generally in the following form:

\[
\sigma - \sigma_0 = \rho_0 U u
\]

(2.3)

In shock wave physics \( \sigma_0 \) is often considered to be negligible.

When viscosity effects and heat conduction effects are neglected, the total energy acquired by a unit mass of a substance as a result of shock compression amounts to \( \sigma (V_0 - V) \), with \( V_0 \) and \( V \) being the specific volume of the substance before and after shock compression, respectively. This total energy per unit mass is divided equally between the change in kinetic energy, \( u^2/2 \) and the internal energy change, \( E - E_0 \). Hence, it is found that:

\[
E - E_0 = \frac{1}{2} \sigma (V_0 - V)
\]

(2.4)

To solve this set of equations a fourth equation is needed. In shock wave physics the most generally accepted equation is the so-called Hugoniot.

**B. The Hugoniot**

The Hugoniot can be written in many forms, but here the Hugoniot is considered as an empirical relation between the shock wave and displacement velocity, i.e.:

\[
U = C_0 + S \ u + Q \ u^2
\]

(2.5)

in which \( C_0 \), \( S \), and \( Q \) are material constants. Usually a linear Hugoniot is used:

\[
U = C_0 + S \ u
\]

(2.6)

In this Hugoniot \( C_0 \) is the bulk sound velocity at standard conditions (\( P=1 \) bar, \( T=300 \) K), that can be estimated from.
\[ C_0 = \sqrt{\frac{K}{\rho_0}} \] (2.7)

with \( K \) being the bulk modulus and \( \rho_0 \) the density of the material at standard conditions. The slope, \( S \), is a material constant. Typical values of \( S \) are 1 to 1.5 for metals.\(^3\)

As mentioned earlier the necessity for a series of experiments arises from the empirical nature of the Hugoniot. This is a major disadvantage, especially in the field of ceramics with its many new and untested materials.

To solve this problem theoretical equations of state were derived for solid and porous ceramics. The derivation of these equations is shown in Chapters 6 and 7, respectively.

2.3 REFERENCES


CHAPTER 3

Experimental Techniques

3.1 THE CYLINDRICAL CONFIGURATION FOR DYNAMIC COMPACTION

In the present experiments a cylindrical configuration has been used as shown in Fig. 3.1(a). In this configuration the ceramic powder is placed in an aluminum tube. The top of the tube is closed with an aluminum plug, and the bottom of the tube is closed with one or more plugs of different materials, but usually aluminum and steel.

The explosive is placed around the powder container, and held by a PVC envelope. The envelope is closed at the bottom with a PVC plug. This plug fits around the powder container and centers it. The top of the envelope is closed with a PVC cap. The detonation of the explosive is initiated with a detonator, which is placed at the center of the top cap. The detonation then travels downward to and alongside the powder container, as shown in Fig. 3.1(b).

![Diagram of cylindrical configuration](image)

**Figure 3.1:** (a) Schematic representation of the cylindrical configuration. (b) Compaction process in the cylindrical configuration.
The explosives which were used are discussed in paragraph 3.2 of this chapter.

Two standard configurations were used, and they will be referred to as 'small' and 'large'. For both configurations the height was the same, but the diameter of the powder containers and the explosive envelopes varied.

The height of the containers was 120 mm, and the height of the envelopes 175 mm for both configurations. In both cases all top and bottom plugs in the metal containers had a thickness of 10 mm, and the bottom plugs of the envelopes were 5 mm thick. The top caps of the envelopes were 10 mm thick. The diameters of the different containers and envelopes are shown in Table 3.1.

**Table 3.1:** The sizes of the containers and envelopes in the small and large cylindrical configurations.

<table>
<thead>
<tr>
<th></th>
<th>Configuration</th>
<th>Small</th>
<th>Large</th>
</tr>
</thead>
<tbody>
<tr>
<td>Container:</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>inner diameter (mm)</td>
<td>16</td>
<td>30</td>
</tr>
<tr>
<td></td>
<td>outer diameter (mm)</td>
<td>20</td>
<td>35</td>
</tr>
<tr>
<td>Envelope:</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>inner diameter (mm)</td>
<td>42</td>
<td>74</td>
</tr>
<tr>
<td></td>
<td>outer diameter (mm)</td>
<td>48</td>
<td>82</td>
</tr>
</tbody>
</table>
3.2 EXPLOSIVES

A. General principles

In non-ideal explosives, such as the blasting agents used in this work, the detonation velocity depends on the diameter of the charge. This effect can be divided into three regions.

In the first region, in which the diameter is smaller than a certain minimum diameter, i.e. the critical diameter for detonation, no detonation occurs.

In the second region in which the diameter of the charge is increased, detonation occurs with a detonation velocity dependent on the diameter. The detonation velocity in this region increases up to a maximum, which is attained at the critical diameter for stable detonation. The detonation velocity throughout a charge can be constant independent of whether the maximum detonation velocity has been attained.

In the third region above the critical diameter for stable detonation, the detonation velocity is constant and independent of the diameter.

In the second region, when the detonation velocity is dependent on the diameter, the detonation velocity is also sensitive to other parameters, such as density. Because the diameters in the experimental setup varied, the detonation velocity was measured, in situ, during several compaction experiments. It is important that the detonation velocity is constant along the entire sample to ensure homogenous densification.

B. Experimental aspects

1. Setup

The detonation velocity measurements are performed in the same configuration as is used for standard densification in a cylindrical setup. The only difference is the presence of 9 ionisation pins, which are inserted through the exterior PVC envelope (Fig. 3.2).

Three sets of ionisation pins are distributed along the envelope in a spiral configuration with a distance of 1 cm between consecutive pins as viewed from the top. In the three sets which are vertically aligned the distance between the pins is 3 cm. The pins are inserted horizontally through a hole in the outer envelope with the head of the pins 5 mm from the inner envelope wall in order to prevent interference from shock reflections on the envelope.
Figure 3.2: Setup used for detonation velocity measurements: (a) side view, and (b) top view.

An ionisation pin consists of an open ended coaxial tube and core, which are isolated from each other by a polymer tube. The ionisation pins used in the present experiments have a diameter of 0.65 mm. The ionisation pins are short-circuited at the open end, when the front of the shock wave arrives. The short circuit is caused by the ionized gasses in the shock wave front.

The passage of the shock wave was recorded with a Krenz Electronics TRC 6070 transient recorder with a time resolution of 50 ns. The ionisation pins were connected to the transient recorder through a trigger unit (designed at TNO-PML), which was used to put a voltage difference of 100 V over the ionisation pins. The passage of the shock wave ionizes the air in the powder assembly and this causes a short circuiting. Subsequently, the trigger unit signal is measured with a transient recorder.

The commercial and self-made explosives, which were used are shown in Table 3.2. With the exception of Wetter-Energit-B (WEB) and Wetter-Permit-B (WPB), all explosives are based on ammonium nitrate and TNT. WEB and WPB are firedamp and coaldust safe explosives, and they consist of gelatinized and powdered ammonium nitrate explosives with alkali chlorides for the reduction
of the energy and temperature.¹

**Table 3.2: The explosives and their composition.**

<table>
<thead>
<tr>
<th>Explosive</th>
<th>Source</th>
<th>Composition⁴)</th>
</tr>
</thead>
<tbody>
<tr>
<td>AMPA1</td>
<td>laboratory</td>
<td>90% AN, 9.8% TNT, 0.2% Al</td>
</tr>
<tr>
<td>AMPA2.xᵇ)</td>
<td>laboratory</td>
<td>81.2% AN, 10% TNT, 8.8% Al</td>
</tr>
<tr>
<td>Alsilite</td>
<td>commercial</td>
<td>81% AN, 18.2% TNT, 0.8% Al</td>
</tr>
<tr>
<td>Triamiteᶜ)</td>
<td>commercial</td>
<td>80% AN, 19.8% TNT, 0.2% Al</td>
</tr>
<tr>
<td>Trimonite</td>
<td>commercial</td>
<td>81.2% AN, 9.8% TNT, 9% Al</td>
</tr>
<tr>
<td>Wetter-Energit-B (WEB)</td>
<td>commercial</td>
<td>Gelatinized ammonium nitrate explosive with alkali chlorides, complex composition</td>
</tr>
<tr>
<td>Wetter-Permit-B (WPB)</td>
<td>commercial</td>
<td>Gelatinized ammonium nitrate explosive with alkali chlorides, complex composition</td>
</tr>
</tbody>
</table>

ᵃ) AN indicates ammonium nitrate.
ᵇ) AMPA2.x, refers to the batches of AMPA2.1, AMPA2.2 etc., these batches have the same overall composition, but differ in grain size. The detonation velocity of different batches of AMPA2.x varied with each batch.
ᶜ) The detonation velocity of different batches of Triamite varied with each batch. The batches were numbered and are referred to as Triamite-1, and Triamite-2.

### 2. Results

The results of the detonation velocity measurements with an explosive thickness of 11 mm are shown in Table 3.3. In Fig. 3.3 an example is shown of the detonation velocity measurement data for AMPA1. The results of the detonation velocity measurements with an explosive thickness of 19 mm are shown in Table 3.4.
Table 3.3: Results of detonation velocity measurements for an explosive thickness of 11 mm.

<table>
<thead>
<tr>
<th>Explosive</th>
<th>Density explosive $\rho_0$ ($10^3$ kg/m$^3$)</th>
<th>Detonation velocity $D$ (km/s)</th>
<th>Correlation coefficient$^2$ $R_{val}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>AMPA1</td>
<td>1.000</td>
<td>2.72</td>
<td>0.9997</td>
</tr>
<tr>
<td>AMPA1</td>
<td>1.020</td>
<td>2.75</td>
<td>0.9995</td>
</tr>
<tr>
<td>AMPA2.1</td>
<td>1.040</td>
<td>2.88</td>
<td>0.9998</td>
</tr>
<tr>
<td>AMPA2.1</td>
<td>1.070</td>
<td>2.76</td>
<td>0.9997</td>
</tr>
<tr>
<td>Triamite1</td>
<td>0.930</td>
<td>3.54</td>
<td>0.9999</td>
</tr>
<tr>
<td>Triamite1</td>
<td>1.000</td>
<td>3.54</td>
<td>0.9999</td>
</tr>
<tr>
<td>Alsilite</td>
<td>1.008</td>
<td>3.65</td>
<td>0.9997</td>
</tr>
<tr>
<td>Alsilite</td>
<td>0.827</td>
<td>3.21</td>
<td>0.9997</td>
</tr>
<tr>
<td>Alsilite</td>
<td>1.070</td>
<td>3.83</td>
<td>0.9996</td>
</tr>
<tr>
<td>Trimonite</td>
<td>1.210</td>
<td>3.55</td>
<td>0.9997</td>
</tr>
<tr>
<td>Trimonite</td>
<td>1.190</td>
<td>3.64</td>
<td>0.9993</td>
</tr>
<tr>
<td>WEB</td>
<td>1.210</td>
<td>1.58</td>
<td>0.9949</td>
</tr>
<tr>
<td>WEB</td>
<td>1.210</td>
<td>1.60</td>
<td>0.9856</td>
</tr>
<tr>
<td>WPB</td>
<td>1.200</td>
<td>1.36</td>
<td>0.8320</td>
</tr>
<tr>
<td>WPB</td>
<td>1.030</td>
<td>...$^a$</td>
<td>...</td>
</tr>
</tbody>
</table>

$^a$) No stable detonation was registered
Figure 3.3: Results of detonation velocity measurement for AMPA1.

Table 3.4: Results of detonation velocity measurements for an explosive thickness of 19 mm.

<table>
<thead>
<tr>
<th>Explosive</th>
<th>Density explosive $\rho_0$ ($10^3$ kg/m$^3$)</th>
<th>Detonation velocity $D$ (km/s)</th>
<th>Correlation coefficient$^2$ $R_{\text{val}}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>AMPA2.1</td>
<td>1.060</td>
<td>3.56</td>
<td>0.9993</td>
</tr>
<tr>
<td>AMPA2.1</td>
<td>1.070</td>
<td>3.56</td>
<td>0.9994</td>
</tr>
<tr>
<td>Triamite2</td>
<td>1.100</td>
<td>3.05</td>
<td>0.9969</td>
</tr>
<tr>
<td>Triamite2</td>
<td>1.110</td>
<td>2.93</td>
<td>0.9984</td>
</tr>
<tr>
<td>WEB</td>
<td>1.170</td>
<td>1.88</td>
<td>0.9981</td>
</tr>
<tr>
<td>WEB</td>
<td>1.160</td>
<td>2.14</td>
<td>0.9488</td>
</tr>
<tr>
<td>WPB</td>
<td>1.200</td>
<td>2.20</td>
<td>0.9993</td>
</tr>
<tr>
<td>WPB</td>
<td>1.210</td>
<td>2.17</td>
<td>0.9988</td>
</tr>
</tbody>
</table>
The effect of the contents of the container are shown in Table 3.5 for an explosive thickness of 11 mm.

**Table 3.5:** Results of detonation velocity measurements for an explosive thickness of 11 mm with an empty container.

<table>
<thead>
<tr>
<th>Explosive</th>
<th>Density explosive $\rho_0$ (10^3 kg/m$^3$)</th>
<th>Detonation velocity $D$ (km/s)</th>
<th>Correlation coefficient$^2$ $R_{val}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>WEB</td>
<td>1.160</td>
<td>1.53</td>
<td>0.9952</td>
</tr>
<tr>
<td>WEB</td>
<td>1.170</td>
<td>1.74</td>
<td>0.9954</td>
</tr>
<tr>
<td>AMPA2.1</td>
<td>1.090</td>
<td>3.24</td>
<td>0.9997</td>
</tr>
</tbody>
</table>

3. Discussion

The values of the correlation coefficient for the detonation velocity measurements, which is a measure for the linear correspondence of the time and the distance travelled,$^2$ is a measure for the stability of the detonation. If the detonation velocity, $D$, is constant, the correlation of the data with a linear fit should be high. The example for AMPA1, shown in Fig. 3.3, illustrates the linearity of the results. The results in Table 3.3 show that the detonation velocity is very stable for the explosives with $D>2$ km/s. The results for WEB indicate that the detonation process in WEB is only marginally stable at this explosive layer thickness. In the second WPB experiment the detonation pressure was probably too low to trigger the ionisation pins. At this diameter WPB is definitely not stable.

Because Trimonite was no longer available, a choice had to be made between Triamite and Alsilite. Triamite was chosen because the detonation velocity of Alsilite showed a strong dependence on the density.

The effect of an increased explosive layer thickness becomes clear when Table 3.3 is compared with Table 3.4. For AMPA2.1, WEB, and WPB the detonation velocity increases with 20 to 60%. The detonation process in WPB appears to be stable for this layer thickness. The detonation in WEB, however,
seems to become less reproducible. The decrease in the detonation velocity of Triamite2 compared to Triamite1 is due to differences in the batches of these explosives. Although this is a disadvantage, it can be obviated by measuring the detonation velocity for each new batch, because the reproducibility per batch appears to be satisfactory.

If the container is left empty, the detonation velocity is expected to decrease because the explosive is less confined. In Table 3.5 it is seen that for WEB the effect is not definite and that for AMPA2.1 the detonation velocity even increases.

4. Conclusions

For the majority of the explosives the detonation velocity is constant throughout the length of the sample. The commercial blasting agents WEB and WPB with detonation velocities of 2 km/s and lower are less stable than the explosives with higher detonation velocities. The stability of WPB increases dramatically with the explosive layer thickness. The reproducibility for AMPA2.1, both Triamite batches, and Trimonite is high. The detonation velocity of Alsilite appears to be sensitive to the density of the explosive.

The effect of the contents of the container on the detonation velocities of AMPA2.1 and WEB is not clear.

For the dynamic compaction experiments in this work AMPA2.1, Triamite, WEB, and WPB were chosen as standard explosives.

3.3 REFERENCES

CHAPTER 4

General shock wave equation of state for solids

ABSTRACT

A theoretical shock wave equation of state has been derived based on the Morse potential function, known from classical spectroscopy. Using this potential function and an interstitial-electron model, a linear relation between the shock wave velocity and the mass displacement velocity can be found, analogous to the common empirical relation, but with parameters derived from easily accessible non-shock-wave data. The equation is applicable to a wide range of inorganic materials, as will be demonstrated in the two following chapters on metals and ceramics. In this chapter examples are shown for silver, and copper. Calculations are within 5% average error between experimental data and the model.
4.1 INTRODUCTION

The application of shock waves in new production methods, such as shock wave compaction of powders\(^1\) or shock-synthesis,\(^2\) requires extensive knowledge of the shock wave behavior of the materials involved. However, the science of material properties under shock wave conditions is a largely empirical field, and this is disadvantageous when dealing with new materials. The theoretical shock wave equation of state, developed in this chapter, which uses easily accessible data, is meant to increase the flexibility of the application of production methods, involving shock waves, to new materials.

In shock wave physics the most generally used equation of state is an empirical equation known as the Rankine-Hugoniot equation, or Hugoniot.\(^3\) This Hugoniot can be expressed as a linear relation between the velocity at which a shock wave travels, the shock wave velocity \(U\), and the velocity at which the material moves directly after passage of the shock wave front, the mass displacement velocity, \(u\). The Hugoniot is then expressed as:

\[
U = C_0 + S u
\]  
(4.1)

in which \(C_0\) can be approximated with the bulk sound velocity, and \(S\) is an empirically determined material constant, which can be approximated with:\(^4\)

\[
S = \frac{1}{2}(1+\Gamma)
\]  
(4.2)

in which \(\Gamma\) is the Grüneisen coefficient, which characterizes the ratio of the thermal pressure, \(P_T\), which is the pressure associated with the thermal motion\(^8\) of the atoms (and electrons), to the thermal energy, \(E_T\), of the lattice:\(^3\)

\[
\Gamma = V \left( \frac{\partial P_T}{\partial E_T} \right)_\nu
\]  
(4.3)

The approximation in Eq. (4.2), however, is valid only at low shock stresses. When data over a very large stress range are available a second order term is sometimes added to the Hugoniot. For many materials, however, a linear relationship fits the experimental data well.\(^5\)

A number of approaches has been explored so far to predict the shock behavior of materials. Ross, and Ree\(^6\) used the pair potential of gases, and scaled them in accordance with the "Law of Corresponding States" to predict the behavior of gases under shock conditions.
For solid materials Dandache, for example, derived an equation for the Grüneisen coefficient as a function of volume \( \Gamma(V) \) for which the parameters can be calculated from the slope of the Hugoniot curve at \( u=0 \), and the Grüneisen coefficient at standard conditions, \( \Gamma_0 \). This \( \Gamma(V) \) function can be combined with the Mie-Grüneisen equation of state\(^4\) to calculate shock wave conditions. Dandache\(^7\) used these equations to calculate the thermodynamic states of Al, Cu, and Pb under shock wave conditions.

The approach used by Dandache is like many other methods\(^7\) based on the Grüneisen coefficient. The Grüneisen coefficient at standard conditions, \( \Gamma_0 \), can be determined with:\(^8\)

\[
\Gamma_0 = \frac{\alpha_v}{C_v \kappa_0 \rho_0}
\]  

(4.4)

in which \( \alpha_v \) is the isobaric volume expansion coefficient at constant pressure, \( C_v \) is the heat capacity at constant volume, \( \kappa_0 \) is the isothermal compressibility at standard conditions (\( T=300 \) K, \( P=0.1 \) MPa), and \( \rho_0 \) is the density at standard conditions. The values of the parameters used to calculate \( \Gamma_0 \) with Eq. (4.4) can be determined experimentally. This would, however, require many experiments. Furthermore, for these experiments a dense sample would be needed, which is often rather difficult to obtain for new materials.

In this chapter it will be shown that a linear shock wave equation of state can be derived using an interatomic potential with parameters that can be determined from infrared spectroscopic data.

Infrared spectroscopic data were chosen as a basis for our calculations because of their general availability, and because of the analogies between infrared spectroscopy, during which deformation of the bonds between the atoms by vibrations is measured, and a shock wave in which the bonds are compressed.

In classic spectroscopy one very well-known example of an equation describing the energy of atomic motion is the interatomic potential. In this equation the potential energy of a diatomic molecule is related to the deviation of the interatomic distance from its equilibrium value.

A well-known interatomic potential is the Morse potential\(^9\) [see Fig. 4.1]. The Morse potential was chosen, because of its successful, widespread use, and its mathematical form. Its relatively simple mathematical structure makes it more attractive for calculations than potentials with multiple exponents. Furthermore, although increasing the number of parameters in a potential increases its accuracy, it also causes complications in their determination. The Morse potential is very often used in spectroscopy, and the required parameters are
easily obtained. This makes this potential a suitable basis for a generally valid shock wave equation of state.

![Graph of the Morse potential curve]

**Figure 4.1**: The Morse potential curve.

In the present model the parameters of a potential are used, which are obtained for a diatomic molecule in the gas phase, to describe the bonds that exist in a lattice. This is accomplished by the application of an interstitial-electron model. Bonds are assumed to exist between an atom and all atoms that border the nearest and next-nearest interstitial sites around it, with the exception of cases in which there is an atom on a straight line between them. Only bonds are assumed to exist between atoms that border adjacent interstitial sites, but no further. In practice this means that bonds are considered at interatomic distances up to slightly more than twice the nearest-neighbor distance (see Appendix C). This model is applicable to lattices with short range atomic interaction, such as metals and covalent materials. For lattices with a strong ionic bond nature, the interstitial-electron model can not be used to determine the bonds, due to the presence of long range Coulombic interaction in these lattices.

The Morse potential describes the relation between the potential energy of atomic vibration, $\Phi$, and the deviation from the equilibrium distance, $r_0$, between the atoms. The Morse potential can be written as:
\[ \varphi(r) = D' \left[1 - e^{-\alpha(r_0 - r)}\right]^2 \] (4.5)

Here \( D' \) is the bond dissociation energy per mol, which is the energy difference between the ground state of a diatomic molecule in the gaseous phase with the atoms at equilibrium distance, and with the atoms at infinite separation, \( \alpha \) is the reciprocal vibration number, and \((r_0 - r)\) is the deviation from the equilibrium distance, with \( r \) being the actual distance. Both \( D' \) and \( r_0 \) can easily be obtained even for new compounds. The reciprocal vibration number, \( \alpha \), can be calculated from infrared spectral data with:

\[ \alpha = 2\pi c_0 \omega_0 \sqrt{\frac{\mu}{2D'}} \] (4.6)

in which \( c_0 \) is the velocity of light in vacuum, \( \mu \) is the reduced mass of the molecule, and \( \omega_0 \) is the wave number (in m\(^{-1}\)) of the zero order transition. The bond dissociation energy, \( D' \), and the wave number, \( \omega_0 \), can be determined from the infrared spectrum.\(^9\) The Morse potential was originally derived for diatomic gases; in the current model, however, the potential is used to describe the interaction in a solid. The equilibrium distance, or bond length between the atoms, \( r_0 \), which is used in the model refers to the average equilibrium distance in the solid and can, therefore, be determined from X-ray data. The average equilibrium distance, \( r_0 \), will be discussed further in paragraph 8.3 of this chapter describing effects of the lattice.

In the current model the adiabatic shock wave compression is calculated by dividing the shock process in two stages; first isothermal compression, and secondly isobaric expansion. Both processes can be described with equations that can easily be derived from the Morse potential.

The assumptions underlying the present derivation of a shock wave equation of state from a potential are as follows:

1. the translational motion of the atoms must be classical,
2. the thermal excitation of electrons is negligible,
3. thermal vibrations in the shock wave state can be approximated by the potential at standard conditions,
4. on the average there is no atomic motion lateral to the shock wave direction, and
5. the true interatomic potential can be approximated with the Morse potential.

At the stress conditions achieved by shock wave experiments the concentration of phonons is sufficiently high that the first assumption, that of
classical motion, is clearly valid. Coffey et al.\textsuperscript{11} calculated that the phonon density at about 2x10\textsuperscript{11} Hz, in a low amplitude compressive wave of 0.5 GPa, with a wave velocity of 2 km/s, would be approximately 10\textsuperscript{27} phonons/m\textsuperscript{3}. The thermal equilibrium density at 2x10\textsuperscript{11} Hz at shock temperatures, would typically\textsuperscript{11} be less than 100 phonons/m\textsuperscript{3}.

The second assumption is reasonable at lattice temperatures below 10,000 K, because the effect of thermal excitation of the electrons is small compared to the thermal vibrations of the atoms.\textsuperscript{3}

The thermal vibrations at "low" stresses can be described accurately by the potential. The effect of a non-negligible external stress on the potential can be represented in a potential plot by adding a linear function of the bond length to the original potential, as is shown in Fig. 4.2. This transformation results in a smaller equilibrium distance and an counterclockwise rotation of the potential. The decrease in the equilibrium distance is accounted for in the model. The third assumption is based on the fact that the shape of the potential near it minimum is rather insensitive to rotation, as shown in Fig. 4.2.

![Diagram](Figure 4.2: Effect of an external stress on the shape of the potential curve. Adding the extra potential energy due to the external stress (dashed line) results in a counterclockwise rotation. The change in the equilibrium distance is accounted for in the model, only the rotation was neglected. The shape of the potential curve in the lower regions, relevant for thermal excitation up to shock temperatures (T<10,000 K), is rather insensitive to this rotation.)
The force balance between the atoms and their bonds in the shock wave state causes the bonds to attain a new equilibrium length, and because there is no overall mass transport perpendicular to the shock wave direction this means that the fourth assumption is valid for the average atom.

The Morse potential has been successfully applied to a wide range of materials. The conditions under which infrared spectroscopy is performed, however, are not as extreme as in a shock wave. At high compressive stresses, the true interatomic potential of materials with an extremely asymmetric interatomic potential might deviate from a Morse potential determined with infrared spectroscopy. Compounds with such an extremely asymmetric potential are few as will be shown in the two following chapters, in which a wide range of metals, and ceramics will be discussed. The calculations in this chapter, and the following chapters reveal that most materials obey the fifth condition.

The aim of this chapter is to develop a theoretical shock wave equation of state with well known non-shock-wave parameters, which if not available can be determined beforehand without shock wave experiments.

In the following sections the basic shock wave equations will be introduced: the three conservation laws of mass, momentum, and energy. After this an example of a generally used empirical shock wave equation of state is given, and after this short introduction a new theoretical shock wave equation of state will be developed in seven stages.

In the first stage the shock wave compression is divided in two processes, first an isothermal, or cold compression, and second an isobaric, or thermal expansion. It should be borne in mind that this division is of course purely theoretical.

In the second and third stages the isothermal compression and isobaric expansion will be related to the internal energy by using the potential.

In the fourth stage the shock wave compression will be derived from combining the isothermal compression and the isobaric expansion. This yields a relation between the internal energy (distributed between isothermal compression, and isobaric expansion), and the bond length in the shock wave. This relation can be expressed in an equation in which the relative shock wave compression is a function of the shock wave velocity, the mass displacement velocity, and the relative amount of internal energy used for isothermal compression.

In the fifth stage a relation will be determined between the bond length, the shock wave velocity, and the mass displacement velocity, using mass conservation.

In the sixth stage the equations found in the fourth and fifth stages will be combined to eliminate the bond length from the equation. This yields an
equation for the shock wave velocity as a function of the mass displacement velocity and the fraction of internal energy used for isothermal compression.

In the seventh and final stage the relative amount of internal energy used for isothermal compression will be determined by a one-step iteration, and some approximations. This yields a shock wave equation of state with the shock velocity as a function of the mass displacement velocity.

After the derivation of this new linear shock wave equation of state the calculation of the relevant parameters will be discussed. It will be demonstrated how to calculate the average bond length in a metal. Finally it will be shown that the parameters of the model can be determined in a second way using the bulk sound velocity (which is sometimes considered to be a shock wave parameter, but can be determined without shock wave experiments) as a key parameter.

4.2 THE MODEL

A. Shock equations

To calculate the shock wave state of a material three balance equations are available. The balance equations in shock wave physics are determined over the shock wave front, moving with the shock wave velocity, \( U \).

The mass conservation law over the shock front dictates, that the mass entering the shock front, with a velocity \( U \) is equal to the mass leaving the shock front with a velocity \( U-u \). This gives:

\[
\rho_0 \ U = \rho \ (U-u) \tag{4.7}
\]

in which \( \rho_0 \) is the density ahead of the shock wave, and \( \rho \) the density directly behind the shock wave front.

The conservation of momentum yields:

\[
\sigma - \sigma_0 = \rho_0 \ U \ u \tag{4.8}
\]

in which \( \sigma \) is the shock stress, or force per unit surface. In shock wave physics the stress before arrival of the shock wave, \( \sigma_0 \), is often considered to be negligible.

When we neglect viscosity effects and heat conduction effects, the internal energy change, \( E_{int} \), is determined by:
\[ E_{\text{int}} = \frac{1}{2} \sigma \Delta V \] (4.9)

in which \( \Delta V \) is the difference in specific volume before and after arrival of the shock wave.

With the use of Eqs. (4.7)-(4.9) the change in internal energy for the shock wave can also be written as:

\[ E_{\text{int}} = \frac{1}{2} \rho u^2 \] (4.10)

These three conservation laws, however, are not sufficient to calculate the shock wave state, and, therefore, a fourth equation is needed. This fourth equation is called the shock wave equation of state, or Hugoniot. An example of such an equation was given earlier [Eq. (4.1)].

**B. Division into two stages**

In the following an equivalent fourth equation will be derived. To this end the thermodynamic state reached after adiabatic shock compression will be calculated in two steps. Firstly an isothermal compression process will be considered, and secondly an isobaric expansion in such a way that the same end state is reached as in a shock compression process. This construction is illustrated in Fig. 4.3(a) to 4.3(d). In Fig. 4.3(a) the Morse potential is shown. The part of the curve for \( r < r_0 \) can also be interpreted as describing the internal energy increase in an isothermal compression. Fig. 4.3(b) shows how for a certain energy level the isobaric expansion can be calculated from the Morse potential by averaging the maximum compression and expansion.

In Fig. 4.3(c) these two steps are combined by considering the material to be compressed from \( (r=r_0, E=0) \) to \( (r_e, E_e) \), and then to expand along an isobar to \( (r_e, E_e + E_T) \). In Fig. 4.3(d) the processes in Fig. 4.3(c) are shown in an alternative plot of the stress, \( \sigma \), against the specific volume, \( V \).
Figure 4.3: (a) The Morse potential curve, the left side of the curve for $r<r_0$ can be considered to represent isothermal compression of the bond. (b) By averaging over the maximum and minimum deviation of the potential curve, the isobaric expansion curve can be found. (c) The shock wave state is constructed by following the isotherm from $(r_p, E=0)$ to $(r_c, E_c)$, and then expanding along the isobar to $(r_{p, E_{int}}=E_c+E_T)$. (d) The construction of the Hugoniot as in Fig. 4.3(c) in a plot of stress, $\sigma$, against specific volume, $V$. 

38
For the mathematical construction first the internal energy increase due to the shock wave $E_{\text{int}}$ is divided into two parts; $E_c$, the isothermal, or cold compression energy increase, and $E_T$ the energy increase due to isobaric expansion (both per unit mass):

$$E_{\text{int}} = E_c + E_T$$  \hspace{1cm} (4.11)

By introducing the fraction, $f$, of isothermal energy over the total internal energy increase:

$$f \equiv \frac{E_c}{E_{\text{int}}}$$  \hspace{1cm} (4.12)

the internal energies can be written as a function of $u$:

$$E_c = f \frac{1}{2} u^2, \text{ and } E_T = \left[ 1-f \right] \frac{1}{2} u^2$$  \hspace{1cm} (4.13)

C. Isothermal compression

The relative isothermal compression, $\varepsilon_c \equiv (r_c-r_0)/r_0$, can be calculated from the isothermal energy increase, or cold compression energy, $E_c$ with the potential [Eq. (4.5)] rewritten to:

$$E_c = D \left[ 1 - e^{-\frac{\alpha}{F} } \right]$$  \hspace{1cm} (4.14)

In the following the bond dissociation energy per unit mass, $D$, will be used instead of the bond dissociation energy per mol, $D'$. This is done in accordance to conventions in shock wave physics, where it is standard procedure to use energies per unit mass.

Rewriting Eq. (4.14) yields $\varepsilon_c$ expressed as a function of the cold compression energy:

$$\varepsilon_c = -\frac{1}{\alpha} \frac{1}{r_0} \ln \left[ 1 + \left( \frac{E_c}{D} \right) \right]$$  \hspace{1cm} (4.15)
D. Isobaric Expansion

The isobaric expansion can be determined from the potential by determining the average deviation from the equilibrium radius, due to the asymmetry of the thermal vibration, as shown in Fig. 4.3(b). In the cold compressed state the thermal vibrations occur around the equilibrium distance in that state, \( r_c \), \([= (1+\varepsilon_c) r_0]\). The thermal energy, \( E_T \), is related to the maximum thermal deviation \( x_T \) \([= (r_s - r_c) / r_c]\) by the potential:

\[
E_T = D \left[ 1 - e^{-\alpha r_c x_T} \right]^2 
\]  \( \text{(4.16)} \)

Rewriting Eq. (4.16) gives:

\[
x_T = -\frac{1}{\alpha r_c} \ln \left[ 1 \pm \sqrt{\frac{E_T}{D}} \right] 
\]  \( \text{(4.17)} \)

The average thermal expansion, \( \varepsilon_T \), which is the isobaric expansion, can be found from averaging \( x_T \) over expansion, \( x_T^+ \), and compression, \( x_T^- \) [shown in Fig. 4.3(b)]:

\[
\varepsilon_T = \frac{x_T^+ + x_T^-}{2} = -\frac{1}{2 \alpha r_0 (1+\varepsilon_c)} \ln \left[ 1 - \frac{E_T}{D} \right] 
\]  \( \text{(4.18)} \)

E. Combination of Stages

The equilibrium radius in the shock wave state \( r_s \) is calculated from the relative isothermal compression, \( \varepsilon_c \), and the relative thermal expansion, \( \varepsilon_T \):

\[
r_s = (1+\varepsilon_c)(1+\varepsilon_T) \ r_0 
\]  \( \text{(4.19)} \)

Substitution of Eqs. (4.15) and (4.18) in (4.19) gives:

\[
\frac{r_s}{r_0} = 1 - \frac{1}{\alpha r_0} \ln \left[ \left(1 + \sqrt{\frac{E_c}{D}}\right) \sqrt{\left(1 - \frac{E_T}{D}\right)} \right] 
\]  \( \text{(4.20)} \)

This yields a relation between the cold and thermal internal energies and the.
bond-compression in the shock state. A schematic representation of this construction is shown in Fig. 4.3(c).

Substitution of Eq. (4.13) in (4.20) gives:

\[
\frac{r_s}{r_0} = 1 - \frac{1}{A} \ln \left[ (1 + B u \sqrt{f}) \sqrt{1 - (1 - f) B^2 u^2} \right]
\]

(4.21)

with:

\[
A = a \ r_0, \ \text{and} \ B = \sqrt{\frac{1}{2D}}
\]

(4.22)

Combining Eq. (4.21) with a second relation between \( r_s, u \) and \( U \) will yield a relation between \( u \), and \( U \), which is the aim of this work. This second relation can be obtained from the conservation of mass.

F. Application of mass conservation

Until now only the relations between the shock wave energy and the average bond length were considered. Changes in the average bond length, however, are also related directly to changes in the overall density. In the following the relations between the bond length and the overall density, as well as Eq. (4.7) resulting from the conservation of mass, will be used to derive a second relation between the average equilibrium bond length in the shock state, \( r_s \), \( u \), and \( U \).

Because shock wave compression in a planar shock wave in solids is always anisotropical on the scale of atomic bonds, the effect of the angle between the interatomic bond and the shock wave should be carefully considered. There is no overall mass transport in lateral direction. Therefore, the average bond will remain uncompressed in directions perpendicular to the shock wave direction.

When these effects are taken into account the following equation results, as is demonstrated in Appendix A:

\[
\frac{u}{U} = 3 \left( 1 - \frac{\langle r_s \rangle}{r_0} \right) + \frac{9}{5} \left( 1 - \frac{\langle r_s \rangle}{r_0} \right)^2 + 2 \sqrt{5} \left( 1 - \frac{\langle r_s \rangle}{r_0} \right)^3
\]

(4.23)
G. Elimination of bond length

Substitution of Eq. (4.21) in (4.23), and expanding to series yields an expression of $U$ as a function of $u$, and $f$:

$$U = \frac{A}{3B\sqrt{f}} + \left(\frac{A}{6f} - \frac{1}{5}\right)u - \left(\frac{A\sqrt{f}}{9} + \frac{2\sqrt{5f}}{9A} - \frac{A}{12f^2} - \frac{3\sqrt{f}}{25A}\right)Bu^2$$  \hspace{1cm} (4.24)

H. Elimination of $f$

The ratio, $f$, of energy used in isothermal compression, $E_a$, and total internal energy, $E_{int}$, can be calculated using the fact that the stress after isothermal compression equals the shock stress, because the expansion is an isobaric process. In Appendix B an equation for $f$ is derived using this equality and the potential. After some approximations it is found that:

$$f \approx 1 - \frac{A}{6U}$$  \hspace{1cm} (4.25)

By using an iteration with Eq. (4.24) and (4.25) an expression for $U$ as a function of $u$ can be obtained. First $f$ is solved by using a simple first order expression with $f=1$ for $U$ from Eq. (4.24), which is substituted in Eq. (4.25):

$$f \approx 1 - \frac{A}{6} \frac{u}{A + \left(\frac{A}{6} - \frac{1}{5}\right)u}$$  \hspace{1cm} (4.26)

Substitution of Eq. (4.26) in (4.24), and discarding terms of second order and higher, yields an equation analogous to the empirical Hugoniot:

$$U = \frac{A}{3B} + \frac{A}{4} \frac{u}{5}$$  \hspace{1cm} (4.27)

in which the parameters $A$, and $B$ can be calculated from non-shock wave data, with:
\[ A = \alpha r_0, \quad \text{and} \quad B = \sqrt{\frac{1}{2D}} \] (4.28)

In the above derivation terms of second order and higher were discarded for the following reasons: (1) it is common practice to use a linear equation of state, which also fits the experimental data very well for many materials, and (2) in view of some assumptions used in the model, and some approximations applied in the derivation the reliability of a second order term would have been questionable. It should be remembered that the linearity has no physical significance. In our calculations we found that if a second order term would have been included, its sign would be negative.

4.3 INFLUENCE OF LATTICE

In the modern bond theory of metals they are considered to consist of a packing of positive ions with a maximum valence electron density in the interstitial sites. According to this theory the electrons are not moving around freely without preference. The electrons in the interstitial sites bind the positive ions together.

In our calculations bonds are assumed to exist between an ion and all ions that border the nearest and next-nearest interstitial sites around it. This means that bonds are assumed to exist between the ions of two adjacent interstitial sites. In this model the average bond length between the ions does not equal the nearest-neighbor distance, which is generally quoted as bond length, but the average distance between an ion, and the ions bordering the nearest and next-nearest interstitial sites around it.

This average bond length is especially important in a shock wave model, because the lattices in a macroscopic polycrystalline sample are anisotropically compacted, and not necessarily in the direction of one of the axes of the lattice. During shock compression of a macroscopic metal sample, which is not a single crystal, every ion bordering an interstitial site can be moved in the direction of every other ion bordering the same, or even the next interstitial site, because of their random orientation with respect to the shock wave direction (due to the polycrystalline nature of the sample). This means that, if the strength of the lattice is described with a bond model, bonds must be considered between all the ions bordering an interstitial site, and those that border the adjacent interstitial sites. In Appendix C [Fig. 4.C1(a)-4.C1(d)] the bonds are determined for a fcc lattice.
The average bond length, \( r_0 \), can be calculated from the lattice structure or packing, and the nearest-neighbor distance. For the regular packings that apply to most metals a constant ratio, \( q \), between the nearest-neighbor distance, and the average bond length can be found applicable to all metals with the same packing. This lattice ratio, \( q \), is found by averaging the distances, \( x = r/R_0 \) with \( R_0 \) the nearest-neighbor distance), between an ion and the ions bordering the interstitial sites around it, and those in a second layer around these, over their number of occurrences, \( n_i \):

\[
q = \frac{\sum n_i x_i}{n_{tot}} \tag{4.29}
\]

The bond length can be calculated from \( q \), and the nearest-neighbor distance, \( R_0 \), in the lattice:

\[
r_0 = q R_0 \tag{4.30}
\]

The value of \( q \), for a fcc lattice is calculated in Appendix C.

### 4.4 ALTERNATIVE CALCULATION OF EQUATION OF STATE

An alternative method is available for the calculation of the parameters of the linear equation of state. This method uses the bulk sound velocity, which can be measured without shock wave experiments, e.g. with ultrasonics.

Analogous to the Hugoniot, the first term can be approximated with the bulk sound velocity, \( C_0 \). For very low mass displacement velocities \( (u \downarrow 0) \) the shock wave velocity \( U \), approaches the bulk sound velocity \( C_0 \). This means that:

\[
U(u \downarrow 0) = \frac{A}{3B} \approx C_0 \tag{4.31}
\]

This has an important consequence for the application of the equation of state [Eq. (4.27)], because it means that if the bulk sound velocity is known, and \( B \) can be calculated from other parameters, an alternative equation can be used:

\[
U = C_{0,\text{exp}} + \left( \frac{3B}{4} C_{0,\text{exp}} - \frac{1}{5} \right) u \tag{4.32}
\]
4.5 CALCULATIONS

In Table 4.1 the necessary data to calculate the equation of state are presented for Ag and Cu, which both have a fcc type lattice.

Table 4.1: The IR data necessary for the calculations with method 1.

<table>
<thead>
<tr>
<th>Metal</th>
<th>Dissociation energy$^{15}$ $D^0$ (kJ/mol)</th>
<th>Mass of diatomic molecule$^{15}$ $M$ (g/mol)</th>
<th>Nearest-neighbor distance$^{15}$ $R_0$ (nm)</th>
<th>Lattice const (App. C) $q$</th>
<th>Wave number$^{12}$ $\omega_0$ (10$^3$ m$^{-1}$)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ag (fcc)</td>
<td>163±8</td>
<td>215.74</td>
<td>0.2889</td>
<td>1.73</td>
<td>20.70</td>
</tr>
<tr>
<td>Cu (fcc)</td>
<td>177±2</td>
<td>127.10</td>
<td>0.2556</td>
<td>1.73</td>
<td>26.89</td>
</tr>
</tbody>
</table>

The calculated intercept ($C_{0,\text{calc}}$) and slope of the equation of state are shown in Table 4.2, together with the range over which data were available, and the average error in the calculations compared to the data.

Table 4.2: Results of calculations with method 1 using spectroscopic data.

<table>
<thead>
<tr>
<th>Metal</th>
<th>Data range$^5$ $u$ (km/s)</th>
<th>Constant $A$ [Eq.(4.28)]</th>
<th>Constant $B$ [Eq.(4.28)] (s/km)</th>
<th>Calculated intercept $C_{0,\text{calc}}$ [Eq.(4.27)] (km/s)</th>
<th>Calculated slope $S$ [Eq.(4.27)]</th>
<th>Average error in calculated shock wave velocity $U$ (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ag</td>
<td>0.5-2.1</td>
<td>7.93</td>
<td>0.814</td>
<td>3.25</td>
<td>1.78</td>
<td>5.0</td>
</tr>
<tr>
<td>Cu</td>
<td>0.2-4.2</td>
<td>6.72</td>
<td>0.600</td>
<td>3.73</td>
<td>1.48</td>
<td>2.7</td>
</tr>
</tbody>
</table>

When not all the IR spectroscopic data are available a second method can be applied in which the bulk sound velocity is used to calculate the parameters of the equation of state [Eq. (4.32)]. In Table 4.3 the parameters are shown, which are necessary to calculate B from the experimental bulk sound velocity.
Table 4.3: The data necessary for the calculations of the constant $B$ for method 2.

<table>
<thead>
<tr>
<th>Metal</th>
<th>Experimental bulk sound velocity(^5)  $C_{0,\text{expt}}$ (km/s)</th>
<th>Dissociation energy(^{15}) $D'$ (kJ/mol)</th>
<th>Mass of diatomic molecule(^{15}) $M$ (g/mol)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ag (fcc)</td>
<td>3.176</td>
<td>163±8</td>
<td>215.74</td>
</tr>
<tr>
<td>Cu (fcc)</td>
<td>3.927</td>
<td>177±2</td>
<td>127.10</td>
</tr>
</tbody>
</table>

The intercept ($C_{0,\text{expt}}$) and the slope of the equation of state, calculated with the experimental bulk sound velocity are shown in Table 4.4, together with the range over which data were available, and the average error in the calculation compared to the data.

Table 4.4: Results of calculations with method 2 using the experimental bulk sound velocity, $C_{0,\text{expt}}$.

<table>
<thead>
<tr>
<th>Metal</th>
<th>Data range(^5) $u$ (km/s)</th>
<th>Intercept (Experimental bulk sound velocity(^5)) $C_{0,\text{expt}}$ (km/s)</th>
<th>Constant $B$ [Eq.(4.28)] (s/km)</th>
<th>Calculated slope $S$ [Eq.(4.33)]</th>
<th>Average error in calculated shock wave velocity (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ag (fcc)</td>
<td>0.5–2.1</td>
<td>3.176</td>
<td>0.81</td>
<td>1.74</td>
<td>2.6</td>
</tr>
<tr>
<td>Cu (fcc)</td>
<td>0.2–4.2</td>
<td>3.927</td>
<td>0.60</td>
<td>1.57</td>
<td>2.6</td>
</tr>
</tbody>
</table>

The linear shock wave equations of state calculated for Ag from infrared (IR) data, and from the sound velocity are compared with literature data\(^5\) in Fig. 4.4.

46
4.6 DISCUSSION

The calculated equations of state are within 5% average error. In Fig. 4.4 it can be seen that the accuracy of the calculations tends to decrease with increasing shock wave velocity. This might be due to the fact that higher order terms were neglected. In this example the calculation with the IR data is less accurate than with the sound velocity, this is, however, a coincidence; in most cases\textsuperscript{13,14} the calculations with IR data are more accurate. For most metals the current model, when used with all spectroscopic data calculates the shock wave velocity within 1-10% average error, as will be shown in Chapter 5 on the equation of state for metals.

![Graph showing shock wave equation with IR data and sound velocity comparison](image)

**Figure 4.4:** The linear shock wave equation of state for Ag calculated with IR data, and with the experimental bulk sound velocity compared with data from Marsh.\textsuperscript{5}

When only the sound velocity, and the dissociation energy are used the calculation for the two model materials is within 3% average error. In general,\textsuperscript{13} the second method is slightly less accurate because the bulk sound velocity is not exactly equal to the intercept of the shock wave curve. For most metals the
current model, when used with only the bulk sound velocity, calculates the shock wave velocity within 2-25% average error, as will be shown in Chapter 5 on the equation of state for metals.

Before applying the present model one should first evaluate whether it is reasonable to assume that the compressive strength of the material can be described with an interatomic potential determined at low stress conditions. The conditions under which infrared spectroscopy are performed are not as extreme as in a shock wave. At high compressive stresses, the true interatomic potential of materials with an extremely asymmetric interatomic potential might deviate from a Morse potential, which was determined with infrared spectroscopy.

Materials that have potentials that are difficult to characterize with the Morse potential are usually recognizable for their low bond strength, or dissociation energy and high thermal expansion coefficient.

The fact that the Morse potential is not applicable to some materials is not a shortcoming of the current model, but merely a result of the choice in potentials. It can be remedied by choosing a different potential, which is applicable to those materials.

The factors that determine the suitability of the model for different materials will be discussed further in two following chapters, the first about metals, the second about ceramics. In these chapters a large range of materials will be considered.

For the two materials Ag and Cu discussed here it appears that the compression in a shock wave can very well be characterized with the Morse interatomic potential.

4.7 CONCLUSIONS

It has been shown that it is possible to derive a shock wave equation of state using the Morse potential function, known from infrared spectroscopy, and an interstitial-electron model. Two methods are demonstrated to calculate a linear shock wave equation of state.

The first method yields:

\[
U = \frac{A}{3B} + \left(\frac{A}{4B} - \frac{1}{5}\right)\mu
\]  

(4.27)

in which \(A\), and \(B\), are material constants that can be determined from infrared spectroscopic and X-ray data:
the dissociation energy, \( D \) (from thermodynamic or IR spectroscopic measurements),
- the wave number of the zero order transition in the infrared spectrum, \( \omega_0 \)
- the atomic lattice (from X-ray data), and
- the nearest-neighbor distance, \( R_0 \), in the lattice (from X-ray data).

The second method which is less accurate but uses fewer data yields:

\[
U = C_{0,\text{exp}} + \left( \frac{3 B C_{0,\text{exp}}}{4} - \frac{1}{5} \right) u
\]  

(4.32)

in which \( C_{0,\text{exp}} \) is the bulk sound velocity, and \( B \) can be determined from the dissociation energy, \( D \) (from thermodynamic or IR spectroscopic measurements).

For the examples Ag, and Cu calculations with method 1, using all data, are within 5% average error of experimental data. Calculations with method 2, using only the bulk sound velocity and the dissociation energy, are within 3% average error. This is sufficiently accurate for most shock wave applications.

4.8 REFERENCES

8 Ya. B. Zeldovich, and Yu. P. Raizer, in Physics of Shock Waves and
APPENDIX A: EFFECT OF VOLUME CHANGE ON BOND LENGTH

In Fig. 4.A1 the effect of the shock wave on the bond is represented schematically. In the figure the shock wave travels downwards. The ratio $a$ over $b$ is a measure of the shock wave compression:

$$\frac{b}{a} = \frac{\rho_0}{\rho} \quad (4.A1)$$

Using the conservation of mass one obtains:

$$\frac{b}{a} = \frac{\rho_0}{\rho} = \frac{U-u}{U} \quad (4.A2)$$

The bond remains uncompressed in lateral direction, hence $e$ is constant. The bond before and after compression is represented by the diagonals hence:

$$\frac{r_s}{r_0} = \frac{d}{c} \quad (4.A3)$$
Figure 4.A1: A schematic representation of bond compression by the shock wave. The shock wave travels downwards parallel to $a$ and $b$. The bond is represented by $c$ before arrival of the shock wave and $d$ during shock compression. The ratio of $b$ over $a$ is proportional to the overall compression. There is no overall compression perpendicular to the shock wave direction, the projection of the bond in the shockwave plane, $e$, therefore, remains constant. The angle of the bond with the shock wave plane changes from $\gamma$ to $\beta$, due to the arrival of the shock wave.

In Fig. 4.A1 it can be seen that:

$$a = c \sin \beta \quad (4.A4)$$

and

$$d = \sqrt{(a \frac{b}{a})^2 + (c \cos \beta)^2} \quad (4.A5)$$

Substitution of (4.A4) in (4.A5) gives:
\[ d = \sqrt{(c \frac{b}{a} \sin \beta)^2 + (c \cos \beta)^2} \]  
\hspace{2cm} (4.A6)

or:
\[ \frac{d}{c} = \sqrt{1 + \left[ \left( \frac{U-u}{U} \right)^2 - 1 \right] \sin^2 \beta} \]  
\hspace{2cm} (4.A7)

Equation (4.A3) now becomes:
\[ \frac{r_s}{r_0} = \sqrt{1 + \left[ \left( \frac{U-u}{U} \right)^2 - 1 \right] \sin^2 \beta} \]  
\hspace{2cm} (4.A8)

When a macroscopic sample of a polycrystalline solid is considered in which the angle of the atomic bond can be considered to vary randomly with respect to the shock wave direction, the average bond can be approximated using a simple hemispherical model. From the position of an atom, atoms with which a bond exists in shock wave direction can then be considered to be distributed over the surface of a hemisphere with radius \( r_0 \), centered around this position. It is assumed that the bound atoms are equally distributed over the surface of the hemisphere. With this assumption the average radius in the shock wave can be found from Eq. (4.A8) by averaging over \( \beta \) using:
\[ \langle \frac{r_s}{r_0} \rangle = \frac{\int_0^{\frac{\pi}{2}} 2\pi \cos \beta \left( \frac{r_s(\beta)}{r_0} \right) d\beta}{\int_0^{\frac{\pi}{2}} 2\pi \cos \beta \ d\beta} \]  
\hspace{2cm} (4.A9)

This yields:
\[ \langle \frac{r_s}{r_0} \rangle = \frac{1}{2} \left[ 1 - \frac{u}{U} + \frac{\arcsin \left[ 1 - \left( \frac{1-u}{U} \right)^2 \right]}{1 - \left( \frac{1-u}{U} \right)^2} \right] \]  
\hspace{2cm} (4.A10)

Expanding to series, with a third order approximation gives:
\[
\langle \frac{r_s}{r_0} \rangle = 1 - \frac{1}{3} \frac{u}{U} + \frac{1}{15} \left( \frac{u}{U} \right)^2 + \frac{1}{35} \left( \frac{u}{U} \right)^3
\]
(4.11)

The physical solution for \( u \) over \( U \) from Eq. (4.11) can be approximated with:

\[
\frac{u}{U} = 3 \left( 1 - \langle \frac{r_s}{r_0} \rangle \right) + \frac{9}{5} \left( 1 - \langle \frac{r_s}{r_0} \rangle \right)^2 + 2\sqrt{5} \left( 1 - \langle \frac{r_s}{r_0} \rangle \right)^3
\]
(4.12)

APPENDIX B: CALCULATION OF \( f \)

The factor \( f \) is defined as the relative amount of energy used in isothermal compression compared to the total internal shock wave energy:

\[
f = \frac{E_c}{E_{int}}
\]
(4.13)

This ratio can be determined with sufficient accuracy by using some simple approximations.

Because the thermal expansion used in the current model is isobaric, the stress after isothermal compression, \( \sigma_c \), is equal to the shock stress, \( \sigma \):

\[
\sigma = \sigma_c
\]
(4.14)

From energy conservation [Eq. (4.9)] it can be derived that:

\[
\sigma = \frac{2E_{int}}{V_0 - V}
\]
(4.15)

Using the Morse potential to describe isothermal compression yields:\(^3\)

\[
\sigma_c = -\left( \frac{d\phi}{dV} \right) = \frac{dr_c}{dV} \frac{-2A}{r_0} \frac{\exp\left[ A(1 - \frac{r_c}{r_0}) \right]}{1 - \exp\left[ A(1 - \frac{r_c}{r_0}) \right]} E_c
\]
(4.16)

Combining Eqs. (4.13)-(4.16) gives:
\[ f = - \frac{r_0}{A} \frac{dV}{dr_c} \frac{1}{(V_0 - V)} \left( \exp \left[ -A \left( 1 - \frac{r_c}{r_0} \right) \right] - 1 \right) \]  

(4.B5)

This equation can be solved using some approximations, and

\[ \frac{dV}{dr_c} = \frac{dV}{de} \frac{de}{dr_s} \frac{dr_s}{dr_c} \]  

(4.B6)

in which:

\[ \epsilon = \frac{u}{U} = \frac{V_0 - V}{V} \]  

(4.B7)

The first approximation, that is used is based on Eq. (4.23):

\[ \frac{r_s}{r_0} \approx 1 - \frac{\epsilon}{3} \]  

(4.B8)

which yields:

\[ \frac{de}{dr_s} = -\frac{3}{r_0} \]  

(4.B9)

From (4.B7) it can be found that:

\[ \frac{dV}{de} = -V_0 \]  

(4.B10)

While furthermore it is assumed that:

\[ \frac{dr_s}{dr_c} \approx 1 \]  

(4.B11)

Substitution of these approximations into Eq. (4.B5) gives:

\[ f \approx -\frac{3}{Ae} \left( \exp \left[ -\frac{Ae}{3} \right] - 1 \right) \]  

(4.B12)

Expanding to series yields in first order approximation:
\[ f = 1 - \frac{A u}{6 U} \]  \hfill (4.8B13)

**APPENDIX C: CALCULATION OF LATTICE RATIO, \( q \)**

For the face-centered-cubic (fcc) packing [8 ions on the corners of a cube and six on the faces of the cube, shown in [Fig. 4.C1(a)] the lattice ratio, \( q \), is calculated from the distances between ion \( i \) and the ions \( I-V \) [shown in Fig. 4.C1(a)] as gathered in Table 4.C1. Using Eq. (4.30) this yields an average ratio, \( q \), for a fcc packing of \( q = 1.73 \).

**Table 4.C1:** The distance between ions in a fcc packing, \( x \), \( (x = r/R_0 \) with \( R_0 \) the nearest-neighbor distance), and their number of occurrences, \( n_i \), for a single ion. The fcc packing is shown in Fig. 4.C1(a). Ions at the opposite corners of the cubes face [such as ion \( IV \) in Fig. 4.C1(a)] are considered to be screened by the ions on the cube face [such as ion \( I \) in Fig. 4.C1(a)], and ions at distances \( x > \sqrt{5} \) [such as ion \( VI \) in Fig. 4.C1(a)] do not border the nearest or next-nearest layer of interstitial sites, and are, therefore, not considered for bonds.

<table>
<thead>
<tr>
<th>Type of ion [Fig. 4.C1(a)]</th>
<th>Distance to ion ( i ) ( x_i ) ( (R_0^{-1}) )</th>
<th>Number of occurrences ( n_i )</th>
</tr>
</thead>
<tbody>
<tr>
<td>( I )</td>
<td>1</td>
<td>12</td>
</tr>
<tr>
<td>( II )</td>
<td>( \sqrt{2} )</td>
<td>12</td>
</tr>
<tr>
<td>( III )</td>
<td>( \sqrt{3} )</td>
<td>24</td>
</tr>
<tr>
<td>( IV )</td>
<td>2</td>
<td>0 (screened)</td>
</tr>
<tr>
<td>( V )</td>
<td>( \sqrt{5} )</td>
<td>24</td>
</tr>
</tbody>
</table>

55
**Figure 4.C1(a):** Schematic representation of a fcc lattice. The ions in the vicinity of ion \( i \) are numbered in order of increasing distance. Ion \( IV \) is screened from ion \( i \) by \( I \). Ion \( V \) is the furthest ion still bordering the next-nearest layer of interstitial sites [see also (d)]. Ion \( VI \) and those that are further away do not border one of the nearest or the next-nearest interstitial sites [see (b) and (d)] and are, therefore, considered screened.

In Fig. 4.C1(b) the adjacent tetrahedral and octahedral sites in the fcc lattice are shown that connect the ions of type \( i \), \( I \), and \( III \). Within these two layers of interstitial sites, ions of type \( III \) are the most distant ions that are still considered for a bond. In Fig. 4.C1(c) two octahedral sites in the nearest layer of interstitial sites are shown that border the ions of type \( i \) and \( II \). In Fig. 4.C1(d) examples of octahedral sites in the nearest and next-nearest layer are shown. The largest distance that can be covered with two layers of interstitial sites is found in this figure; between ions of type \( i \) and type \( V \).
Figure 4.C1(b): Examples of the nearest and next-nearest layer of interstitial sites in the fcc lattice: a tetrahedral interstitial site in the nearest layer and an adjacent octahedral site in the next-nearest layer. The longest distance between the ions in these layers is between ion $i$ and $III$.

Figure 4.C1(c): Examples from the first layer of octahedral sites in the fcc lattice. The longest distance within this layer is found between the ions $i$ and $II$. 

57
Figure 4.C1(d): Examples of connected nearest and next-nearest octahedral sites. The longest distance between ions in the first and second layer is found between the ions $i$ and $V$. 
CHAPTER 5

Shock wave equation of state for metals

ABSTRACT

A new theoretical shock wave equation of state was used to calculate the shock wave state of 35 different metals. The linear equation is applicable in two ways; (1) with data from infrared and X-ray measurements, and (2) with the experimental sound velocity and the bond dissociation energy.

With the first method the model calculations are within 1-10% accuracy for metals, which have an electron configuration in the gaseous atomic state with non-filled orbitals, and/or a dissociation energy of 40 kJ mol$^{-1}$ or higher.

With the second method the calculations are within 2-24% for metals with non-filled orbitals.
5.1 INTRODUCTION

In an earlier paper a theoretical expression for the shock wave equation of state or Rankine-Hugoniot equation of state (also called Hugoniot) was derived, that could be determined without any shock wave measurements using data from X-ray and infrared (IR) spectroscopy measurements.¹

In general a Hugoniot can be expressed as a linear relation between the velocity at which a shock wave travels, the shock wave velocity $U$, and the velocity at which the material moves directly after passage of the shock wave front, the mass displacement velocity, $u$. The Hugoniot is then written as:

$$U = C_0 + S u$$  \hspace{1cm} (5.1)

in which $C_0$ can be approximated with the bulk sound velocity, and $S$ is a material constant. The intercept $C_0$ will be higher than the experimental sound velocity, because the first is determined under plastic deformation conditions, and the latter under elastic deformation conditions.

Because many complex experiments are required to accurately determine the parameters of the Hugoniot, several models have been developed to calculate the parameters beforehand.

Rice for example derived an expression for $S$, that is valid at low stresses:²

$$S = \frac{1}{2}(1+\Gamma)$$  \hspace{1cm} (5.2)

in which $\Gamma$ is the Grüneisen coefficient, which characterizes the ratio of the thermal pressure, $P_T$, which is the pressure associated with the thermal motion of the ions and valence electrons, and the thermal energy, $E_T$, of the lattice:³

$$\Gamma = V \left( \frac{\partial P_T}{\partial E_T} \right)_V$$  \hspace{1cm} (5.3)

Dandache⁴ derived an equation for the Grüneisen coefficient as a function of volume [$\Gamma(V)$] for which the parameters can be calculated from the slope of the Hugoniot curve at $u=0$ km/s, and the Grüneisen coefficient, $\Gamma_0$, at standard conditions ($T=300$ K, $P=0.1$ MPa). This $\Gamma(V)$ function can be combined with the Mie-Grüneisen equation of state to calculate shock wave conditions.³ Dandache⁴ used these equations to calculate the thermodynamic states of Al, Cu, and Pb under shock wave conditions.

The approach used by Dandache is like many other methods based on the
Grüneisen coefficient. The Grüneisen coefficient at standard conditions, $\Gamma_0$, can be determined with:

$$\Gamma_0 = \frac{\alpha_v}{C_v \kappa_o \rho_0} \quad (5.4)$$

in which $\alpha_v$ is the isobaric volume expansion coefficient at constant pressure, $C_v$ is the heat capacity at constant volume, $\kappa_o$ is the isothermal compressibility at standard conditions ($T=300$ K, $P=0.1$ MPa), and $\rho_0$ is the density at standard conditions. The values of the parameters used to calculate $\Gamma_0$ with Eq. (5.4) can be determined experimentally. This would, however, require many experiments.

The two equations of state derived in our earlier paper, however, are based on parameters that can be calculated from non-shock wave data.

The first method uses:

$$U = \frac{A}{3B} + \left(\frac{A}{4} - \frac{1}{5}\right)u \quad (5.5)$$

in which parameters $A$ and $B$ can be calculated from IR data of the diatomic molecule:

$$A = \alpha \; r_0 \quad \text{and} \quad B = \sqrt{\frac{M}{2D}} \quad (5.6)$$

in which $r_0$ is the equilibrium distance, or bond length between the atoms in the solid, $M$ is the mass of the diatomic molecule, $D$ is the bond dissociation energy, which is the energy difference between a diatomic molecule in the gaseous phase in the ground state and with its atoms at infinite separation, and:

$$\alpha = 2\pi c \; \omega_0 \sqrt{\frac{\mu}{2D}} \quad (5.7)$$

in which $c_0$ is the velocity of light in vacuum, $\mu$ is the reduced mass of the diatomic molecule, and $\omega_0$ is the wavenumber (in m$^{-1}$) of the zero-order transition. The bond dissociation energy, $D$, and the wavenumber, $\omega_0$, can be determined from the infrared spectrum of the diatomic molecule, while the equilibrium distance, or bond length between the atoms, $r_0$, can be determined from X-ray data.

The second method, based on the bulk sound velocity, can be used to calculate the parameters if the data for the wavenumber of the zero-order
transition, \( \omega_0 \), are not available. This method is based on the fact that the first term of the Hugoniot can be approximated with the bulk sound velocity, \( C_0 \). This means that:

\[
U(\mu \downarrow 0) = \frac{A}{3B} \approx C_0
\] (5.8)

To calculate \( B \) only the dissociation energy, \( D \), and the mass of the diatomic molecule are needed [Eq. (5.6)], and if the bulk sound velocity \( C_{0,\text{expt}} \) is known, the equation of state becomes:

\[
U = C_{0,\text{expt}} + \left( \frac{3BC_{0,\text{expt}}}{4} - \frac{1}{5} \right) u
\] (5.9)

This second method is somewhat less accurate, because in practice there is a small difference between the intercept and the bulk sound velocity,\(^6\) due to the difference in elastic and plastic deformation mentioned earlier.

Terms of second order or higher were omitted in Eqs. (5.5) and (5.9), in view of the limited reliability of these higher order terms, and because commonly a linear equation is used [Eq.(5.1)] that in general fits the experimental data well. In our calculations we found that the second order term would be negative. Therefore, the calculated slope will in general be slightly higher than the slope of a linear fit through a non-linear experimental data set.

When applying the present equation of state it should be borne in mind that the model was derived from the Morse potential curve for diatomic molecules.\(^1\) Although the Morse potential has been applied successfully to a wide range of materials in infrared spectroscopy,\(^5\) it should be remembered that the conditions under which infrared spectroscopy is performed are not as extreme as in a shock wave. At high compressive stresses, the true interatomic potential of materials with an extremely asymmetric interatomic potential might deviate from a Morse potential determined with infrared spectroscopy. This criterion is not a severe limit to the model, because most metals do not show this asymmetric potential as will be shown in this paper. In a following paper this criterion will be discussed for ceramics and elemental boron.\(^7\)
5.1 BOND THEORY

In the present model\(^1\) bonds are considered between all the metal-ions around an interstitial site, and one adjacent interstitial site in the packing. The determination of these bonds was based on an interstitial-electron model\(^8\) for metals. In our present model bonds are assumed to exist between an ion and all ions that border the nearest and next-nearest interstitial sites around it. This means that bonds are assumed to exist between the ions of two adjacent interstitial sites. In this model the average bond length between the ions does not equal the nearest-neighbor distance, which is generally quoted as bond length,\(^9\) but the average distance between an ion, and the ions bordering nearest and next-nearest interstitial sites around it.

During shock compression of a polycrystalline metal sample every atom bordering an interstitial site can be moved in the direction of every other atom bordering the same site or an adjacent site (shown in Appendix A), because of the random orientation of the crystals with regard to the shock wave direction. This means that, if the strength of the lattice is described with a bond model, bonds must be considered between all ions around an interstitial site, and the adjacent interstitial sites.

The average bond length can be calculated from the lattice structure or packing, and the nearest-neighbor distance. For the regular packings that apply to most metals a constant ratio, \(q\), between the nearest-neighbor distance, and the average bond length can be found to apply to all metals with the same packing.

This ratio, \(q\), is found by averaging the dimensionless distances, \(x\) (relative to the nearest-neighbor distance, \(R_0\)), between an ion and the ions bordering the nearest and next-nearest interstitial sites around it over their number of occurrences, \(n_i\):

\[
q = \frac{\sum n_i x_i}{n_{tot}} \quad (5.10)
\]

The average bond length, \(r_0\), can be calculated from \(q\), and the nearest-neighbor distance, \(R_0\), in the lattice:

\[
r_0 = q R_0 \quad (5.11)
\]

The values of \(q\), for body centred cubic (bcc), face centred cubic (fcc), the hexagonal close (hcp) packings, and the layer structures of Bi and Sb are calculated in Appendix A.

63
5.3 CALCULATIONS WITH METHOD 1 (USING IR PARAMETERS)

In Table 5.1 the parameters necessary to calculate the shock state with the first method are shown for a number of metals. In Table 5.2 the results of the calculations with the first method are shown with the constants $A$, and $B$ determined with Eq. (5.6) from the data in Table 5.1. The average error is found from the deviation of the calculated shock velocity, relative to the experimental value, over the entire data range.

**Table 5.1:** The data necessary for calculations with method 1 for a number of metals (IR data). The metals Bi and Sb have a graphite-type layer structure.

<table>
<thead>
<tr>
<th>Metal</th>
<th>Disso-</th>
<th>Molar</th>
<th>Nearest-</th>
<th>Lattice</th>
<th>Wave</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>ciation</td>
<td>mass$^b$</td>
<td>neighbor</td>
<td>ratio,</td>
<td>number$^c$</td>
</tr>
<tr>
<td></td>
<td>energy$^a$ $D$</td>
<td>$M$ (g/mol)</td>
<td>distance$^b$ $R_0$ (nm)</td>
<td>$q$</td>
<td>$\omega_0$ ($10^3$ m$^{-1}$)</td>
</tr>
<tr>
<td>Ag (fcc)</td>
<td>163</td>
<td>215.74</td>
<td>0.2889</td>
<td>1.73</td>
<td>20.70</td>
</tr>
<tr>
<td>Au (fcc)</td>
<td>221.3</td>
<td>393.94</td>
<td>0.2884</td>
<td>1.73</td>
<td>19.09</td>
</tr>
<tr>
<td>Bi (layer)</td>
<td>200.22</td>
<td>417.96</td>
<td>0.309</td>
<td>1.13</td>
<td>17.271</td>
</tr>
<tr>
<td>Ca (fcc)</td>
<td>11.24$^c$</td>
<td>80.16</td>
<td>0.3947</td>
<td>1.73</td>
<td>6.50</td>
</tr>
<tr>
<td>Cs (bcc)</td>
<td>44.77</td>
<td>265.82</td>
<td>0.5309</td>
<td>1.61</td>
<td>4.20</td>
</tr>
<tr>
<td>Cu (fcc)</td>
<td>176.52</td>
<td>127.10</td>
<td>0.2556</td>
<td>1.73</td>
<td>26.089</td>
</tr>
<tr>
<td>K (bcc)</td>
<td>57.3</td>
<td>78.20</td>
<td>0.4544</td>
<td>1.61</td>
<td>9.264</td>
</tr>
<tr>
<td>Li (bcc)</td>
<td>106.48</td>
<td>13.88</td>
<td>0.3039</td>
<td>1.61</td>
<td>35.143</td>
</tr>
<tr>
<td>Mg (hcp)</td>
<td>8.55</td>
<td>48.62</td>
<td>0.31971</td>
<td>1.56</td>
<td>5.112</td>
</tr>
<tr>
<td>Na (bcc)</td>
<td>73.6</td>
<td>45.98</td>
<td>0.37157</td>
<td>1.61</td>
<td>15.913</td>
</tr>
<tr>
<td>Pb (fcc)</td>
<td>362.2</td>
<td>414.38</td>
<td>0.35003</td>
<td>1.73</td>
<td>11.91</td>
</tr>
<tr>
<td>Rb (bcc)</td>
<td>45.6</td>
<td>170.94</td>
<td>0.495</td>
<td>1.61</td>
<td>5.731</td>
</tr>
<tr>
<td>Sb (layer)</td>
<td>299.2</td>
<td>243.50</td>
<td>0.290</td>
<td>1.13</td>
<td>26.99</td>
</tr>
</tbody>
</table>

$^a$ Values are from Reference 9 unless indicated otherwise.
$^b$ Reference 9.
$^c$ Values from Reference 5.
Table 5.2: The results of the calculations with method 1 compared with the experimental shock data.\(^a\)

<table>
<thead>
<tr>
<th>Metal</th>
<th>Range(^a) in (u) (km/s)</th>
<th>Constant (A) [Eq.(5.6)]</th>
<th>Constant (B) [Eq.(5.6)] (s/km)</th>
<th>Calculated intercept (S) [Eq.(5.6)] (C_{0,calc}) (km/s)</th>
<th>Calculated slope (S)</th>
<th>Average error in calculated (U) (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ag</td>
<td>0.5-2.1</td>
<td>7.93</td>
<td>0.81</td>
<td>3.25</td>
<td>1.78</td>
<td>5.0</td>
</tr>
<tr>
<td>Au</td>
<td>0.4-1.7</td>
<td>8.46</td>
<td>0.94</td>
<td>2.99</td>
<td>1.92</td>
<td>6.7</td>
</tr>
<tr>
<td>Bi</td>
<td>0.6-2.5</td>
<td>5.80</td>
<td>1.02</td>
<td>1.89</td>
<td>1.25</td>
<td>5.9</td>
</tr>
<tr>
<td>Ca</td>
<td>0.5-4.7</td>
<td>7.89</td>
<td>1.89</td>
<td>1.39</td>
<td>1.77</td>
<td>21</td>
</tr>
<tr>
<td>Cs</td>
<td>1.3-3.8</td>
<td>5.83</td>
<td>1.72</td>
<td>1.13</td>
<td>1.26</td>
<td>8.1</td>
</tr>
<tr>
<td>Cu</td>
<td>0.2-4.2</td>
<td>6.72</td>
<td>0.60</td>
<td>3.73</td>
<td>1.48</td>
<td>2.7</td>
</tr>
<tr>
<td>K</td>
<td>1.3-4.5</td>
<td>5.27</td>
<td>0.83</td>
<td>2.13</td>
<td>1.12</td>
<td>0.98</td>
</tr>
<tr>
<td>Li</td>
<td>1.4-4.8</td>
<td>4.13</td>
<td>0.26</td>
<td>5.40</td>
<td>0.83</td>
<td>4.1</td>
</tr>
<tr>
<td>Mg</td>
<td>0.9-4.3</td>
<td>4.05</td>
<td>1.69</td>
<td>0.80</td>
<td>0.81</td>
<td>64</td>
</tr>
<tr>
<td>Na</td>
<td>1.3-4.3</td>
<td>5.01</td>
<td>0.56</td>
<td>2.99</td>
<td>1.05</td>
<td>2.2</td>
</tr>
<tr>
<td>Pb</td>
<td>0.3-2.8</td>
<td>5.14</td>
<td>0.76</td>
<td>2.26</td>
<td>1.08</td>
<td>9.6</td>
</tr>
<tr>
<td>Rb</td>
<td>1.2-4.0</td>
<td>5.89</td>
<td>1.37</td>
<td>1.43</td>
<td>1.27</td>
<td>7.2</td>
</tr>
<tr>
<td>Sb</td>
<td>1.0-2.7</td>
<td>5.31</td>
<td>0.64</td>
<td>2.78</td>
<td>1.13</td>
<td>6.4</td>
</tr>
</tbody>
</table>

\(^a\)Reference 6.

5.4 DISCUSSION METHOD 1

In Table 5.2 the results of the calculations with method 1 are shown. For two metals; Ca and Mg, the average deviation in the calculated shock wave velocity is much larger than 10%. When the data in Table 5.1 are studied these two metals have only one property in common; they have an extremely low dissociation energy. The results of the calculations for; Ag, Au, Cu, and Pb show that the fcc packing of Ca is an unlikely cause for the large deviation in
the calculated shock wave velocity. And although Mg is the only metal in Table 5.1 with a hcp structure calculations with method 2 will show that the hcp structure does not necessarily lead to a large deviation.

In Table 5.3 the results of the calculations with method 1 are shown with the dissociation energy and the electron configuration in the gaseous phase, the metals are given in order of increasing dissociation energy.

Table 5.3: The average error in the calculations of the shock wave velocity with method 1 of the metals in Table 5.1 in order of increasing dissociation energy, with their electron configuration in the gaseous phase.

<table>
<thead>
<tr>
<th>Metal</th>
<th>Electron configuration in gaseous state</th>
<th>Dissociation energy $D$ (kJ/mol)</th>
<th>Average error in calculated $U$ (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Mg</td>
<td>(Ne)3s$^2$</td>
<td>8.552</td>
<td>64</td>
</tr>
<tr>
<td>Ca</td>
<td>(Ar)4s$^2$</td>
<td>11.24$^c$</td>
<td>21</td>
</tr>
<tr>
<td>Cs</td>
<td>(Xe)6s$^1$</td>
<td>44.77</td>
<td>8.1</td>
</tr>
<tr>
<td>Rb</td>
<td>(Kr)5s$^1$</td>
<td>45.6</td>
<td>7.2</td>
</tr>
<tr>
<td>K</td>
<td>(Ar)4s$^1$</td>
<td>57.3</td>
<td>0.98</td>
</tr>
<tr>
<td>Na</td>
<td>(Ne)3s$^1$</td>
<td>73.6</td>
<td>2.2</td>
</tr>
<tr>
<td>Li</td>
<td>1s$^2$2s$^1$</td>
<td>106.48</td>
<td>4.1</td>
</tr>
<tr>
<td>Ag</td>
<td>(Kr)4d$^{10}$5s$^1$</td>
<td>163</td>
<td>5.0</td>
</tr>
<tr>
<td>Cu</td>
<td>(Ar)3d$^{10}$4s$^1$</td>
<td>176.52</td>
<td>2.7</td>
</tr>
<tr>
<td>Bi</td>
<td>(Xe)4f$^{14}$5d$^{10}$6s$^2$p$^3$</td>
<td>200.4</td>
<td>5.9</td>
</tr>
<tr>
<td>Au</td>
<td>(Xe)4f$^{14}$5d$^{10}$6s$^1$</td>
<td>221.3</td>
<td>6.7</td>
</tr>
<tr>
<td>Sb</td>
<td>(Kr)4d$^{10}$5s$^2$p$^3$</td>
<td>299.2</td>
<td>6.4</td>
</tr>
<tr>
<td>Pb</td>
<td>(Xe)4f$^{14}$5d$^{10}$6s$^2$p$^2$</td>
<td>362.2</td>
<td>9.6</td>
</tr>
</tbody>
</table>

$^a$ Reference 9.
$^b$ Values are from Reference 9 unless indicated otherwise.
$^c$ Value from Reference 5.
This table shows that Mg and Ca, which have fully filled outer orbitals and an extremely low dissociation energy can clearly be distinguished from metals for which method 1 works successfully. The calculations are within 1-10% average error for metals with unfilled outer orbitals in the gaseous state. The low dissociation energy and large error in Ca and Mg indicate that these metals have orbitals that can not accurately be described with a Morse interatomic potential. Apparently the model is not applicable to metals with filled outer orbitals, which can often also be recognized by their low dissociation energy.

5.5 CALCULATIONS WITH METHOD 2 (USING $C_{0,expt}$)

Shock wave parameters calculated from the experimental sound velocity and dissociation energy, without spectroscopic data, are shown in Table 5.4 for a large range of metals. The results of the calculations with method 2 are shown in Table 5.5. The average error is found by averaging the relative error in the calculated shock velocity, compared to the experimental value over the entire data range.

Table 5.4: The data for the calculations of shock wave parameters with method 2 for the metals for which the experimental bulk sound velocity, $C_{0,expt}$, was available.

<table>
<thead>
<tr>
<th>Metal</th>
<th>Experimental bulk sound velocity</th>
<th>Dissociation energy</th>
<th>Mass of the diatomic molecule</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>$C_{0,expt}$ (km/s)</td>
<td>$D$ (kJ/mol)</td>
<td>$M$ (g/mol)</td>
</tr>
<tr>
<td>Ag (fcc)</td>
<td>3.176</td>
<td>163 ±8</td>
<td>107.87</td>
</tr>
<tr>
<td>Au (fcc)</td>
<td>2.945</td>
<td>221 ±2</td>
<td>196.97</td>
</tr>
<tr>
<td>Be (hcp)</td>
<td>8.102</td>
<td>59</td>
<td>9.01</td>
</tr>
<tr>
<td>Bi (layer)</td>
<td>1.864</td>
<td>200 ±8</td>
<td>208.98</td>
</tr>
<tr>
<td>Ca (fcc)</td>
<td>3.317</td>
<td>11.24$^d$</td>
<td>40.08</td>
</tr>
<tr>
<td>Cd (hcp)</td>
<td>2.571</td>
<td>7.37</td>
<td>112.41</td>
</tr>
<tr>
<td>Ce (fcc)</td>
<td>1.742</td>
<td>245.2</td>
<td>140.12</td>
</tr>
<tr>
<td>Element</td>
<td>Value 1</td>
<td>Value 2</td>
<td>Value 3</td>
</tr>
<tr>
<td>---------</td>
<td>---------</td>
<td>---------</td>
<td>---------</td>
</tr>
<tr>
<td>Co (hcp)</td>
<td>4.529</td>
<td>167 ±25</td>
<td>58.93</td>
</tr>
<tr>
<td>Cu (fcc)</td>
<td>3.927</td>
<td>177 ±2</td>
<td>63.55</td>
</tr>
<tr>
<td>Hg (liq.)</td>
<td>1.451</td>
<td>8 ±2</td>
<td>200.59</td>
</tr>
<tr>
<td>Ho (hcp)</td>
<td>2.386</td>
<td>84 ±20</td>
<td>164.93</td>
</tr>
<tr>
<td>La (hcp)</td>
<td>2.048</td>
<td>247 ±20</td>
<td>138.91</td>
</tr>
<tr>
<td>Mg (hcp)</td>
<td>4.440</td>
<td>8.552±0.004</td>
<td>24.31</td>
</tr>
<tr>
<td>Mo (bcc)</td>
<td>5.033</td>
<td>406 ±20</td>
<td>95.94</td>
</tr>
<tr>
<td>Nd (hcp)</td>
<td>2.157</td>
<td>≤ 163</td>
<td>144.24</td>
</tr>
<tr>
<td>Ni (fcc)</td>
<td>4.523</td>
<td>203.3±1.0</td>
<td>58.70</td>
</tr>
<tr>
<td>Pb (fcc)</td>
<td>2.002</td>
<td>362 ±4</td>
<td>207.2</td>
</tr>
<tr>
<td>Pd (fcc)</td>
<td>3.829</td>
<td>75</td>
<td>106.4</td>
</tr>
<tr>
<td>Pt (fcc)</td>
<td>3.528</td>
<td>357 ±15</td>
<td>195.97</td>
</tr>
<tr>
<td>Rh (fcc)</td>
<td>4.282</td>
<td>285 ±20</td>
<td>102.91</td>
</tr>
<tr>
<td>Sb (layer)</td>
<td>3.166</td>
<td>299 ±6</td>
<td>121.75</td>
</tr>
<tr>
<td>Sn (tetr.)</td>
<td>2.755</td>
<td>195 ±20</td>
<td>118.69</td>
</tr>
<tr>
<td>Sr (fcc)</td>
<td>2.118</td>
<td>15.5±0.4</td>
<td>87.62</td>
</tr>
<tr>
<td>Tb (hcp)</td>
<td>2.199</td>
<td>131 ±25</td>
<td>158.93</td>
</tr>
<tr>
<td>Th (fcc)</td>
<td>2.327</td>
<td>≤ 289</td>
<td>232.04</td>
</tr>
<tr>
<td>Ti (hcp)</td>
<td>4.937</td>
<td>141 ±20</td>
<td>47.90</td>
</tr>
<tr>
<td>U (ortho.)</td>
<td>2.431</td>
<td>222 ±20</td>
<td>238.03</td>
</tr>
<tr>
<td>V (bcc)</td>
<td>5.307</td>
<td>242 ±20</td>
<td>50.94</td>
</tr>
<tr>
<td>Y (hcp)</td>
<td>3.274</td>
<td>159 ±20</td>
<td>88.91</td>
</tr>
<tr>
<td>Yb (fcc)</td>
<td>1.446</td>
<td>20 ±17</td>
<td>173.04</td>
</tr>
</tbody>
</table>

* Reference 6.
* Values are from Reference 9 unless indicated otherwise.
* Reference 9.
* Value from Reference 5.
Table 5.5: The results of the calculations with method 2 compared with the experimental shock data.

<table>
<thead>
<tr>
<th>Metal</th>
<th>Data range in $u$ (km/s)</th>
<th>Intercept ($C_{0,\text{expt}}$ (km/s))</th>
<th>Constant $B$ [Eq.(5.6)] (s/km)</th>
<th>Calculated slope $S$ [Eq.(5.9)]</th>
<th>Average error in calculated $U$ (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ag (fcc)</td>
<td>0.5-2.1</td>
<td>3.176</td>
<td>0.81</td>
<td>1.74</td>
<td>2.6</td>
</tr>
<tr>
<td>Au (fcc)</td>
<td>0.4-1.7</td>
<td>2.945</td>
<td>0.94</td>
<td>1.88</td>
<td>5.1</td>
</tr>
<tr>
<td>Be (hcp)</td>
<td>0.5-3.9</td>
<td>8.102</td>
<td>0.39</td>
<td>2.17</td>
<td>20</td>
</tr>
<tr>
<td>Bi (layer)</td>
<td>0.6-2.5</td>
<td>1.864</td>
<td>1.02</td>
<td>1.23</td>
<td>7.1</td>
</tr>
<tr>
<td>Ca (fcc)</td>
<td>0.5-4.7</td>
<td>3.317</td>
<td>1.88</td>
<td>4.50</td>
<td>121</td>
</tr>
<tr>
<td>Cd (hcp)</td>
<td>0.6-2.4</td>
<td>2.571</td>
<td>3.91</td>
<td>7.33</td>
<td>160</td>
</tr>
<tr>
<td>Ce (fcc)</td>
<td>0.4-3.2</td>
<td>1.742</td>
<td>0.75</td>
<td>0.79</td>
<td>23</td>
</tr>
<tr>
<td>Co (hcp)</td>
<td>0.5-2.3</td>
<td>4.529</td>
<td>0.59</td>
<td>1.82</td>
<td>8.2</td>
</tr>
<tr>
<td>Cu (fcc)</td>
<td>0.2-4.2</td>
<td>3.927</td>
<td>0.60</td>
<td>1.57</td>
<td>2.6</td>
</tr>
<tr>
<td>Hg (liq.)</td>
<td>0.6-1.0</td>
<td>1.451</td>
<td>5.01</td>
<td>5.24</td>
<td>58</td>
</tr>
<tr>
<td>Ho (hcp)</td>
<td>0.4-3.0</td>
<td>2.386</td>
<td>1.40</td>
<td>2.31</td>
<td>51</td>
</tr>
<tr>
<td>La (hcp)</td>
<td>0.4-3.3</td>
<td>2.048</td>
<td>0.74</td>
<td>0.95</td>
<td>11</td>
</tr>
<tr>
<td>Mg (hcp)</td>
<td>0.9-4.3</td>
<td>4.440</td>
<td>1.69</td>
<td>5.41</td>
<td>130</td>
</tr>
<tr>
<td>Mo (bcc)</td>
<td>0.4-2.5</td>
<td>5.033</td>
<td>0.48</td>
<td>1.64</td>
<td>6.3</td>
</tr>
<tr>
<td>Nd (hcp)</td>
<td>0.3-3.1</td>
<td>2.157</td>
<td>0.94</td>
<td>1.32</td>
<td>11</td>
</tr>
<tr>
<td>Ni (fcc)</td>
<td>0.5-2.1</td>
<td>4.523</td>
<td>0.53</td>
<td>1.62</td>
<td>2.4</td>
</tr>
<tr>
<td>Pb (fcc)</td>
<td>0.3-2.8</td>
<td>2.002</td>
<td>0.76</td>
<td>0.94</td>
<td>13</td>
</tr>
<tr>
<td>Pd (fcc)</td>
<td>0.4-2.3</td>
<td>3.829</td>
<td>1.19</td>
<td>3.22</td>
<td>28</td>
</tr>
<tr>
<td>Pt (fcc)</td>
<td>0.3-3.6</td>
<td>3.528</td>
<td>0.73</td>
<td>1.76</td>
<td>7.0</td>
</tr>
<tr>
<td>Rh (fcc)</td>
<td>0.4-2.2</td>
<td>4.282</td>
<td>0.60</td>
<td>1.73</td>
<td>3.1</td>
</tr>
<tr>
<td>Sb (layer)</td>
<td>1.0-2.7</td>
<td>3.166</td>
<td>0.64</td>
<td>1.31</td>
<td>12</td>
</tr>
<tr>
<td>Sn (tet.r.)</td>
<td>0.3-3.1</td>
<td>2.755</td>
<td>0.77</td>
<td>1.41</td>
<td>1.9</td>
</tr>
</tbody>
</table>

69
(Table 5.5 continued)

<table>
<thead>
<tr>
<th>Metal</th>
<th>Electron configuration</th>
<th>Dissociation energy $D$ (kJ/mol)</th>
<th>Average error in $U$ (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Sr (fcc)</td>
<td>0.5-4.2</td>
<td>2.118</td>
<td>2.38</td>
</tr>
<tr>
<td>Tb (hcp)</td>
<td>0.7-3.1</td>
<td>2.199</td>
<td>1.10</td>
</tr>
<tr>
<td>Th (fcc)</td>
<td>0.5-2.3</td>
<td>2.327</td>
<td>0.89</td>
</tr>
<tr>
<td>Ti (hcp)</td>
<td>0.4-3.2</td>
<td>4.937</td>
<td>0.58</td>
</tr>
<tr>
<td>U (ortho.)</td>
<td>0.3-3.5</td>
<td>2.431</td>
<td>1.04</td>
</tr>
<tr>
<td>V (bcc)</td>
<td>0.6-2.6</td>
<td>5.307</td>
<td>0.46</td>
</tr>
<tr>
<td>Y (hcp)</td>
<td>0.3-3.6</td>
<td>3.274</td>
<td>0.75</td>
</tr>
<tr>
<td>Yb (fcc)</td>
<td>0.3-3.3</td>
<td>1.446</td>
<td>2.91</td>
</tr>
</tbody>
</table>

*Reference 6.

### 5.6 DISCUSSION METHOD 2

In Table 5.6 the results of the calculations with method 2 are shown with the electron configuration and dissociation energy of the metals.

#### Table 5.6: The average errors in the calculations of the shock wave velocity with method 2 of the metals in Tables 5.4 and 5.5 in order of increasing dissociation energy, with their electron configuration in gaseous phase.

<table>
<thead>
<tr>
<th>Metal</th>
<th>Electron configuration in gaseous phase</th>
<th>Dissociation energy $D$ (kJ/mol)</th>
<th>Average error in $U$ (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Mg</td>
<td>(Ne)$3s^2$</td>
<td>8.552</td>
<td>130</td>
</tr>
<tr>
<td>Ca</td>
<td>(Ar)$4s^2$</td>
<td>11.24</td>
<td>121</td>
</tr>
<tr>
<td>Sr</td>
<td>(Kr)$5s^2$</td>
<td>15.5</td>
<td>110</td>
</tr>
<tr>
<td>Be</td>
<td>$1s^22s^2$</td>
<td>59</td>
<td>20</td>
</tr>
<tr>
<td>Pd</td>
<td>(Kr)$4d^{10}$</td>
<td>75</td>
<td>28</td>
</tr>
<tr>
<td>Cd</td>
<td>(Kr)$4d^{10}5s^2$</td>
<td>7.37</td>
<td>160</td>
</tr>
</tbody>
</table>

70
(Table 5.6 continued)

<table>
<thead>
<tr>
<th>Element</th>
<th>Electron Configuration</th>
<th>Symbol</th>
<th>Value</th>
</tr>
</thead>
<tbody>
<tr>
<td>Hg</td>
<td>(Xe)4f^45d^106s^2</td>
<td>Hg</td>
<td>8</td>
</tr>
<tr>
<td>Yb</td>
<td>(Xe)4f^46s^2</td>
<td>Yb</td>
<td>20.5</td>
</tr>
<tr>
<td>Ho</td>
<td>(Xe)4f^416s^2</td>
<td>Ho</td>
<td>84</td>
</tr>
<tr>
<td>Tb</td>
<td>(Xe)4f^46s^2</td>
<td>Tb</td>
<td>131.4</td>
</tr>
<tr>
<td>Ti</td>
<td>(Ar)3d^24s^2</td>
<td>Ti</td>
<td>141.4</td>
</tr>
<tr>
<td>Y</td>
<td>(Kr)4d^15s^2</td>
<td>Y</td>
<td>159</td>
</tr>
<tr>
<td>Nd</td>
<td>(Xe)4f^46s^2</td>
<td>Nd</td>
<td>≤163</td>
</tr>
<tr>
<td>Co</td>
<td>(Ar)3d^74s^2</td>
<td>Co</td>
<td>167</td>
</tr>
<tr>
<td>Ni</td>
<td>(Ar)3d^84s^2</td>
<td>Ni</td>
<td>203.26</td>
</tr>
<tr>
<td>U</td>
<td>(Rn)5f^66d^17s^2</td>
<td>U</td>
<td>222</td>
</tr>
<tr>
<td>V</td>
<td>(Ar)3d^34s^2</td>
<td>V</td>
<td>242.3</td>
</tr>
<tr>
<td>Ce</td>
<td>(Xe)4f^55d^16s^2</td>
<td>Ce</td>
<td>245.2</td>
</tr>
<tr>
<td>La</td>
<td>(Xe)5d^16s^2</td>
<td>La</td>
<td>247</td>
</tr>
<tr>
<td>Th</td>
<td>(Rn)6d^27s^2</td>
<td>Th</td>
<td>≤289</td>
</tr>
<tr>
<td>Sn</td>
<td>(Kr)4d^{10}5s^2p^2</td>
<td>Sn</td>
<td>195.4</td>
</tr>
<tr>
<td>Bi</td>
<td>(Xe)4f^45d^{10}6s^2p^3</td>
<td>Bi</td>
<td>200.4</td>
</tr>
<tr>
<td>Pb</td>
<td>(Xe)4f^45d^{10}6s^2p^2</td>
<td>Pb</td>
<td>362.2</td>
</tr>
<tr>
<td>Sb</td>
<td>(Kr)4d^{10}5s^2p^3</td>
<td>Sb</td>
<td>299.2</td>
</tr>
<tr>
<td>Ag</td>
<td>(Kr)4d^{10}5s^1</td>
<td>Ag</td>
<td>163</td>
</tr>
<tr>
<td>Cu</td>
<td>(Ar)3d^{10}4s^1</td>
<td>Cu</td>
<td>176.52</td>
</tr>
<tr>
<td>Au</td>
<td>(Xe)4f^45d^{10}6s^1</td>
<td>Au</td>
<td>221.3</td>
</tr>
<tr>
<td>Rh</td>
<td>(Kr)4d^85s^1</td>
<td>Rh</td>
<td>285.4</td>
</tr>
<tr>
<td>Pt</td>
<td>(Xe)4f^45d^6s^1</td>
<td>Pt</td>
<td>257.3</td>
</tr>
<tr>
<td>Mo</td>
<td>(Kr)4d^55s^1</td>
<td>Mo</td>
<td>406</td>
</tr>
</tbody>
</table>

^a Reference 9.
^b Values are from Reference 9 unless indicated otherwise.
^c Value from Reference 5.
The calculations are within 2-24% average error for metals with unfilled outer orbitals with the exception of Ho, which has a very low bond dissociation energy. The calculations with method 2 using $C_{0,\text{expt}}$ are generally less accurate than with method 1, which uses more parameters. This can be explained by the fact that $C_{0,\text{expt}}$ is only an approximation of the intercept. This can be seen in the Tables 5.2 and 5.4 where for Pb the difference between $C_{0,\text{calc}}$ and $C_{0,\text{expt}}$ is larger than the average error in $U$.

For most metals that have fully filled outer orbitals in free atomic gaseous state the calculations are not within 25% error. These metals also have a low dissociation energy. The low dissociation energy and large error indicate that these metals have orbitals that can not accurately be described with a Morse interatomic potential. Apparently method 2 is not applicable to metals with filled outer orbitals either.

It is interesting to note that the shock wave velocity, $U$, for Be, which has a relatively high bond dissociation energy compared with metals with a similar electron configuration (Mg, Sr, and Ca), is calculated within 20% accuracy. In Mg the valence electrons are screened from the nucleus by the 1s², 2s², and 2p⁶ orbitals, in Ca and Sr this screening effect is even stronger. In Be the only orbital between the valence electrons and the nucleus is the 1s² orbital. The resulting increase in the bonding character of the valence electrons to the Be nucleus could explain the relatively high value of $D$. This high value for $D$ increases the symmetry of the real potential and therefore the success of the calculation based on the Morse potential. A similar effect might occur with Pd. Although the valence electrons are screened from the nucleus by a large number of orbitals, the high charge (10) of the nucleus increases the attraction on the valence electrons, causing a high value of $D$, and a relatively low error in the calculations.

5.7 COMPARISON WITH LITERATURE

In Table 5.7 the slope, $S$, is shown as calculated with Eq. (5.2) using the Grüneisen coefficients given by Rice,² and the average error in the calculation of the shock wave velocity, $U$, with this $S$ using Eq. (5.1). These results with Rice's parameters are compared with the results of methods 1 and 2 of the present model. In Fig. 1 the results of the calculations with both methods of the present model, and Rice's model² are compared with experimental data from Marsh² for gold (Au). Typically all models yield a very good result for the low mass displacement velocity, $u$, region, and a somewhat less accurate calculation for higher values of $u$. Because Rice's model and method 2 both use the
experimental sound velocity as intercept this result is to be expected. The bulk sound velocity can almost be considered to be a shock wave measurement, and calculations near this value are, therefore, often accurate. Method 1 is apparently capable of calculating the intercept. The deviation at high values for \( u \) is probably due to the non-linearity of the shock wave properties, which is not covered by either model. The deviation indicates a negative second order term as we expected from our calculations.\(^1\)

**Table 5.7:** Comparison of the results with Rice's model\(^a\) [Eq. (5.2)], and methods 1 and 2 of the present model. The large error for method 2 for Ti is caused by a phase transformation\(^b\) (see Fig. 5.2).

<table>
<thead>
<tr>
<th>metal</th>
<th>slope from Rice(^a) ( S ) [Eq.(5.2)]</th>
<th>average error in ( U ) with ( S ) from Rice (%)</th>
<th>average error in ( U ) with method 1 (%)</th>
<th>average error in ( U ) with method 2 (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ag</td>
<td>1.74</td>
<td>2.6</td>
<td>5.0</td>
<td>2.6</td>
</tr>
<tr>
<td>Au</td>
<td>2.03</td>
<td>8.2</td>
<td>6.7</td>
<td>5.1</td>
</tr>
<tr>
<td>Co</td>
<td>1.50</td>
<td>2.3</td>
<td></td>
<td>8.2</td>
</tr>
<tr>
<td>Cu</td>
<td>1.52</td>
<td>1.4</td>
<td>2.7</td>
<td>2.6</td>
</tr>
<tr>
<td>Mo</td>
<td>1.29</td>
<td>0.7</td>
<td></td>
<td>6.3</td>
</tr>
<tr>
<td>Pb</td>
<td>1.89</td>
<td>9.2</td>
<td>9.6</td>
<td>13</td>
</tr>
<tr>
<td>Pt</td>
<td>1.82</td>
<td>8.7</td>
<td></td>
<td>7.0</td>
</tr>
<tr>
<td>Rh</td>
<td>1.63</td>
<td>3.6</td>
<td></td>
<td>3.1</td>
</tr>
<tr>
<td>Sn</td>
<td>1.52</td>
<td>4.3</td>
<td></td>
<td>1.9</td>
</tr>
<tr>
<td>Ti</td>
<td>1.09</td>
<td>2.0</td>
<td></td>
<td>22</td>
</tr>
<tr>
<td>Th</td>
<td>1.06</td>
<td>3.0</td>
<td></td>
<td>7.6</td>
</tr>
<tr>
<td>overall</td>
<td></td>
<td>4.18</td>
<td>(5.35)</td>
<td>6.00</td>
</tr>
</tbody>
</table>

\(^a\)Reference 2.
\(^b\)Reference 10.
With the Rice's model\textsuperscript{2} the shock wave states of Be, Cd, Mg, and Pd can also be calculated. Because Rice\textsuperscript{2} uses experimental data, his model is not sensitive for the shape of the potential curve, as is our present model. The results for these metals are not compared, because the metals do not satisfy the criterion of the present model, viz. the presence of an unfilled outer orbital.

For four of the metals in Table 5.7 all IR data necessary for the calculations with method 1 of the present model were known. For these metals calculations with Rice's parameters show an overall average error of 5.4\%. Calculations with method 1 show an overall average error of 6.0\%. The difference in the accuracy of these models is small, favouring Rice's model. The real difference between the models is then found in the source of the parameters.

![Graph showing comparison of Rice's model and results of methods 1 and 2 with experimental data for Au.]

**Figure 5.1:** Comparison of Rice's model and results of methods 1 and 2 of the present model with experimental data\textsuperscript{6} for Au.
For the calculations with Rice's parameters the experimental sound velocity and the Grüneisen coefficient must be known. The Grüneisen coefficients used by Rice are calculated from experimental data for the bulk modulus, the thermal expansion coefficient, the theoretical maximum density, and the heat capacity, as shown in Eq. (5.4). In the case of metals these required data are usually readily available, but for materials such as ceramics, which will be treated in a following paper, the experimental determination of all five above-mentioned parameters often yields problems, one example being the difficulty in obtaining a pure, fully dense sample of the material.

For the calculations with method 1 also five parameters need to be found: the nearest-neighbor distance, $R_0$, and its ratio, $q$, over the bond length, the atomic mass of the elements, the bond dissociation energy, and the wavenumber of the zero-order transition. The first two parameters can be found from X-ray measurements. The atomic mass of the elements is known. And the last two parameters can be found from IR spectroscopy. Both methods, X-ray and IR spectroscopy, can be performed on small, even porous samples, and are, therefore, ideally suited for new and ceramic materials.

When applied to new materials the small difference in accuracy, which is not really significant considering the small number of metals compared, is
completely outweighed by the difference in accessibility of the necessary data. 

For the 11 metals shown in Table 5.7 the calculations with Rice's parameters have an overall average deviation of 4.2%. Calculations with method 2 of the present model have an overall average deviation of 7.2%. This relatively large average deviation is mainly due to the large error in the calculations for Ti. This large error is caused by a phase transformation at \( u = 0.5 \) km/s, discussed extensively by Zhukov,\(^6\) as shown in Fig. 5.2. Omitting the result for Ti, because of the phase transformation, the calculations with method 2 show an overall average deviation of 5.7%. It is not clear why Rice's model does not show a large deviation for Ti. For the calculations with method 2 of the present model it is also necessary to know the experimental sound velocity, but beside the sound velocity only the bond dissociation energy, and the atomic mass have to be known. The atomic mass for all elements is known,\(^9\) and the bond dissociation energy can be found by e.g. IR spectroscopy, if not already known.\(^9\)

When not considering the difference in the calculation for Ti, because of the phase transformation, the difference in accuracy between Rice's model and method 2 is small (4.2% compared to 5.7% overall average deviation); it should be borne in mind that there are five experimental parameters needed for Rice's model, and only two for method 2. One parameter, the bulk sound velocity, they even have in common. This advantage of method 2, and the fact that its accuracy is acceptable for most applications makes method 2 an attractive model for new and ceramic materials.

5.8 CONCLUSIONS

Calculations on shock wave data\(^6\) of 35 different metals show that the present model is applicable in two ways; 1. with data from infrared and X-ray measurements, or 2. with the experimental sound velocity and the bond dissociation energy.

Using method 1 the model calculates the shock velocity, \( U \), from the mass displacement velocity, \( u \), within 1-10% accuracy for metals that have an electron configuration in the gaseous atomic state with non-filled orbitals, and/or a dissociation energy of about 40 kJ/mol or higher.

Using method 2 the accuracy of the calculations decreases to 2-24% for metals with non-filled orbitals, and about 100 kJ/mol seems a safe lower limit for the dissociation energy.

With both methods the accuracy of the calculations increases with the dissociation energy for groups of metals with similar electron configuration.
Comparison with other models, like Rice's model show that the present model is attractive for calculations on new materials, because of the comparatively easy accessibility of the required parameters. The results indicate that the model is reliable for the calculation of shock parameters for metals that comply with certain well-defined criteria.

5.9 REFERENCES

1 Chapter 4 of this work.
7 Chapter 6 of this work.
APPENDIX A: CALCULATION OF LATTICE CONSTANTS

For the body-centered-cubic (bcc) packing [8 atoms on the corners of a cube and one in the center, see Fig. 5.A1(a)] the ratio, $q$, is calculated from the distances in Table 5.A1. The average ratio, $q$, for a bcc packing calculated with Eq. (5.10) from Table 5.A1 is 1.61.

Figure 5.A1(a): Schematic representation of a bcc lattice. Bonds are shown between ion $i$ and ions of type $I$ to $IV$.

Table 5.A1: The dimensionless distances, $x$, ($x=r_i/R_o$ with $R_o$ the nearest-neighbor distance), between atoms in a bcc packing [shown in Fig. 5.A1(a)], and their number of occurrences, $n$, for a single atom. Ions at distances $x>\sqrt{11/3}$ do not border one of the nearest or next nearest interstitial sites, and are, therefore, considered to be screened.

<table>
<thead>
<tr>
<th>Ion No. [Fig. 5.A1(a)]</th>
<th>Distance to ion $i$</th>
<th>Number of occurrences $n$</th>
</tr>
</thead>
<tbody>
<tr>
<td>$I$</td>
<td>1</td>
<td>8</td>
</tr>
<tr>
<td>$II$</td>
<td>$\sqrt{4/3}$</td>
<td>6</td>
</tr>
<tr>
<td>$III$</td>
<td>$\sqrt{8/3}$</td>
<td>12</td>
</tr>
<tr>
<td>$IV$</td>
<td>$\sqrt{11/3}$</td>
<td>24</td>
</tr>
</tbody>
</table>

78
Figure 5.A1(b): The octahedral interstitial site that connects ions of type I and II to ion i.

Figure 5.A1(c): Schematic representation of the nearest and next-nearest octahedral interstitial sites in the bcc lattice, which connect ions of type III and IV to ion i.
In the bcc packing ion \( i \), and the ions of type \( I \) and \( II \) border an octahedral interstitial site, as shown in Fig. 5.A1(b). The ions of type \( III \) and \( IV \) are connected to ion \( i \) by two octahedral interstitial sites, as shown in Fig. 5.A1(c). Ions further away than type \( IV \) do not border a next-nearest interstitial site.

For the face-centered-cubic (fcc) packing [8 ions on the corners of a cube and six on the faces of the cube, shown in [Fig. 5.A2(a)] the lattice ratio, \( q \), is calculated from the distances between ion \( i \) and the ions \( I-V \) [shown in Fig. 5.A2(a)] as gathered in Table 5.A2. Using Eq. (5.10) this yields an average ratio, \( q \), for a fcc packing of \( q=1.73 \).

**Table 5.A2:** The distance between ions in a fcc packing, \( x \), \((x=r/R_o \) with \( R_o \) the nearest-neighbor distance), and their number of occurrences, \( n \), for a single ion. The fcc packing is shown in Fig. 5.A2(a). Ions at the opposite corners of the cubes face [such as ion \( IV \) in Fig. 5.A2(a)] are considered to be screened by the ions on the cube face [such as ion \( I \) in Fig. 5.A2(a)], and ions at distances \( x>\sqrt{5} \) [such as ion \( VI \) in Fig. 5.A2(a)] do not border the nearest or next-nearest layer of interstitial sites, and are, therefore, not considered for bonds.

<table>
<thead>
<tr>
<th>Type of ion [Fig. 5.A2(a)]</th>
<th>Distance to ion ( i ) ((R_o^{-1}))</th>
<th>Number of occurrences ( n_i )</th>
</tr>
</thead>
<tbody>
<tr>
<td>( I )</td>
<td>1</td>
<td>12</td>
</tr>
<tr>
<td>( II )</td>
<td>( \sqrt{2} )</td>
<td>12</td>
</tr>
<tr>
<td>( III )</td>
<td>( \sqrt{3} )</td>
<td>24</td>
</tr>
<tr>
<td>( IV )</td>
<td>2</td>
<td>0 (screened)</td>
</tr>
<tr>
<td>( V )</td>
<td>( \sqrt{5} )</td>
<td>24</td>
</tr>
</tbody>
</table>
Figure 5.2A(a): Schematic representation of a fcc lattice. The ions in the vicinity of ion $i$ are numbered in order of increasing distance. Ion $IV$ is screened from ion $i$ by $I$. Ion $V$ is the furthest ion still bordering the next-nearest layer of interstitial sites [see also (d)]. Ion $VI$ and those that are further away do not border one of the nearest or the next-nearest interstitial sites [see (b) and (d)] and are, therefore, considered screened.

In Fig. 5.2A(b) the adjacent tetrahedral and octahedral sites in the fcc lattice are shown that connect the ions of type $i$, $I$, and $III$. Within these two layers of interstitial sites, ions of type $III$ are the most distant ions that are still considered for a bond. In Fig. 5.2A(c) two octahedral sites in the nearest layer of interstitial sites are shown that border the ions of type $i$ and $II$. In Fig. 5.2A(d) examples of octahedral sites in the nearest and next-nearest layer are shown. The largest distance that can be covered with two layers of interstitial sites is found in this figure; between ions of type $i$ and type $V$.
Figure 5.A2(b): Examples of the nearest and next-nearest layer of interstitial sites in the fcc lattice: a tetrahedral interstitial site in the nearest layer and an adjacent octahedral site in the next-nearest layer. The longest distance between the ions in these layers is between ion $i$ and $III$.

Figure 5.A2(c): Examples from the first layer of octahedral sites in the fcc lattice. The longest distance within this layer is found between the ions $i$ and $II$. 

82
The graphite-like layer structure of Bi and Sb is shown in Fig. 5.A3. The structures are not regular packings and the value of $q$ is, therefore, calculated somewhat differently. In this layer structure it is assumed that a layer functions as a screen for the electrons. Bonds are, therefore, only considered between the three direct neighbors, the three nearest ions of the next layer, and the ions directly above and below. The ratio, $q$, is calculated from the distances in Table 5.A3. The average ratio, $q$, for Bi and Sb is 1.13.
Figure 5.A3: Schematic representation of the layered packing of Bi and Sb with the relevant bonds.

Table 5.A3: The distances, $x$, ($x = r_i/R_0$ with $R_0$ the nearest-neighbor distance), between atoms in the layered packings of Bi and Sb (shown in Fig. 5.A3), and their number of occurrences, $n$, for a single atom. Ions "behind" a layer are considered to be screened.

<table>
<thead>
<tr>
<th>Metal</th>
<th>Ion No. [Fig. 5.A3]</th>
<th>Distance to ion $i$ ($x$)</th>
<th>Number of occurrences ($n$)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Bi</td>
<td>I</td>
<td>1</td>
<td>3</td>
</tr>
<tr>
<td></td>
<td>II</td>
<td>1.15</td>
<td>3</td>
</tr>
<tr>
<td></td>
<td>III</td>
<td>1.29</td>
<td>2</td>
</tr>
<tr>
<td>Sb</td>
<td>I</td>
<td>1</td>
<td>3</td>
</tr>
<tr>
<td></td>
<td>II</td>
<td>1.15</td>
<td>3</td>
</tr>
<tr>
<td></td>
<td>III</td>
<td>1.30</td>
<td>2</td>
</tr>
</tbody>
</table>

*Reference 11.
For the hexagonal-close-packing (hcp) [see Fig. 5.A4(a)] the ratio, \( q \), is calculated from the distances in Table 5.A4. The average ratio, \( q \), for a hcp structure calculated with Eq. (5.10) from Table 5.A4 is 1.56.

**Table 5.A4:** The dimensionless distances, \( x \), (\( x = r_i / R_0 \) with \( R_0 \) the nearest-neighbor distance), between atoms in a hcp packing (shown in Fig. 5.A4), and their number of occurrences, \( n \), for a single atom. The distance between atoms in a hcp structure, ions at distances \( x > \sqrt{(11/3)} \) do not border one of the nearest or next-nearest interstitial sites, and are, therefore, considered to be screened.

<table>
<thead>
<tr>
<th>Ion No. [Fig. 5.A4(b)]</th>
<th>Distance to ion ( i )</th>
<th>Number of occurrences</th>
</tr>
</thead>
<tbody>
<tr>
<td>( I )</td>
<td>1</td>
<td>12</td>
</tr>
<tr>
<td>( II )</td>
<td>( \sqrt{2} )</td>
<td>6</td>
</tr>
<tr>
<td>( III )</td>
<td>( \sqrt{3} )</td>
<td>18</td>
</tr>
<tr>
<td>( IV )</td>
<td>( 2\sqrt{(2/3)} )</td>
<td>2</td>
</tr>
<tr>
<td>( V )</td>
<td>( \sqrt{(11/3)} )</td>
<td>12</td>
</tr>
</tbody>
</table>

In Fig. 5.A4(b) the unit cell of the hcp structure in Fig 5.A4(a) is expanded to include an extra layer of ions on the first and second level of the cell. In this figure all the ions are shown that can be connected to ion \( i \) through a maximum of two interstitial sites, with the corresponding bonds.
Figure 5.A4(a): Schematic representation of the unit cell of the hcp lattice.

Figure 5.A4(b): Expanded hcp lattice including all ions with which a bond exists with ion \( i \). Bonds are shown between ion \( i \) and ions of type \( I \) to \( V \).
In Fig. 5.A4(c) the octahedral interstitial site is shown that connects ion \( i \) with ions of type \( II \). In Fig. 5.A4(d) a combination of an octahedral and a tetrahedral site is shown that connects ions of type \( III \) with ion \( i \). Ions of type \( IV \) are connected with ion \( i \) through two tetrahedral sites, which are each others mirror-image in the central plane of the unit cell [shown in Fig. 5.A4(a)]. In Fig. A4(e) only a part of the hcp structure is shown for clarity. In this figure a pair of octahedral sites is shown that connects ion \( i \) with ions of type \( V \).

**Figure 5.A4(c):** The octahedral interstitial site that connects ions of type \( I \) and \( II \) to ion \( i \).
Figure 5.A4(d): Schematic representation of the tetrahedral and octahedral interstitial sites in the hcp lattice of Fig. 5.A4(b), which connect ions of type III to ion $i$.

Figure 5.A4(e): Schematic representation of the pair of octahedral interstitial sites in the hcp packing that connects ions of type $V$ to ion $i$. 
CHAPTER 6

Shock wave equation of state for ceramics and boron

ABSTRACT

A new theoretical shock wave equation of state was used to calculate the shock wave behaviour of AlN, Al₂O₃, B, B₄C, BeO, SiC, Si₃N₄, TiB₂, TiO₂, and UO₂. The linear equation is applicable in two ways; 1, with data from infrared spectroscopic, and X-ray measurements, and 2, with the experimental sound velocity and the bond dissociation energy.

With the first method calculations were performed for Al₂O₃, B, BeO, and TiO₂ results were within 5% accuracy, as long as no phase transformation occurred.

With the second method calculations were performed for AlN, Al₂O₃, B, B₄C, BeO, SiC, Si₃N₄, TiB₂, and UO₂ the accuracy varied between 4 to 10%, as long as no phase transformation occurred.

Furthermore, the slope of the shock wave equation of state after a phase transformation was determined by approximation using theory and experimental evidence, and an example is given for B₄C how to estimate the intercept after a phase transformation.
6.1 INTRODUCTION

In Chapter 4 a theoretical expression for the shock wave equation of state, or Rankine-Hugoniot equation of state (also called Hugoniot) was derived, that could be determined in two ways without any shock wave measurements. Method 1 uses data from X-ray and infrared (IR) spectroscopy measurements, and method 2 uses the experimental sound velocity.¹

In general, a Hugoniot can be expressed as a linear relation between the velocity at which a shock wave travels, the shock wave velocity \( U \), and the velocity at which the material moves directly after passage of the shock wave front, the mass displacement velocity, \( u \). The Hugoniot is then written as:

\[
U = C_0 + S u
\]

in which \( C_0 \) can be approximated with the bulk sound velocity, and \( S \) is a material constant.

Concerning the equation of state properties there is only information available for a small range of ceramics,²³⁴⁵ and often this information is only fragmentary.⁵ Accurate determination of these properties requires complicated and time-consuming labour.

Several models were developed to determine the parameters of the Hugoniot from non-shock wave data.¹ These models, however, all required experimental data for the isobaric volume expansion coefficient at constant pressure, the heat capacity at constant volume, the isothermal compressibility at standard conditions \( (T=300 \text{ K}, \textit{P}=0.1 \text{ MPa}) \), and the density at standard conditions. For newly developed ceramics even the theoretical maximum density at standard conditions might be unknown.

All before-mentioned parameters can only be determined from a solid sample of macroscopic dimensions. This poses a serious problem when these newly developed ceramics are to be compacted for the first time with the dynamic compaction process, because it uses a shock wave to compact a powder.⁶ This process can be used, for example, on materials that are difficult to sinter because of their high melting temperature⁷, or those which decompose during sintering.⁶⁸ The importance of the equation of state derived in Chapter 4 is, therefore, found in the source of its parameters.

When applying the current equation of state it should be borne in mind that the model was derived from the Morse potential curve for diatomic molecules.¹ Although the Morse potential has been applied successfully to a wide range of materials in infrared spectroscopy,⁹ it should be noted that the conditions under which infrared spectroscopy is performed are not as extreme as in a shock wave. At high compressive stresses, the true interatomic potential
of materials with an extremely asymmetric interatomic potential might deviate from a Morse potential, which was determined with infrared spectroscopy. For example; the high pressure properties of some of the alkali halides, like LiF, and LiCl can not be described accurately with an exponential law, such as the Morse potential.

Furthermore, the model was developed for application to ceramic materials, which are often covalent materials. The model is not based on Coulombic attraction and repulsion, such as is often applied to ionic solids. Coulombic repulsion between ions with the same charges (either positive or negative) is not incorporated, and neither is long range ionic interaction. The model is, therefore, not suitable for solids with a strong ionic bond character.

In the following chapter the two methods will be introduced and applied to a number of ceramics. It will be demonstrated that phase transformations occur during shock loading, and the effect of a phase transformation on the Hugoniot will be evaluated from theory and experiments. After this, the results of this evaluation will be used to demonstrate that similarities in the lattices of two materials can be used to estimate the Hugoniot of a material after a phase transformation.
6.2 METHOD 1; HUGONIOT FROM IR DATA

A. The model

Method 1 uses a linear equation of state:

\[ U = \frac{A}{3B} + \left( \frac{A}{4} - \frac{1}{5} \right) u \]  

(6.2)

For a substance \( M, X_j \):

\[ A = \alpha \ r_0, \ \text{and} \ B = \sqrt{\frac{M}{2D}} \]  

(6.3)

in which \( r_0 \) is the equilibrium distance, or bond length between the atoms in the solid at standard conditions, and:

\[ \alpha = 2\pi c \ \omega_0 \sqrt{\frac{\mu}{2D}} \]  

(6.4)

in which \( c \) is the velocity of light in vacuum, \( \omega_0 \) is the wavenumber (in m\(^{-1}\)) of the zero order transition, \( \mu \) is the reduced mass of the diatomic molecule \( MX \), and \( D \) is the bond dissociation energy of the diatomic molecule, which is the energy difference between the diatomic molecule in the gaseous phase with its atoms at equilibrium distance, and at infinite separation.

The mass, \( M \), in Eq. (6.3) originates from the energy balance between the kinetic shock wave energy, and bond potential energy. The bond energy is proportional to the dissociation energy, \( D \), of a diatomic molecule. Analogous to the distribution of electrostatic bond strength, used by Wells\(^{12}\), the bond strength of the diatomic molecule is considered to be distributed equally over the bonds around one atom in the solid. The mass, \( M \), for the \( M, X_j \) molecule is, therefore, determined by the least occurring atom (\( M \) or \( X \)), and the atoms of the other kind that share its bonds:

\[ \text{for } i \leq j : M = A_M + \frac{i}{i} A_X, \ \text{and for } j < i : M = A_X + \frac{i}{j} A_M \]  

(6.5)

in which \( A_M \), and \( A_X \) are the atomic masses of the atoms \( M \) and \( X \), respectively.

The bond dissociation energy, \( D \), and the wavenumber, \( \omega_0 \), can be determined from the infrared spectrum,\(^{9}\) while the equilibrium distance, or bond length, between the atoms, \( r_0 \), can be determined from X-ray data. The IR as
well as the X-ray measurements can be performed without a solid sample of macroscopic dimensions.

B. Bond theory

In the present model\(^1\) bonds in a solid with composition \(M_iX_j\) are considered between the atoms \(M\) and the \(X\) atoms bordering the nearest and next-nearest interstitial sites in the packing. In this model the average bond length between the atoms does not equal the nearest neighbor distance, which is generally quoted as bond length,\(^{13}\) but the average distance between an atom \(M_i\) and the atoms \(X\) bordering the nearest and next-nearest interstitial sites around it.

This concept of interstitial bonding was used in Chapter 5 on metals,\(^{14}\) for which it is well accepted.\(^{15}\) While not standard practice for solids with covalent bonding it will be explained why, especially during shock wave compression, this concept can also be applied to these solids.

In representations of di- and polyatomic molecules the bonds are usually\(^{16,17}\) depicted as orbitals. These orbitals define the space in which the chance for the electrons to be present is about 95%. When solids are considered the bonds are usually shown as a single line between nearest neighbors.\(^{18,19,20}\) This simplification is used because the determination of the bonding electron orbitals in covalent solids is very difficult. These electron orbitals in a solid are influenced by all atoms in the vicinity. When besides this effect, it is considered that orbitals only represent the space in which there is a chance to find the valence electrons, it becomes clear that the orbital model itself suggests that bonding between \(M\) atoms and \(X\) atoms around the nearest or next-nearest interstitial sites is likely to occur.

As mentioned before, bonding between atoms which are not neighbors is especially important during shock wave compression. During shock compression of a polycrystalline solid every atom, \(M\), can be moved into the direction of every other atom, \(X\), bordering the nearest or next-nearest interstitial sites, because of the random orientation of the crystals with regard to the shock wave direction. This means that, if the strength of the lattice is described with a bond model, bonds must be considered between the pairs of \(M\) and \(X\) atoms around the nearest and next-nearest interstitial sites.

For regular packings of metals the average bond length can be calculated from the lattice structure and the nearest neighbor distance. For a regular packing like that of elemental boron (B),\(^{21}\) distances between neighboring atoms are different. For these the average bond length can be expressed as a function
of the 'nearest' neighbor distances. The 'nearest' neighbor distances will be labelled \( R_{0,1}, R_{0,2}, \) etc. in order of increasing length. By expressing the average bond length in terms of \( R_{0,1}, R_{0,2}, \) etc. the calculations can be applied to any solid with a similar structure.

In Appendix A the average bond lengths are calculated for \( \text{Al}_2\text{O}_3 \) (corundum), \( \text{B} (\alpha\text{-rhombohedral boron}), \text{BeO} \) (wurtzite), and \( \text{TiO}_2 \) (rutile). It is difficult to determine an expression for the average bond length, when the solid has no unique crystal structure or when its structure does not comprise a rigid lattice. An example of the former is sulphur (S) that is generally found in an allotropic mixture containing at least three forms: orthorhombic, monoclinic, and polymeric sulphur.\(^{22}\) Examples of the latter are graphite and polymers.

For these type of solids the strength of the material is not determined by the lattice and bonds, but by the interaction between sublattices, like the layers in graphite, or the chains in polymers. For these solids neither method 1 nor method 2 is applicable.

For amorphous solids the derivation of a general expression is still difficult, but if their strength is governed by interatomic bonds, method 2, which does not use the bond length, but only the sound velocity, should still be applicable.

C. Calculations

In Table 6.1 the necessary IR data are shown for three ceramic materials and elemental boron. The average bond lengths are calculated in Appendix A.
Table 6.1: The IR data for the calculations with method 1.

<table>
<thead>
<tr>
<th>Compound (lattice)</th>
<th>Dissociation energy(^a) (D) (kJ/mol)</th>
<th>Mass of (M) ([\text{g/mol}])</th>
<th>Average bond-length (r_0) (nm)</th>
<th>Wave number of zero-order transition(^b) (\omega_0) ((10^2/\text{m}))</th>
</tr>
</thead>
<tbody>
<tr>
<td>(\text{Al}_2\text{O}_3) (corundum)</td>
<td>512</td>
<td>50.98</td>
<td>0.322</td>
<td>979.23</td>
</tr>
<tr>
<td>B ((\alpha)-rhombohedral)</td>
<td>297</td>
<td>21.62</td>
<td>0.300</td>
<td>1051.30</td>
</tr>
<tr>
<td>BeO (wurtzite)</td>
<td>435</td>
<td>25.01</td>
<td>0.206</td>
<td>1487.32</td>
</tr>
<tr>
<td>(\text{TiO}_2) (rutile)</td>
<td>672</td>
<td>79.9</td>
<td>0.305</td>
<td>1008.2</td>
</tr>
</tbody>
</table>

\(^a\) Reference 13.

\(^b\) Reference 9.

For B, BeO, and \(\text{TiO}_2\) the shock wave data given by Marsh were used.\(^2\) The density of the samples which were used by Marsh\(^2\), relative to their theoretical maximum density (TMD), can be determined easily for BeO and \(\text{TiO}_2\), being 99.3% TMD and 99.6% TMD respectively. The fact that B is usually found as a mixture of polymorphs makes it hard to estimate its relative density. Using the range for the TMD given by Lide et al.\(^{13}\) the density of Marsh's sample is 98.6-100% TMD. For \(\text{Al}_2\text{O}_3\) the shock wave data reported by Gust (1971)\(^4\) for hot-pressed corundum with a density of 99.8% TMD were used.

The parameters calculated from the IR data in Table 6.1 are shown in Table 6.2 together with the density of the sample, and a comparison of the calculated and experimental sound velocity. As can be seen, the calculation of the parameters is within 12% for \(\text{Al}_2\text{O}_3\), B, and BeO.
Table 6.2: The parameters of the linear shock wave equation of state, and the difference between the calculated, and the experimental sound velocity.

<table>
<thead>
<tr>
<th>Compound</th>
<th>Sample density (%TMD)</th>
<th>Experimental sound-velocity(^a) (C_{0,\text{exp}}) (km/s)</th>
<th>Material constant (A) [Eq.(6.3)]</th>
<th>Material constant (B) [Eq.(6.3)] (s/km)</th>
<th>Calculated sound-velocity (C_{0,\text{calc}}) (km/s)</th>
<th>Error in (C_0) (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Al(_2)O(_3)</td>
<td>99.8</td>
<td>7.83(^b)</td>
<td>5.88</td>
<td>0.223</td>
<td>8.79</td>
<td>12</td>
</tr>
<tr>
<td>B</td>
<td>98.6-100</td>
<td>9.23</td>
<td>5.67</td>
<td>0.191</td>
<td>9.90</td>
<td>7</td>
</tr>
<tr>
<td>BeO</td>
<td>99.3</td>
<td>8.44</td>
<td>4.70</td>
<td>0.170</td>
<td>9.23</td>
<td>9</td>
</tr>
<tr>
<td>TiO(_2)</td>
<td>99.6</td>
<td>...</td>
<td>5.47</td>
<td>0.244</td>
<td>7.48</td>
<td>...</td>
</tr>
</tbody>
</table>

\(^a\) Values for \(C_{0,\text{exp}}\) are from Reference 2, unless indicated otherwise.

\(^b\) Reference 5.

The calculated intercept and slope of the equation of state [Eq.(6.3)] are shown in Table 6.3 together with the average deviation of the calculated value over the given range of mass displacement velocities. The results for Al\(_2\)O\(_3\) and BeO are rather good, the average deviation being less than 5.3%. The large deviations for B and TiO\(_2\) are due to phase transformations, which will be discussed in paragraphs 6.4 and 6.5 of this chapter.
Table 6.3: The intercept, and slope of the linear equation of state from the calculations with the IR data, and the mass displacement velocity (u) range over which experimental shock wave data were available.

<table>
<thead>
<tr>
<th>Compound</th>
<th>Data range u (km/s)</th>
<th>Intercept (or sound velocity)</th>
<th>Slope S</th>
<th>Average error in U (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Al₂O₃</td>
<td>0.61-2.32</td>
<td>8.79</td>
<td>1.27</td>
<td>5</td>
</tr>
<tr>
<td>B</td>
<td>1.47-3.94</td>
<td>9.92</td>
<td>1.22</td>
<td>16</td>
</tr>
<tr>
<td>BeO</td>
<td>0.32-2.82</td>
<td>9.23</td>
<td>0.97</td>
<td>4</td>
</tr>
<tr>
<td>TiO₂</td>
<td>0.47-3.19</td>
<td>7.47</td>
<td>1.17</td>
<td>21 (6)</td>
</tr>
</tbody>
</table>

* Reference 2.
* Value in parentheses is found for data up to the phase transformation.

6.3 METHOD 2; HUGONIOT FROM SOUND VELOCITY

A. The model

The second method, is based on the bulk sound velocity, and can be used to calculate the parameters if the data for the wavenumber of the zero order transition, ω₀, are not available. Although the determination of the sound velocity requires a solid sample of macroscopic dimensions, this determination is far more simple than the determination of parameters, like the cubic expansion coefficient, for the alternative models. In this method the first term of the Hugoniot can be approximated with the bulk sound velocity, C₀,exp, because for u<0 the shock wave velocity U, approaches the bulk sound velocity C₀,exp. This means that:

\[ U(u<0) = \frac{A}{3B} \approx C₀,exp \]  (6.6)

To calculate B only the dissociation energy, D, and the mass M are needed [Eq. (6.3)] and if the bulk sound velocity C₀,exp is known, the equation of state becomes:

97
\[ U = C_{0,\text{exp}} + \left( \frac{3BC_{0,\text{exp}}}{4} - \frac{1}{5} \right) u \] (6.7)

This second method is somewhat less accurate, because in practice there is a small difference between the intercept and the bulk sound velocity.\textsuperscript{2}

B. Calculations

In Table 6.4 the necessary data for method 2 and the parameter \( B \) calculated for nine ceramics and elemental boron are shown, together with the density of the sample.

The Hugoniot parameters calculated from the data in Table 6.4 are shown in Table 6.5 with a comparison of the calculated and experimental shock wave velocity. It can be seen that the calculation of the shock wave velocity is within an average deviation of 10\% for all materials except for B\textsubscript{2}C and Si\textsubscript{3}N\textsubscript{4}. The large deviation for these two can be attributed to a phase transformation as will be discussed in paragraph 6.5. Phase transformations also occur in some of the other materials, but for these the effect is not as pronounced.
Table 6.4: The experimental data for method 2, along with the calculated parameters.

| Compound   | Density of sample (%TMD) | Experimental sound-velocity $C_{0,exp}$ (km/s) | Disassociation energy $D$ (kJ/mol) | Mass of $M_1X_{(i,j)}$ [Eq.(6.5)] (g/mol) | Constant $B$ [Eq.(6.6)] (s/km) |
|------------|--------------------------|-----------------------------------------------|-----------------------------------|-------------------------------------------|---------------------------------
| AlN        | 99.0                     | 7.91                                          | 297                               | 40.99                                     | 0.263                           |
| Al$_2$O$_3$ | 99.8                     | 7.83$^c$                                      | 512                               | 50.98                                     | 0.223                           |
| Corundum   |                          |                                               |                                   |                                           |                                 |
| B          | 98.6-100                 | 9.23                                          | 297                               | 21.62                                     | 0.191                           |
| B$_4$C     | 95.2                     | 9.63$^c$                                      | 448                               | 55.25                                     | 0.248                           |
| BeO        | 99.3                     | 8.44                                          | 435                               | 25.01                                     | 0.170                           |
| SiC        | 96.0                     | 8.00                                          | 452                               | 40.10                                     | 0.211                           |
| Si$_3$N$_4$| ±92                      | 8.82                                          | 435                               | 46.77                                     | 0.232                           |
| (5 wt% MgO)|                          |                                               |                                   |                                           |                                 |
| TiB$_2$    | 99.6                     | 7.46$^d$                                      | 276                               | 69.52                                     | 0.355                           |
| UO$_2$     | 94.0                     | 3.99                                          | 759                               | 270.03                                    | 0.422                           |

$^a$ Values for the experimental sound velocity are from Marsh (Reference 2), unless indicated otherwise.
$^b$ Reference 13.
$^c$ Reference 4.
$^d$ Reference 5.
Table 6.5: The intercept, and slope of the linear equation of state from the calculations with the experimental sound velocity, and the range of the mass displacement velocity ($u$) over which experimental shock wave data\textsuperscript{a} were available.

<table>
<thead>
<tr>
<th>Compound</th>
<th>Data range $u$ (km/s)</th>
<th>Intercept (or sound velocity $C_{0,\text{exp}}$ km/s)</th>
<th>Slope $S$ [Eq.(6.7)]</th>
<th>Average error in $U$ (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>AlN\textsuperscript{b}</td>
<td>0.30-0.73</td>
<td>7.91</td>
<td>1.36</td>
<td>10</td>
</tr>
<tr>
<td>Al\textsubscript{2}O\textsubscript{3}</td>
<td>0.61-2.32</td>
<td>7.83</td>
<td>1.11</td>
<td>7</td>
</tr>
<tr>
<td>B</td>
<td>1.47-3.94</td>
<td>9.23</td>
<td>1.12</td>
<td>10</td>
</tr>
<tr>
<td>B\textsubscript{4}C</td>
<td>0.54-3.78</td>
<td>9.63</td>
<td>1.59</td>
<td>24</td>
</tr>
<tr>
<td>BeO</td>
<td>0.32-2.82</td>
<td>8.44</td>
<td>0.87</td>
<td>9</td>
</tr>
<tr>
<td>SiC</td>
<td>0.46-2.91</td>
<td>8.00</td>
<td>1.06</td>
<td>4</td>
</tr>
<tr>
<td>Si\textsubscript{3}N\textsubscript{4}</td>
<td>2.48-3.76</td>
<td>8.82</td>
<td>1.33</td>
<td>33</td>
</tr>
<tr>
<td>TiB\textsubscript{2}</td>
<td>0.81-2.98</td>
<td>7.46</td>
<td>1.79</td>
<td>8</td>
</tr>
<tr>
<td>UO\textsubscript{2}</td>
<td>0.57-2.49</td>
<td>3.99</td>
<td>1.06</td>
<td>10</td>
</tr>
</tbody>
</table>

\textsuperscript{a}Reference 2.

\textsuperscript{b}Experimental data are from Rosenberg (Reference 3). In the original paper $u$ and $U$ were given as a function of the longitudinal shock stress, $\sigma$. With the use of the momentum conservation law; $\sigma=\rho_0uU$ (with $\rho_0$ the TMD at standard conditions) these were converted to $U-u$ data.

6.4 DISCUSSION OF CALCULATIONS WITH BOTH METHODS

The results for both methods show good agreement with the experimental data as long as the material shows linear shock wave behavior. Examples are Al\textsubscript{2}O\textsubscript{3} (corundum) and UO\textsubscript{2} as shown in Figs. 6.1 and 6.2, respectively.
Figure 6.1: The shock wave equation of state for Al₂O₃ as calculated with method 1 (using IR data) and method 2 (using the experimental sound velocity), compared with experimental data for corundum reported by Gust (1971).³

Figure 6.2: The shock wave equation of state for UO₂ as calculated with method 2 (using the experimental sound velocity) compared with experimental data reported by Marsh.⁵
All other materials show deviations from linear behavior. The deviations can be divided into two types.

The first type is very clearly discernible in the results for BeO and SiC, as shown in Figs. 6.3 and 6.4, respectively. At low mass displacements velocities these materials show a region of very high shock wave velocities. The source of these humps is considered to be a two wave structure. In the low stress (low u) region an elastic wave with a high velocity is recorded first by the sensors. In the high stress region the material is deformed plastically, and a relatively slow plastic shock wave is registered. The decrease of the recorded shock wave with increasing mass displacement velocity probably occurs in situations when the elastic wave still arrives before the plastic wave, but is too weak to be registered. The fact that both materials show the same effect might very well be due to the similarities in the wurtzite lattice of BeO, and the carborundum or zinc blende lattices in SiC. The deviation for SiC after the phase transformation is only 2.1% in the region of 1.5<u<3 km/s.

![Graph](image_url)

**Figure 6.3:** The shock wave equation of state for BeO as calculated with method 1 (using IR data) and method 2 (using the experimental sound velocity), compared with experimental data reported by Marsh. The origin of the high shock wave velocities at low mass displacements velocities is considered to be a two wave structure with an elastic and a plastic component.
Figure 6.4: The shock wave equation of state for SiC as calculated with method 2 (using the experimental sound velocity), compared with experimental data reported by Marsh. At low mass displacement velocities the same effect is observed as found for BeO (Fig. 6.3).

The relative density under shock wave conditions of both materials can be calculated using:

\[
\varepsilon = \frac{U - u}{U}
\]  \hspace{1cm} (6.8)

At the end of the phase transformation the relative density of BeO is about 90%, and 84% for SiC. Considering the error in the determination of the locus of the end of the phase transformation, these two values are remarkably similar, as would be expected if the phase transformation depends on the lattice structure.

Although the data range covers only a very low mass displacement region, the results for AlN with the wurtzite structure shown in Fig. 6.5 show a similar effect.
Figure 6.5: The shock wave equation of state for AlN as calculated with method 2 (using the experimental sound velocity), compared with experimental data reported by Rosenberg. The deviations are most probably due to the same effect as was found for BeO and SiC (Figs. 6.3 and 6.4). The experimental data were converted from shock stress data as explained in Table 6.5 [o from \((\sigma, u)\)-data and + from \((\sigma, U)\)-data].

For materials exhibiting the first type of deviation, the low-stress shock wave velocity data are high compared to the experimental sound velocity. The results over the entire data range are, however, within 10% average deviation for both methods. If experimental techniques were to be used which would only record the plastic wave the results would probably be even better.

A second type of deviation exerts a larger effect on the results. This type of behavior is found in, for example, TiO$_2$ and TiB$_2$ as shown in Figs. 6.6 and 6.7, respectively. For these materials the calculated Hugoniot agree well with the experimental data up to a region in which the shock wave velocity remains constant. According to thermodynamic principles, it is found that for a single phase the shock wave velocity must increase with the mass displacement. The constant shock wave velocity in this region is, therefore, attributed to a phase transformation.
Figure 6.6: The shock wave equation of state for TiO₂ as calculated with method 1 (using IR data), compared with experimental data for rutile reported by Marsh.² The region in which the shock wave velocity remains constant is attributed to a phase transformation. A parallel equation of state curve with θ=2.2 is shown.

Figure 6.7: The shock wave equation of state for TiB₂ as calculated with method 2 (using the experimental sound velocity), compared with experimental data reported by Gust (1973).³ The region in which the shock wave velocity remains constant is attributed to a phase transformation. A parallel equation of state curve with θ=1.6 is shown.
In the Figs. 6.6 and 6.7 a Hugoniot is drawn parallel to the original Hugoniot. It can be seen that the slope of the Hugoniot after the phase transformation can be approximated with the slope before the phase transformation. This fact and the similarity in behavior found for AlN, BeO, and SiC, which have similar lattices can be combined with knowledge of phase transformation behavior in order to obtain a model for phase transformations that can be used to estimate the shock Hugoniot after a phase transformation.

6.5 PHASE TRANSFORMATIONS IN SHOCK WAVES

A. The difference between a static and a dynamic phase transformation

Stress-induced phase transformations in shock waves are found in many ceramics; Linde et al. mention a high pressure phase of TiO₂, and Gust (1973)⁵ finds proof for phase transformations in the shock wave data of TiB₂, SiC, and Be₂B.

When phase transformations under shock wave conditions are studied, it should be remembered that although many examples are found of first order agreement with static phase transformations, the differences between the mechanisms involved are significant and reveal effects controlled by the physical and chemical nature of the imposed deformations.²⁵ To date there is no generally accepted model for the basic mechanisms of phase transformations in shock waves.²⁵

Shock-induced phase transformations in solids can be divided into three types; elastic/plastic transformations, polymorphic phase transformations, and melting. The first two types are determined by lattice bond arrangements,²⁵ and will be discussed in detail, while the latter will not be discussed further. The first type that was discussed for AlN, BeO, and SiC (Figs. 6.3-6.5) will be considered to be a special version of the second type. In the following, when the term phase transformation is used, it will refer to the second type (shown in Figs. 6.6 and 6.7).

The phase transformations in shock waves are always similar in type to martensitic transitions. The rapid transition of one type of lattice into another is facilitated by non-diffusional martensitic rearrangements, i.e. they are based on the cooperative motion of many atoms over small distances.²⁵

An important difference between compression-induced static and dynamic phase transformations is caused by the anisotropic nature of the stresses in a shock wave. When the longitudinal stresses are higher than the normal stresses the lattice structure will deform stronger in longitudinal direction. This distortion of the lattice might give rise to phases of a type that would not occur under
isotropic loading conditions.

The concept of different mechanisms for static and dynamic phase transformations does not exclude the possibility of similar phase transformations for static and dynamic conditions. When a phase transformation under static conditions results in a phase with an increased density, it is very likely that this phase also has an optimum structure for dynamic conditions. The most important consequence of the concept is that phases can exist under shock conditions, which can not exist under isotropic, static conditions. These phases can, therefore, not be recovered.

When these metastable shock phases are part of a complex shock wave phase diagram with multiple phases it is possible that a material with a phase A lattice, before shocking, is converted to a metastable phase B that, upon unloading, turns into a stable phase C that also exists under static conditions. This would, for example, explain the polymorphic behavior of TiO$_2$ as found by Linde et al. In their experiments they recover an orthorhombic TiO$_2$ phase after shocking of the rutile phase. They find proof for a denser metastable phase at shock stresses above 20 GPa, but can not deduce its structure. This could be explained by the existence of a highly anisotropic structure that is only stable under shock wave conditions.

A special kind of phase transformation is found for rare earth metals. The fact that their lattices consist of several types of closest packing, and their outer electron shells remain unchanged with increasing atomic number indicate that a transformation to a denser phase must be due to a change in the electron distribution. It is suggested that for instance, 5d electrons are promoted to unfilled 4f-levels.

**B. The effect of a phase transformation on the equation of state**

When developing a shock wave equation of state for ceramics, it would be an advantage to know what effect a phase transformation would have on shock parameters. Because our present model is based on a description of the crystal lattice, it is well suited for such a study.

The parameter $A$ [Eq. (6.3)] depends on the reciprocal vibration constant, $\alpha$, and the average equilibrium bond length, $r_0$. The constant $\alpha$ is determined by the interatomic interactions, which do not change as long as the chemical nature of the bond does not change. Only when mechanisms occur, as in the earlier mentioned special phase transformations in the rare earth metals, the bonds, and,
therefore, \( \alpha \), would change.

When two phases of the same material are compared it seems clear that the average equilibrium bond length, \( r_0 \), differs from phase to phase. However, when the process of the phase transformation in a shock wave is considered, this effect is not very large. This will be demonstrated by analysing the phase transformation of TiO\(_2\) from rutile (theoretical maximum density; TMD=4.26 \( 10^3 \) kg/m\(^3\)) to the orthorhombic \( \alpha \)-PbO\(_2\) phase (TMD=4.34 \( 10^3 \) kg/m\(^3\)) found after shock wave experiments by Linde \textit{et al.}.

The effect of the volume change on the bond length can be evaluated without an elaborate study of both phases. The phase transformation is rapid and diffusionless,\(^{28}\) which means that there is no material transport over distances larger than one atomic cell. This in turn means that the volume in both phases can be considered to be proportional to \( r_0^3 \). The volume change from rutile to the orthorhombic phase is 1.9%. The change in \( r_0 \) is, therefore, approximately 0.6%. Even if the phase transformation with a much larger volume change is considered e.g. from rutile to anatase (TMD=3.89 \( 10^3 \) kg/m\(^3\)), a volume change of 8.7% only would result in a change of 3.0% in the average equilibrium distance.

Because all phase transformations in shock waves are rapid and diffusionless, and volume changes for these transformations are in general less than 10\%,\(^{29}\) changes in the average equilibrium bond length due to phase transformations in shock waves are expected to be small. This means that, according to the present model, the slope of the Hugoniot, which is determined solely by \( A \) [Eq. (6.2)], will not change much upon phase transformations. This effect could also be observed in Figs. 6.6 and 6.7.

Equation (6.3) suggests that parameter \( B \) must be insensitive to a phase transformation. Neither the mass, \( M \), nor the bond strength, \( D \), should depend on the phase (as long as the bond type does not change as was supposed to occur in the rare earth metals). This is, however, entirely due to the fact that the present model initially was not developed to incorporate phase transformations.\(^1\)

The parameter \( B (=\sqrt{(M/2D)}) \) originates from the energy balance between the internal shock wave energy and the bond potential energy:

\[
\frac{1}{2} M u^2 = D g(r) \tag{6.9}
\]

in which \( g(r) \) is a complex exponential expression depending on the average bond length, \( r \). The left-hand part of the expression gives the amount of internal shock wave energy of mass \( M \). The righthand part of the expression gives the amount of energy increase in the bonds in mass \( M \) due to the shock wave.

A phase transformation can affect the balance Eq. (6.8) in several ways.
Three effects will be considered here,
(1) The transformation to an anisotropical phase. This would change the fraction of bonds which are perpendicular to the shock wave direction, and which, therefore, do not contribute to the shock balance for the Hugoniot equation of state. This is due to the fact that for the Hugoniot only the longitudinal part of the stresses are considered.
(2) A change in the enthalpy associated with the volume change due to the phase transformation. 29
(3) Energy dissipation of mechanical energy into thermal energy due to the phase transformation. 30

The first effect that is suggested could not occur under the isotropic conditions associated with static phase transformations. It could, however, occur under anisotropic shock wave conditions.

In the present shock wave model it was assumed that the bond angles were equally distributed over a hemisphere, because of the random orientation of the crystals in the sample. When the concept of an anisotropic metastable shock phase is used, the denser phase could be a phase in which the bond angles are changed in such a way that a fraction of the bonds becomes approximately perpendicular to the shock wave direction. In this phase only a fraction of the bonds which were originally compressed in the shock wave direction will still be orientated in their original direction. The bonds perpendicular to the shock wave direction will no longer contribute to the materials resistance to compression in the direction of the shock wave. This reduction in the number of bonds which are compressed by the longitudinal shock stress results in an increased compressibility of the material in longitudinal direction. The compressibility would increase because there are fewer bonds to resist compression.

In the balance Eq. (6.8) this would result in an increase of internal shock energy per bond. This increase of internal energy would effectively increase the parameter \( B \):

\[
B = \sqrt[\frac{\theta M}{2D}} \quad (6.10)
\]

with \( \theta > 1 \). This would result in a lower intercept for the equation of state [Eq. (6.2)].

In this analysis of the phase transformation it is assumed that the bonds which contribute to the shock wave equilibrium are still evenly distributed over a hemisphere after the phase transformation. If this distribution changes this
would affect the model. Proof for or against this assumption, however, is extremely hard to obtain.

The second effect, a variation in the enthalpy, $\Delta H$, associated with the volume reduction, would have a comparable effect. If the phase transformation is endothermic some of the internal shock wave energy will be spent in generating the phase transformation. The balance equation becomes:

$$\frac{1}{2} M u^2 - \Delta H = D g(r)$$ (6.11)

If the enthalpy change is proportional to the internal shock wave energy Eq. (6.10) could also be used to incorporate this effect. If, however, the enthalpy change is independent of the internal shock wave energy, the parameter $B$ becomes a function of the mass displacement velocity, $u$. In this case $B$ will increase with $u$ and this will result in a reduced slope of the Hugoniot. In case of an exothermic effect of the volume change the parameter $B$ will first increase due to the phase transformation and then decrease with $u$. This would also result in a reduced slope.

The third effect, energy dissipation of mechanical energy to thermal energy, will have exactly the same effect as an enthalpy change during an endothermic phase transformation. Zhukov$^{30}$ studied this effect in the metals Fe and Ti, and found that the amount of dissipated energy remains constant over a 'fairly wide range' of mass displacement velocities. It is, therefore, to be expected that this effect would also reduce the slope of the Hugoniot.

As a first approach it will be assumed that the slope of the Hugoniot does not change due to the phase transformation, and that the change in the intercept can be described by the introduction of the parameter $\theta$, as shown in Eq. (6.10). If the phase transformation is determined by the lattice structure the parameter $\theta$ in Eq. (6.10) should be approximately the same for materials with a comparable lattice structure.

C. Calculations with a parallel Hugoniot after a phase transformation

In Fig. 6.8 the results are shown for elemental boron (B). Rigid use of the principle, that for a single phase the shock wave velocity must increase with the mass displacement velocity,$^{23}$ would indicate that the phase transformation affects the data in the region for $u<3.3$ km/s. In the region for $u>3.3$ km/s the slope of the $U(u)$ curve seems to correspond well with the slope calculated with method 1. A linear fit with this calculated slope using the proposed Eq. (6.10) for the calculation of $B$, yields an average deviation of 2.2% for $\theta=1.8$. 

110
**Figure 6.8:** The shock wave equation of state for elemental boron as calculated with method 1 (using IR data) and method 2 (using the experimental sound velocity), compared with experimental data reported by Marsh.² An equation of state curve parallel to the equation of state curve as calculated with method 1 with θ=1.8 is shown.

**Figure 6.9** The shock wave equation of state for B₄C as calculated with method 2 (using the experimental sound velocity), compared with experimental data reported by Marsh.² Two parallel equation of state curves are shown; the first with θ=2.1 was obtained by fitting the experimental data after the phase transformation, the second was obtained by using the value 1.8 for θ found for elemental boron (Fig. 6.8).
In Fig. 6.9 the results are shown for B$_4$C. In this figure it can be seen, that a phase transformation occurs in the region $0.6<\nu<1.3$ km/s, because the shock velocity does not increase. In the figure there are more examples of a fluctuation in the shock wave velocity, but these are small compared to the effect in this region and are, therefore, considered to be scatter. The best fit for a parallel Hugoniot [using B from Eq. (6.10)] is found for $\theta=2.1$ with an average deviation of 2.4%. However, the structure of B$_4$C shows strong similarities with the structure of boron,$^{31}$ and a comparison of Figs. 6.8 and 6.9 shows that their shock behavior undergoes the same kind of phase transformation. When the parameters for B$_4$C found with method 2 are combined with the value of $\theta=1.8$, that was found for elemental boron, the deviation for this new Hugoniot is only 5.7% for $\nu>1.5$ km/s (see also Fig. 6.9).

The results for B with method 1 were used, because this method is supposed to be more reliable as the results for Al$_2$O$_3$ and BeO also indicate. It must be borne in mind that in order to obtain a parallel equation of state with method 2 only the intercept is adapted with:

\[
C_{0,2} = \frac{C_{0,\text{exp}}}{\sqrt{\theta}} \quad (6.12)
\]

to obtain the same result as with method 1.

The large deviation for Si$_3$N$_4$ is clearly due to a phase transformation as can be seen in Fig. 6.10. A parallel equation of state with $\theta=3.0$ fits the experimental data with an average deviation of 2.1%.
Figure 6.10: The shock wave equation of state for Si₃N₄ as calculated with method 2 (using the experimental sound velocity), compared with experimental data for Si₃N₄ with 5 Wt% MgO reported by Marsh.² A parallel equation of state curve with θ=3.0 is shown.

6.6 CONCLUSIONS

Calculations using the shock wave data² of 9 different ceramics, and elemental boron show that the current model is applicable in two ways, i.e. 1, with data from X-ray and infrared measurements, and 2, with the experimental sound velocity and the bond dissociation energy.

Using method 1 the shock velocity, \( U \), can be calculated from the mass displacement velocity, \( u \), within a 5% average deviation, as long as no phase transformation occurs for \( \text{Al}_2\text{O}_3 \), B, BeO, and \( \text{TiO}_2 \).

Using method 2 the accuracy varied between 4 and 10% for AIN, \( \text{Al}_2\text{O}_3 \), B, B₄C, BeO, SiC, \( \text{TiB}_2 \), and \( \text{UO}_2 \) in the regions before a phase transformation, occurred, if at all.

Phase transformations were discussed for B, B₄C, \( \text{TiB}_2 \), \( \text{TiO}_2 \), and Si₃N₄. Experimental evaluation of the phase transformations indicates, that the slope of the Hugoniot curve after a phase transformation is comparable with the slope before the phase transformation. Calculations with data for elemental
boron and B\textsubscript{2}C show furthermore that phase transformation behavior of compounds with similar lattices follow similar rules. This can be used to calculate the shock wave behavior after a phase transformation for a new material, if the phase transformation behavior of a material with a similar lattice is known.

6.7 REFERENCES

1 Chapter 4 of this work.
14 Chapter 5 of this work.
16 Reference 11, p. 482
18 Reference 11, p. 17
19 Reference 17, p. 67
24 Reference 12, p.985
25 R.A. Graham, Solids under High-Pressure Shock Compression, (Springer-Verlag, New York, 1993)
33 Reference 12, p. 545
34 Table of Periodic Properties of the Elements, (Sargent-Welch Scientific Company, Skokie, Illinois, 1980)
35 Reference 12, p. 289
36 Reference 12, p. 248

115
APPENDIX A: CALCULATION OF AVERAGE BOND LENGTH

Because of the complexity of the corundum lattice the average bond length is calculated with the C-M₂O₃ structure as suggested by Wells, shown in Fig. 6.A1.

![Diagram of C-M₂O₃ structure]

**Figure 6.A1:** Schematic representation of the C-M₂O₃ structure proposed by Wells. The O ions in the vicinity of ion i (an Al ion) are numbered in order of increasing distance. Ions of type II are the furthest ions still bordering the next-nearest layer of interstitial sites. Ions which are further away do not border one of the nearest or the next-nearest interstitial sites and are, therefore, considered to be screened.

For this regular packing the average Al-O nearest neighbor distance reported by McCollm is used, i.e., \( R_0 = 0.191 \text{ nm} \). The dimensionless distances, \( x_i \), relative to \( R_0 \), and its number of occurrences \( n_i \), are shown in Table 6.A1. Averaging over the number of occurrences in Table 6.A1 gives a value for \( x \) of 1.69. The average bond length in \( \alpha \)-Al₂O₃ (corundum) is, therefore,

\[
r_0 = 1.69 \times 0.191 = 0.322 \text{ nm}.
\]
Table 6.A1: The dimensionless distances, $x_i$ (relative to $R_0$), between an Al atom, and the O atoms bordering the same interstitial sites, and their number of occurrences in an Al$_2$O$_4$ (corundum) lattice (see Fig. 6.A1). Atoms at distances $x_i > \sqrt[3]{11/3}$ do not border one of the nearest or next-nearest interstitial sites and are, therefore, considered to be screened.

<table>
<thead>
<tr>
<th>Type of atom</th>
<th>$x_i$</th>
<th>$n$</th>
</tr>
</thead>
<tbody>
<tr>
<td>I</td>
<td>1</td>
<td>6</td>
</tr>
<tr>
<td>II</td>
<td>$\sqrt[3]{11/3}$</td>
<td>18</td>
</tr>
</tbody>
</table>

Boron (B) as used in the experiments of Marsh is considered to be $\alpha$-rhombohedral boron as described by Bullett,$^{21}$ and shown in Fig. 6.A2.

![Diagram of the structure of $\alpha$-rhombohedral boron](image)

Figure 6.A2: Schematic representation of the structure of $\alpha$-rhombohedral boron as described by Bullett.$^{21}$ The B atoms in the vicinity of atom $i$ are numbered in order of increasing distance. Atoms of type VII are the furthest atoms still bordering the next-nearest layer of interstitial sites. Atoms which are further away do not border one of the nearest or the next-nearest interstitial sites and are, therefore, considered to be screened.
In this structure two 'nearest' neighbor distances occur: intercluster; \( R_{0,1} = 0.167 \) nm, and intra-icosahedral; \( R_{0,2} = 0.178 \) nm (average of the values given by Bultet\(^{21}\)). The average bond length in this crystal structure is calculated using the interatomic distances between B-atoms bordering the same interstitial site as shown in Table 6.A2.

The average bond length \( r_0 \) as calculated for an \( \alpha \)-rhombohedral packing is, therefore:

\[
\frac{\left(\frac{33}{2} + \frac{\sqrt{13}}{2} + 2\sqrt{3}\right)R_{0,1} + (6 + 2\sqrt{2} + 2\sqrt{3})R_{0,2} + 6\sqrt{\frac{9}{4}R_{0,1}^2 + \sqrt{3}R_{0,1}R_{0,2} + R_{0,2}^2}}{29} \tag{6.A1}
\]

Substitution of \( R_{0,1} \), and \( R_{0,2} \) in Eq. (6.A1) gives \( r_0 = 0.300 \) nm.

**Table 6.A2:** The distances, \( y \), expressed in the 'nearest' neighbor distances \( R_{0,1} \), and \( R_{0,2} \), between atoms in an \( \alpha \)-rhombohedral packing as found in B,\(^*\) and their number of occurrences, \( n \), for a single atom (see Fig. 6.A2). Ions at distances \( y > \sqrt{\{(3/2) R_{0,1}^2 + (R_{0,2} + \sqrt{3/4} R_{0,1})^2 \}} \) do not border one of the nearest or next-nearest interstitial sites and are, therefore, considered to be screened.

<table>
<thead>
<tr>
<th>Type of atom</th>
<th>( y )</th>
<th>( n )</th>
</tr>
</thead>
<tbody>
<tr>
<td>intercluster:</td>
<td>( R_{0,1} )</td>
<td>5</td>
</tr>
<tr>
<td>( II )</td>
<td>( 3/2 \times R_{0,1} )</td>
<td>5</td>
</tr>
<tr>
<td>( III )</td>
<td>( \sqrt{(13/4)} \times R_{0,1} )</td>
<td>1</td>
</tr>
<tr>
<td>intra-icosahedral: (direct)</td>
<td>( R_{0,2} )</td>
<td>2</td>
</tr>
<tr>
<td>( V )</td>
<td>( \sqrt{2} \times R_{0,2} )</td>
<td>2</td>
</tr>
<tr>
<td>intra-icosahedral: (large distances)</td>
<td>( \sqrt{(3/4)} \times (R_{0,1} + R_{0,2}) )</td>
<td>4</td>
</tr>
<tr>
<td>( VII )</td>
<td>( (R_{0,1} + R_{0,2}) )</td>
<td>4</td>
</tr>
<tr>
<td>( VIII )</td>
<td>( \sqrt{{(3/2) R_{0,1}^2 + (R_{0,2} + \sqrt{(3/4)} R_{0,1})^2 }} )</td>
<td>6</td>
</tr>
</tbody>
</table>

\(^*\) Reference 21.
The low-temperature phase of BeO has a wurtzite-type lattice shown in Fig. 6.A3. The average bond length is calculated with the dimensionless distance, \(x_i\), relative to the nearest neighbor distance, \(R_0\), and its number of occurrences \(n_i\), which are shown in Table 6.A3.

**Table 6.A3:** The dimensionless distances, \(x_i\) (relative to \(R_0\)), between Be, and O atoms bordering the same interstitial sites, and their number of occurrences in a BeO (wurtzite) lattice (see Fig. A3). Atoms at distances \(x_i > 2\) do not border one of the nearest or next-nearest interstitial sites and are, therefore, considered to be screened.

<table>
<thead>
<tr>
<th>Type of atom</th>
<th>(x)</th>
<th>(n)</th>
</tr>
</thead>
<tbody>
<tr>
<td>I</td>
<td>1</td>
<td>4</td>
</tr>
<tr>
<td>II</td>
<td>(\sqrt{5/2})</td>
<td>6</td>
</tr>
<tr>
<td>III</td>
<td>2</td>
<td>1</td>
</tr>
</tbody>
</table>

Averaging over the number of occurrences in Table 6.A3 yields an average value for \(x\) of 1.41. The nearest neighbor distance, \(R_0\), in BeO can be calculated from the covalent radii of Be and O \((R_{C,Be} = 0.90 \text{ nm} \text{ and } R_{C,O} = 0.73 \text{ nm}, \text{ respectively}^{34})\), and their Pauling electronegativities \((\chi_{Be} = 1.57, \text{ and } \chi_O = 3.44, \text{ respectively}^{34})\) with the empirical equation:\(^{35}\)

\[
R_0 = R_{C,Be} + R_{C,O} - 0.09(\chi_{Be} - \chi_O) = 0.146 \text{ nm}
\]

(6.A2)

The average bond length in BeO is, therefore:

\[r_0 = 1.41 \times 0.146 = 0.206 \text{ nm}.
\]
Figure 6.A3: Schematic representation of the wurtzite structure of BeO. The O ions in the vicinity of ion $i$ (a Be ion) are numbered in order of increasing distance. Ions of type III are the furthest ions still bordering the next-nearest layer of interstitial sites. Ions which are further away do not border one of the nearest or the next-nearest interstitial sites and are, therefore, considered to be screened.

The TiO$_2$ in Marsh’s experiments$^2$ had a rutile lattice, as shown in Fig. 6.A4. The average bond length is also calculated with the dimensionless distance, $x_i$, relative to the nearest neighbor distance, $R_0$, and its number of occurrences $n_i$, which are shown in Table 6.A4.

Averaging over the number of occurrences in Table 6.A4 gives an average value for $x$ of 1.57. The nearest neighbor distance in TiO$_2$ is $R_0 = 0.194$ nm.$^{36}$ Hence the average bond length in TiO$_2$ is, therefore,

$$r_0 = 1.57 \times 0.194 = 0.305 \text{ nm}.$$
Figure 6.4: Schematic representation of TiO$_2$ with the rutile structure. The O ions in the vicinity of ion $i$ (a Ti ion) are numbered in order of increasing distance. Ions of type $II$ are the furthest ions still bordering the next-nearest layer of interstitial sites. Ions which are further away do not border one of the nearest or the next-nearest interstitial sites and are, therefore, considered to be screened.

Table 6.4: The dimensionless distances, $x$, (relative to $R_o$), between Ti, and O atoms bordering the same interstitial sites, and their number of occurrences in a TiO$_2$ (rutile) lattice (see Fig. 6.4). Atoms at distances $x > 2$ do not border one of the nearest or next-nearest interstitial sites and are, therefore, considered to be screened.

<table>
<thead>
<tr>
<th>Type of atom</th>
<th>$x$</th>
<th>$n$</th>
</tr>
</thead>
<tbody>
<tr>
<td>I</td>
<td>1</td>
<td>6</td>
</tr>
<tr>
<td>$II$</td>
<td>2</td>
<td>8</td>
</tr>
</tbody>
</table>

121
CHAPTER 7

Shock wave mechanics in porous ceramic assemblies

ABSTRACT

The propagation of shock waves in ceramic particle assemblies is described with a simple mechanical model. Shock wave velocities in particle assemblies of BeO, SiC, and UO$_2$ are predicted within 9% from measurements at a different density, and solid material properties.

Assembly properties of several BeO, SiC, and UO$_2$ porous assemblies are compared. The results indicate that it is possible to discriminate between material effects and assembly effects. This yields the possibility of calculating shock waves in a porous ceramic assembly using generally applicable assembly properties, and the solid material properties of the ceramic.
7.1 INTRODUCTION

When shock waves are applied to porous assemblies, e.g. for the compaction of ceramic powders, the effect of the shock wave on the structure of the material is very important. Several theoretical models for the propagation of a shock wave in a porous assembly\textsuperscript{1,2,3} were developed based on a continuum description of the porous assembly. These models, however, only consider overall assembly parameters, like the density.

So far only micromechanical simulations have shown promising results in describing shock waves in particle assemblies while including their effect on the particle structure\textsuperscript{4,5}. These simulations, however, require a large computational capacity to simulate even the smallest assemblies.

The present model is a description of a shock wave travelling through a collection of solid spheres. The model assumes that inside these spheres the shock wave travels as if through a solid, but that a delay is caused during the transmission of the shock from sphere to sphere. This delay occurs due to the deformation of the spheres, when the shock wave is transmitted.

The model aims to predict the shock wave velocities in porous assemblies using data available for assemblies of the same material at other densities, while in the meantime acquiring a description of the changes in a particle assembly due to the passage of a shock wave.

The model describes shock wave equilibrium conditions, and incorporates no absorption of shock energy. No energy dissipation effects due to e.g. surface melting, friction and such are included. The model describes a shock wave travelling through a porous assembly. Only the longitudinal velocity component normal to the shock wave plane, and the corresponding stresses are considered. The solid spheres are assumed to behave as a solid material under equilibrium shock wave conditions. The model is valid only for assemblies in which compaction mainly occurs due to particle deformation and does not incorporate particle fracture.

Firstly the principles of the model are introduced. It is shown that the concept of shock wave delay due to particle deformation is supported by experimental evidence, and the approximations necessary for the model are discussed. These lead to an expression for the stress in the solid spheres.

Secondly, the model itself is developed in two steps, i.e.: (a) the determination of the particle deformation in a loosely packed assembly in which the spheres have only point contacts, and (b) the formulation of the relation between the deformation in a loosely packed, and a precompacted assembly.

Thirdly, the deformation curves of three ceramics at several densities
are calculated, and discussed.

Fourthly, the relation between the deformation curves in two precompacted assemblies with different densities is formulated.

And finally, these relations are applied to predict the shock wave velocity in a porous assembly, from experimental data obtained at another density.

7.2 THEORY

The model is based on the assumption that a certain contact area is created during the transmission of a shock wave from particle to particle. This contact area is created by deformation of the particles.

Several experimental observations clearly suggest this deformation effect, i.e. (a) The shock wave velocity in a porous assembly is always less than in a fully dense sample of the same material at the same stress level. (b) The density of a porous assembly is changed irreversibly by the passage of a shock wave. (c) After passage of a shock wave through a porous assembly the compact shows micromechanical effects. Severe plastic deformation is observed at the grain boundaries in metals and ceramics. Local melting and decomposition also occur specifically at grain boundaries, and not inside the grains.

Simulations of shock waves through an array of metal cylinders by Flinn and Gao show a good correlation with the experiments. In these simulations the particles show deformation in and immediately after the shock wave front. This also indicates that the particle-particle contact surface area has to increase in order to allow the transmission of the stationary shock stress.

The stationary shock stress in a porous assembly is the constant stress attained a short distance after the front of a shock wave. For shock waves in porous substances in particular the shock wave has a blurred precursor due to shock reflections at the particle surfaces.

The present model only applies to the situation in which the relative density is large enough to guarantee particle contact. Initial particle contact can be assumed to exist above the loose packing density. The density of a random loose packing of randomly-shaped particles varies between 45% theoretical maximum density (TMD) and 55% TMD. At lower density the effect of particle rearrangement is too profound. This effect will also delay the shock wave, but is not considered in the model.

The model also does not incorporate particle fracture at stresses well above those at which plastic deformation occurs. It only describes the plastic-
flow regime and should not be applied to other regimes.

In the model the behaviour of a porous assembly is described with an array of solid spheres. In the solid spheres the shock stress is assumed to remain constant. Furthermore it is assumed that the shock stress components perpendicular to the shock wave direction compensate each other. In reality the particles in a porous ceramic assembly will hardly ever be spherical. However a large number of randomly shaped particles, with random orientation can be described with an array of spheres as a good first approximation.

Furthermore, for the current model it is assumed that the many small shock waves inside the particles, can be described with one collective planar shock wave. In addition, it is assumed that this averaged shock wave can be described with shock wave parameters that apply to bulk solid materials.

For the deformation model it is necessary to know the average stress in the solid material in the porous assembly. By using an analogy with a static situation this stress inside the solid material can be approximated. The average stress in the solid material can then be calculated from the assembly density and the stress on the assembly.

In the experiments, used to determine shock wave velocities in porous assemblies, a planar shock wave, of stress $\sigma_{\text{assembly}}$ is introduced in the porous assembly by planar impact.

In a static situation the average internal stress in the solid material, $\sigma_{\text{solid, static}}$, can be calculated from the solid part of the cross-sectional surface of the assembly. In a cross-section of a porous assembly, with a relative density $\epsilon$ compared to the solid, the solid surface covers a surface of $\epsilon$ times the total cross-section. Thus the stress, $\sigma_{\text{solid, static}}$, in the solid can be found from the stress, $\sigma_{\text{assembly, static}}$, on the porous assembly:

$$\sigma_{\text{solid, static}} = \sigma_{\text{assembly, static}} \frac{S_{\text{assembly}}}{S_{\text{solid}}} = \frac{\sigma_{\text{assembly, static}}}{\epsilon} \tag{7.1}$$

in which $S_{\text{assembly}}$ is the cross-section surface area of the porous assembly and $S_{\text{solid}}$ the cross-section surface area of the solid.

An analogous equation can be applied to a dynamic situation if $\sigma_{\text{solid, static}}$ is replaced with the average shock stress, $\sigma$, in the solid phase of the assembly in the plane of shock and $\sigma_{\text{assembly, static}}$ is replaced with the dynamic stress, $\sigma_{\text{assembly}}$, on the assembly.

In the present model the shock wave velocity, $U_{s, \text{solid}}$, and mass displacement velocity, $u_{p, \text{solid}}$, in the solid part of the assembly will be calculated with the stress, $\sigma$, calculated with Eq. (7.1). It should be borne in mind that the $U_{s, \text{solid}}(\sigma)$ and $u_{p, \text{solid}}(\sigma)$ relations that will be used, are basically
only valid for solid bulk materials, while the variables used in our derivation have values averaged over the particles. The correct relations between the average variables might differ considerably and even systematically from the relations for the bulk materials. The latter relations will nevertheless be used as a first approximation.

Before the stationary shock stress is reached small shock waves of lower stress are already present in the particles. The effect of the solid material densification, due to these waves, on the shape of the particles is not incorporated in the model.

7.3 THE MODEL

A. Introduction

The aim of the model is to be able to use shock wave velocity data from a porous assembly to predict shock wave velocities in porous assemblies of the same or perhaps another material at other densities. In addition it aims to describe the microstructural changes in a particle assembly due to the passage of a shock wave.

To develop the model, firstly the particle deformation in a loosely packed assembly is determined. In a loosely packed assembly there are only point contacts between the spheres, as shown in Fig. 7.1(a). Any deformation of the spheres is solely due to the shock wave, as shown in Fig. 7.1(b).

In the second part the relation between the shock wave deformation in a loosely packed assembly, and a precompacted assembly is derived. In an assembly precompacted by for instance sintering or static pressing the particles are already deformed, before the shock wave arrives, as shown in Fig. 7.1(c). The shock wave then compresses the particles as shown in Fig. 7.1(d), which is comparable to the state shown in Fig. 7.1(b).

In the third part the relation between the shock wave deformation in two precompacted assemblies with a different starting density is derived.

In the fourth part this relation is used to calculate the shock wave velocity in a precompacted assembly using the deformation data of a precompacted assembly with an other density.
Figure 7.1: Schematic representation of impacting spheres: (a) For spheres, with a point contact (loosely packed assembly, with a density $\varepsilon = \varepsilon_0$), at the time the shock wave arrives (with shock wave velocity $U_s$) at the center of the impacting sphere ($t=0$). (b) For spheres that initially have point contact, at the time the shock wave arrives at the center of the target sphere ($t=t_s+t_d$). (c) For spheres, with an initial contact surface (precompacted assembly, with a density $\varepsilon > \varepsilon_0$), at the time the shock wave arrives at the center of the impacting sphere ($t=0$). (d) For spheres that initially have a contact surface, at the time the shock wave arrives at the center of the target sphere ($t=t_s+t_d$).

B. Deformation in a loosely packed assembly

The deformation in the assembly is the result of the transmission and reflection of many small shock waves that travel in different directions and interfere. In the present model this complex situation is treated by the introduction of a delay time $t_d$. In this delay time the deformation of the
spheres is assumed to occur with the mass displacement velocity.

In Fig. 7.2 the particle is shown when the shock wave arrives at the centre of the impacting sphere \((r=0)\), and after the transmission of the shock wave, when the particles are fully deformed \((t=t_s+t_d)\).

\[
\begin{align*}
R & \quad R \\
2t_d u_p & \quad t = 0 \\
1 = t_s + t_d & \quad \Delta x = 2R
\end{align*}
\]

**Figure 7.2:** Schematic representation of impacting spheres with the deformation as a function of the mass displacement velocity, \(u_p\). The spheres have only point contact at \(t = 0\).

The shock wave velocity through the porous assembly, \(U_{s,\text{assembly}}\) can be found from the distance travelled and the corresponding time needed. In travelling from particle centre to particle centre the distance travelled is:

\[
\Delta x = 2R
\]

(7.2)

in which \(R\) is the particle radius.

The corresponding time, \(t\), consists of two parts i.e. first the time, \(t_s\), for the shock wave to travel through the solid material:
\[ t_s = \frac{2R}{U_{s,\text{solid}}} \quad (7.3) \]

in which \( U_{s,\text{solid}} \) is the average shock wave velocity in the solid particles comprising the porous assembly. The second part is the delay time \( t_d \) introduced to take into account that the deformation process during the shock wave transmission delays the shock wave.

Introduction of \( t_d \) results in the following equation for the shock wave velocity in the porous assembly, \( U_{s,\text{assembly}} \):

\[ U_{s,\text{assembly}} = \frac{2R}{\frac{2R}{U_{s,\text{solid}}} + t_d} \quad (7.4) \]

It is assumed that the delay time \( t_d \) is determined by the velocity at which the impacting sphere is deformed. In a vacuum or a medium with a low density such as air the velocity at which the surface of the impacting sphere moves is twice the mass displacement velocity: \( 2u_{p,\text{solid}} \). The distance over which the surface of the impacting sphere at the edge of the contact surface has travelled at \( t=t_d \) is \( 2u_{p,\text{solid}} t_d \) as can be seen in Fig. 7.2. At the contact surface the material moves with the mass displacement velocity, this causes the deformation shown in Fig. 7.2.

We now define a dimensionless deformation parameter, \( \Delta r_0 \) as:

\[ \Delta r_0 = \frac{t_d u_{p,\text{solid}}}{R} \quad (7.5) \]

in which \( u_{p,\text{solid}} \) is the average mass displacement velocity of the material in the particle, and \( R \) is the particle radius. This means that \( \Delta r_0 \) is the relative compression due to the shock wave.

Combining Eqs. (7.4) and (7.5) gives:

\[ \frac{1}{U_{s,\text{assembly}}} = \frac{1}{U_{s,\text{solid}}} + \frac{\Delta r_0}{2 u_{p,\text{solid}}} \quad (7.6) \]

in which \( U_{s,\text{assembly}} \) is a function of, \( \sigma_{\text{assembly}} \), the shock stress in the porous assembly, and \( u_{p,\text{solid}} \) and \( U_{s,\text{solid}} \) are functions of, \( \sigma \), the shock stress in the solid phase in the assembly. These two stresses are related through Eq. (7.1), which makes it possible to determine the \( \Delta r_0(\sigma) \)-curve as a function of one stress parameter only.
C. Deformation in a precompacted assembly

In an assembly that is precompacted by sintering or static pressing, the particles are already deformed, before the shock wave arrives. If the deformation by pressing or sintering is assumed to be isotropic this initial deformation can be calculated from the initial density. This calculation shown in Appendix A leads to the following expression for the initial deformation, $\Delta l$:

$$\Delta l = 1 - \left(\frac{\varepsilon_0}{\varepsilon}\right)^{\frac{1}{3}}$$

(7.7)

in which $\varepsilon_0$ and $\varepsilon$ are the relative densities of a loosely packed and precompacted assembly, respectively, compared to solid material.

The density of a random loose packing of irregular particles varies between 45% theoretical maximum density (TMD) and 55% TMD. In the following $\Delta l$ will be calculated with $\varepsilon_0=50$% TMD. The maximum error of about 10% in the relative density leads to a maximum error of about 3% in the initial deformation, $\Delta l$.

If an assembly is precompacted before a shock wave is applied the particles deform. This initial deformation in the direction of the shock wave is $\Delta l$ as shown in Fig. 7.1(c) ($t=0$). It is assumed that the shape of the contact area due to initial deformation is the same as would occur in a shock wave, $\Delta r_0=\Delta l$ [Fig. 7.1(b), $t=t_s+t_d$]. The deformation of a prepressed or sintered porous assembly can then be related to the curve of a loosely packed assembly.

The shock wave delay in a prepressed or sintered assembly can be calculated analogous to the delay in a loosely packed assembly.

In a precompacted assembly the distance from particle centre to particle centre is:

$$\Delta x = 2R (1-\Delta l)$$

(7.8)

The time needed for the shock wave to travel through the solid material becomes:

$$t_s = \frac{2R (1-\Delta l)}{U_{s,solid}}$$

(7.9)

The shock wave velocity in the porous assembly, $U_{s,assembly}$ is than found from:
\[ U_{\text{assembly}} = \frac{2R (1 - \Delta l)}{2R (1 - \Delta l) + t_d} U_{s,\text{solid}} \]  
\[ (7.10) \]

The delay time, \( t_d \), can now be found from the total deformation, which is the shock wave deformation for the loosely packed assembly, \( \Delta r_0 \), minus the initial deformation, \( \Delta l \):
\[ t_d = \frac{R (\Delta r_0 - \Delta l)}{u_{p,\text{solid}}} \]  
\[ (7.11) \]

Combining Eqs. (7.10) and (7.11) gives an equation analogous to (7.6):
\[ \frac{1}{U_{s,\text{assembly}}} = \frac{1}{U_{s,\text{solid}}} + \frac{(\Delta r_0 - \Delta l)}{(1 - \Delta l)} \frac{1}{2 u_{p,\text{solid}}} \]  
\[ (7.12) \]

in which \( U_{s,\text{assembly}} \) is a function of, \( \sigma_{\text{assembly}} \), the stress on the porous assembly, and \( u_{p,\text{solid}} \) and \( U_{s,\text{solid}} \) are functions of, \( \sigma \), the stress in the solid phase in the assembly. These two stresses are related through Eq. (7.1), which makes it possible to determine the \( \Delta r_0(\sigma) \)-curve as a function of one stress parameter only.

The shock wave deformation of the spheres, \( \Delta r \), which is reached when the stable shock stress is attained, can be calculated from the total deformation, \( \Delta r_0 \), and the initial deformation, \( \Delta l \) using Eq. (7.12) and:
\[ \Delta r = \Delta r_0 - \Delta l \]  
\[ (7.13) \]

When the \( \Delta r_0 \)-curve is known for a certain ceramic the shock wave velocity, \( U_{s,\text{assembly}} \), in any porous assembly can be calculated with Eq. (7.12). Because the aim of the present model was not only to find the shock wave velocity, but also to study the effects of the shock wave on the porous assembly, we first analyze the deformation curves before applying them to the calculation of shock wave velocities.
7.4 SHOCK WAVE DEFORMATION CURVES

A. Calculations

For the calculation of the particle deformation with Eq. (7.12), it is necessary to have equations describing the shock wave velocities, \( U_{s,\text{solid}} \) and \( U_{s,\text{assembly}} \), and the mass displacement velocity, \( u_{p,\text{solid}} \), as a function of the dynamic stress. In this case data were used from Marsh\(^6\). The shock wave velocity and the mass displacement velocity, were correlated to the dynamic stress applied to the assembly, \( \sigma_{\text{assembly}} \), by a second order polynomial.

The fits are performed for solid BeO, solid SiC, and solid UO\(_2\) and a number of particle assemblies of these materials. These materials were the only ceramics for which enough data were available. The parameters of the polynomials are shown in Table 7.1(a) and 7.1(b). For the materials data were only available for a limited stress range. The stress ranges within which the data were available are shown in Table 7.2. Because data for the pure 100% TMD ceramics were not available we used the data of 99.3% TMD BeO, 97.0% TMD SiC, and 94.0% TMD UO\(_2\) to determine \( U_{s,\text{solid}}(\sigma) \) and \( u_{p,\text{solid}}(\sigma) \).

**Table 7.1(a):** Parameters of the least squares second order polynomial fit of the shock wave velocity, \( U_{s,\text{assembly}} \), in the assembly, to the stress, \( \sigma_{\text{assembly}} \), for BeO, SiC, and UO\(_2\), at several relative densities, \( \varepsilon \) \((U_{s,\text{assembly}} = a_0 + a_1\sigma_{\text{assembly}} + a_2\sigma_{\text{assembly}}^2)\). Data are from Marsh\(^6\).

<table>
<thead>
<tr>
<th>Compound</th>
<th>( \varepsilon ) (%)</th>
<th>( a_0 ) ( (\text{km s}^{-1}) )</th>
<th>( a_1 ) ( (\text{km s}^{-1} \text{ GPa}^{-1}) )</th>
<th>( a_2 ) ( (\text{km s}^{-1} \text{ GPa}^{-2}) )</th>
</tr>
</thead>
<tbody>
<tr>
<td>BeO</td>
<td>99.3</td>
<td>+1.070( \cdot )10(^{-1} )</td>
<td>-2.413( \cdot )10(^{-2} )</td>
<td>+3.771( \cdot )10(^{-4} )</td>
</tr>
<tr>
<td></td>
<td>92.4</td>
<td>+8.077</td>
<td>+2.016( \cdot )10(^{-3} )</td>
<td>+3.571( \cdot )10(^{-4} )</td>
</tr>
<tr>
<td></td>
<td>81.4</td>
<td>+4.019</td>
<td>+1.085( \cdot )10(^{-1} )</td>
<td>-4.500( \cdot )10(^{-4} )</td>
</tr>
<tr>
<td>SiC</td>
<td>97.0</td>
<td>+1.120( \cdot )10(^{-1} )</td>
<td>-5.731( \cdot )10(^{-2} )</td>
<td>+5.611( \cdot )10(^{-4} )</td>
</tr>
<tr>
<td></td>
<td>94.2</td>
<td>+8.772</td>
<td>-1.113( \cdot )10(^{-2} )</td>
<td>+3.158( \cdot )10(^{-4} )</td>
</tr>
<tr>
<td></td>
<td>72.5</td>
<td>+2.717</td>
<td>+1.322( \cdot )10(^{-1} )</td>
<td>-6.898( \cdot )10(^{-4} )</td>
</tr>
<tr>
<td>UO(_2)</td>
<td>94.0</td>
<td>+3.802</td>
<td>+1.378( \cdot )10(^{-2} )</td>
<td>+1.013( \cdot )10(^{-4} )</td>
</tr>
<tr>
<td></td>
<td>57.9</td>
<td>+1.415</td>
<td>+5.822( \cdot )10(^{-2} )</td>
<td>-1.810( \cdot )10(^{-4} )</td>
</tr>
</tbody>
</table>
Table 7.1(b): Parameters of the least squares second order polynomial fit of the mass displacement velocity, $u_{d,\text{assembly}}$, to the stress, $\sigma_{\text{assembly}}$, for BeO, SiC, and UO$_2$, at several relative densities, $\varepsilon$ ($u_{d,\text{assembly}} = b_0 + b_1\sigma_{\text{assembly}} + b_2\sigma_{\text{assembly}}^2$). Data are from Marsh.$^6$

<table>
<thead>
<tr>
<th>Compound</th>
<th>$\varepsilon$ (%)</th>
<th>$b_0$ (km s$^{-1}$)</th>
<th>$b_1$ (km s$^{-1}$ GPa$^{-1}$)</th>
<th>$b_2$ (km s$^{-1}$ GPa$^{-2}$)</th>
</tr>
</thead>
<tbody>
<tr>
<td>BeO</td>
<td>99.3</td>
<td>$-6.959 \cdot 10^{-2}$</td>
<td>$+3.824 \cdot 10^{-2}$</td>
<td>$-9.596 \cdot 10^{-5}$</td>
</tr>
<tr>
<td></td>
<td>92.4</td>
<td>$+2.558 \cdot 10^{-2}$</td>
<td>$+4.626 \cdot 10^{-2}$</td>
<td>$-1.589 \cdot 10^{-4}$</td>
</tr>
<tr>
<td></td>
<td>81.4</td>
<td>$+7.877 \cdot 10^{-1}$</td>
<td>$+3.460 \cdot 10^{-2}$</td>
<td>$-3.379 \cdot 10^{-5}$</td>
</tr>
<tr>
<td>SiC</td>
<td>97.0</td>
<td>$-1.668 \cdot 10^{-1}$</td>
<td>$+4.151 \cdot 10^{-2}$</td>
<td>$-1.049 \cdot 10^{-4}$</td>
</tr>
<tr>
<td></td>
<td>94.2</td>
<td>$-2.848 \cdot 10^{-1}$</td>
<td>$+5.172 \cdot 10^{-2}$</td>
<td>$-1.857 \cdot 10^{-4}$</td>
</tr>
<tr>
<td></td>
<td>72.5</td>
<td>$+8.844 \cdot 10^{-1}$</td>
<td>$+4.328 \cdot 10^{-2}$</td>
<td>$-8.651 \cdot 10^{-5}$</td>
</tr>
<tr>
<td>UO$_2$</td>
<td>94.0</td>
<td>$+5.662 \cdot 10^{-2}$</td>
<td>$+2.244 \cdot 10^{-2}$</td>
<td>$-4.651 \cdot 10^{-5}$</td>
</tr>
<tr>
<td></td>
<td>57.9</td>
<td>$+6.579 \cdot 10^{-1}$</td>
<td>$+3.067 \cdot 10^{-2}$</td>
<td>$-7.802 \cdot 10^{-5}$</td>
</tr>
</tbody>
</table>

Table 7.2: The stress ranges in which shock velocity data were available.$^6$

<table>
<thead>
<tr>
<th>Compound</th>
<th>Density $\varepsilon_0$ (% TMD)</th>
<th>Lower stress limit (GPa)</th>
<th>Upper stress limit (GPa)</th>
</tr>
</thead>
<tbody>
<tr>
<td>BeO</td>
<td>99.3</td>
<td>10</td>
<td>102</td>
</tr>
<tr>
<td></td>
<td>92.4</td>
<td>9</td>
<td>93</td>
</tr>
<tr>
<td></td>
<td>81.4</td>
<td>30</td>
<td>80</td>
</tr>
<tr>
<td>SiC</td>
<td>97.0</td>
<td>16</td>
<td>98</td>
</tr>
<tr>
<td></td>
<td>94.2</td>
<td>42</td>
<td>88</td>
</tr>
<tr>
<td></td>
<td>72.5</td>
<td>29</td>
<td>69</td>
</tr>
<tr>
<td>UO$_2$</td>
<td>94.0</td>
<td>24</td>
<td>161</td>
</tr>
<tr>
<td></td>
<td>57.9</td>
<td>14</td>
<td>121</td>
</tr>
</tbody>
</table>
The values of $\Delta l$ were calculated with Eq. (7.7) with $\varepsilon_0=50\%$ TMD. In Fig. 7.3 all the $\Delta r$-curves for the ceramics are shown together, plotted against, $\sigma$, the shock stress in the solid phase in the assembly.

\begin{figure}[h]
\centering
\includegraphics[width=0.5\textwidth]{fig73.png}
\caption{The shock deformation curves for 81.4\% TMD, and 92.5\% TMD BeO, 72.5\% TMD, and 94.2\% TMD SiC, and 57.9\% TMD UO$_2$. The curves were calculated using data from Marsh$^6$.}
\end{figure}

**B. Discussion**

The deformation curves increase with decreasing relative density, $\varepsilon$, as can be seen in Fig. 7.3. This can be explained from the fact that in these assemblies (with $\varepsilon>50\%$ TMD) the particles already have an initial contact surface which increases with the density. Therefore less deformation occurs in the shock wave for an assembly with a high starting density. This leads to a comparatively low $\Delta r$-curve for assemblies with a high initial density as can be seen in Fig. 7.3.

In Fig. 7.3 it can be seen that for BeO, SiC, and UO$_2$ the deformation
shows an overall increase with decreasing relative density. This effect appears
to be material independent for these materials. This indicates that the particle
deformation depends more on assembly properties than on solid material
properties. The results suggest that the deformation curves for the three
ceramics are mutually exchangeable.

In Fig. 7.3 the deformation curves of 57.9% TMD UO₂ and 92.4%
TMD BeO show a maximum. The initial rise in the deformation curves can
easily be explained. At low stresses the shock wave can be transmitted
through a small contact area, so there is little delay.

The deformation curves show a decline for stresses above ca. 40 GPa.
The effect is strongest for low densities. This is an unexpected effect,
because the deformation is expected to increase with increasing stress to a
theoretical maximum. A possible explanation for this might be the occurrence
of particle rearrangement, which was not accounted for in the model.

Because the shock wave compaction that occurs in shocked porous
assemblies is a complicated process, involving more then only plastic
deformation, the interpretation of the shape of the deformation curves must
be approached with care. Furthermore, the simplifications and assumptions
that have been applied in the model might affect this shape. Due to the lack
of sufficient data on the compaction process in relation to the shock state,
though study is, as yet, not possible.

However, when the deformation curves are used as an intermediate to
calculate the Hugoniot of a porous material only the relative magnitude of the
two different deformation curves is important. Calculations show that an error
of 10% in the value of the deformation would result in an error of only about
3% in the calculated shock wave velocity.

7.5 RELATION BETWEEN DEFORMATION CURVES

A. Introduction

The aim of the present model is to relate the shock wave velocities in
two assemblies with different initial densities. Most of the available data
consider precompacted assemblies. It is, therefore, necessary to have a
relation between the shock wave velocities in two precompacted assemblies.
This relation can be derived from the relation between the Δρ-curves of a
precompacted assembly and the Δρ₀-curves of a loosely packed assembly
found earlier.
B. Theory

The shock wave deformation, $\Delta r_i$, in assembly $i$, with a relative density of $\varepsilon_i$ can be found from the total deformation $\Delta r_0$ and the initial deformation $\Delta l_i$:

$$\Delta r_i = \Delta r_0 - \Delta l_i$$  \hspace{1cm} (7.14)

The same applies for assembly $j$:

$$\Delta r_j = \Delta r_0 - \Delta l_j$$  \hspace{1cm} (7.15)

This means that:

$$\Delta r_i = \Delta r_j + \Delta l_j - \Delta l_i$$  \hspace{1cm} (7.16)

C. Calculations

The $\Delta r$-curve calculated with Eq. (7.16) for 81.4% TMD BeO from the 92.4% TMD BeO $\Delta r$-curve is shown in Fig. 7.4. The 72.5% TMD SiC curve calculated from the 94.2% TMD SiC $\Delta r$-curve is shown in Fig. 7.5. For the calculation of $\Delta l$, Eq. (7.7) was used with a loose packing density\textsuperscript{10} of $\varepsilon_0=50\%$ TMD.

To see if the $\Delta r$-curves are material dependent, the $\Delta r$-curve for a 72.5% TMD assembly was calculated from all BeO, SiC, and UO$_2$ curves. In Fig. 7.6 these $\Delta r$-curves, calculated from 92.4% TMD BeO, 81.4% TMD BeO, and 57.9% TMD UO$_2$ data are shown compared to the curve of the 72.5% TMD SiC assembly.
Figure 7.4: Calculated deformation curves for 81.4% TMD BeO. The solid lines were calculated with Eq. (7.12) using data from Marsh\textsuperscript{6}. The dashed line was calculated with Eq. (7.13) from the Δ\textit{r}-curve of 92.4% TMD BeO.

Figure 7.5: Calculated deformation curves for 72.5% TMD SiC, the solid lines were calculated with Eq. (7.12) using data from Marsh\textsuperscript{6}. The dashed line was calculated with Eq. (7.13) from the Δ\textit{r}-curve of 94.2% TMD SiC.
**Figure 7.6:** Calculated deformation curves for 72.5% TMD using Δr-curves from different densities compared to the experimental Δr-curve of 72.5% TMD SiC. The experimental curves were calculated with experimental data from Marsh⁶.

### D. Discussion

In the Figs. 7.4 and 7.5 the predicted deformation curves for BeO and SiC are shown. In both calculations the calculated curves are lower than the curves to be predicted. The largest difference (33%) is found for SiC (see Fig. 7.5).

The Δr-curves do not change shape when they are adapted in the present model to a different density with Eq. (7.16). This is due to the fact that the present model is a first order approximation.

All three ceramics seem to have curves that are mutually exchangeable. The fact that the best predictions are made with the deformation curve of 57.9% TMD UO₂ and 81.4% TMD BeO indicates that the curves for BeO, SiC, and UO₂ are very similar.

The best predictions are made with the data of assemblies with densities closest to the density of the predicted curve. This is to be expected, because according to the model the Δr-curves are an assembly property, and all assemblies are made of ceramics. Solid material properties are no longer
incorporated in the $\Delta r$-curves. Thus the error in the approximation should depend mainly on the relative density, $\varepsilon$.

If a loose packing density of $\varepsilon_0=50\%$ TMD is assumed, the initial deformation for a 72.5\% dense assembly, calculated with Eq. (7.7) is $\Delta l_0=0.12$. If the maximum shock wave deformation ($\Delta r=0.18$ in Fig. 7.6 for 57.9\% TMD UO$_2$) is added, the total deformation is $\Delta r_{0,\text{max}}=0.30$.

The final contact area, $A$, after passage of the shock wave front can be calculated from:

$$A = \pi R^2 (2-\Delta r_0)\Delta r_0$$  \hspace{1cm} (7.17)

Thus the maximum total deformation in Fig. 7.6, $\Delta r_{0,\text{max}}=0.30$ corresponds with a final contact area, on transmission of the stable shock pressure of 51\% of the maximum sphere cross-section ($=\pi R^2$).

### 7.6 SHOCK WAVE VELOCITY FROM DEFORMATION CURVE

**A. Theory**

With the relation between the deformation curves shock wave velocity data of one assembly can be used to predict the shock wave velocity in assemblies with other initial densities. The relation between the shock wave deformation, $\Delta r_i$, and the shock wave velocity $U_{s,i}$ in assembly $i$ can be found from Eq. (7.12):

$$\frac{1}{U_{s,i}} = \frac{1}{U_{s,\text{solid}}} + \frac{(\Delta r_i)}{(1-\Delta l_i)} \frac{1}{2 u_{p,\text{solid}}}$$  \hspace{1cm} (7.18)

in which $\Delta r_i=\Delta r_0-\Delta l_i$.

Substitution of Eq. (7.16) in (7.18) gives:

$$\frac{1}{U_{s,i}} = \frac{1}{U_{s,\text{solid}}} + \frac{(\Delta r_j+\Delta l_j-\Delta l_i)}{(1-\Delta l_i)} \frac{1}{2 u_{p,\text{solid}}}$$  \hspace{1cm} (7.19)

The shock wave velocity $U_{s,i}$ in a porous assembly with density $\varepsilon_i$, therefore, can be predicted with the deformation curve of a porous assembly of density $\varepsilon_i$. The fact that the results in earlier calculations indicate that the deformation curves are not very sensitive to the type of ceramic suggests that the results for an assembly $i$ of ceramic A could be used for calculations on
assembly $j$ of the ceramic B.

B. Calculations

For BeO and SiC assemblies there were two sets of data for different densities, which makes comparison possible.

The $U_{s,i}$-curve calculated with Eq. (7.19) for 81.4% TMD BeO from the 92.4% TMD BeO $\Delta r$-curve is shown in Fig. 7.7. The $U_{s,i}$-curve for 72.5% TMD SiC calculated from the 94.2% TMD SiC $\Delta r$-curve is shown in Fig. 7.8. In Figs. 7.7 and 7.8 the calculations are compared with the experimental data from Marsh$^6$, and with the original shock wave data from which the $\Delta r$-curves were calculated.

![Graph showing shock wave velocity vs. assembly stress](image)

**Figure 7.7:** The shock wave velocity, $U_{s,i}$, calculated for a 81.4% dense BeO assembly using the $\Delta r$-curve from a 92.4% dense BeO assembly. Data are from Marsh$^6$. 

141
Figure 7.8: The shock wave velocity, $U_{s,i}$, calculated for a 72.5% dense SiC assembly using the $\Delta r$-curve from a 94.2% dense SiC assembly. Data are from Marsh.  

There was only one set of shock wave velocity data available for a porous UO$_2$ assembly with a starting density above 50% TMD, apart from the 94.0% TMD data that were used to derive the "solid" Hugoniot. This prevented comparison with another UO$_2$ assembly. However, because the $\Delta r$-curves seem to be material independent the $\Delta r$-curve of 72.5% TMD SiC was used to calculate the $U_{s,i}$-curve for 57.9% TMD UO$_2$, with Eq. (7.19). The result is shown in Fig. 7.9.

To further study the effect of the material independence of the $\Delta r$-curves on the calculation of $U_{s,i}$-curves the $U_{s,i}$-curve for 72.5% TMD SiC was calculated from the 81.4% TMD BeO $\Delta r$-curve and the 57.9% TMD UO$_2$ $\Delta r$-curve. The result is shown in Fig. 7.10.
Figure 7.9: The shock wave velocity, $U_{k,i}$, calculated for a 57.9% dense UO$_2$ assembly using the $\Delta r$-curve from a 72.5% dense SiC assembly. Data are from Marsh$^6$.

Figure 7.10: The shock wave velocity, $U_{k,i}$, calculated for a 72.5% dense SiC assembly using the $\Delta r$-curve from a 57.9% dense UO$_2$ assembly, and the $\Delta r$-curve from a 81.4% dense BeO assembly. Data are from Marsh$^6$. 

143
C. Discussion

In Figs. 7.7 and 7.8 the predicted shock wave velocity curves for 81.4% TMD BeO and 72.5% TMD SiC are shown. These curves are predicted using the calculated $\Delta r$-curves shown in Figs. 7.4 and 7.5. Within the range of available data the prediction of $U_{s,\text{assembly}}$ is always within 9% for BeO and SiC, when compared to data from Marsh.

The average deviation from the experimental curves is 3.9% for BeO and 5.7% for SiC. The calculation of the shock wave velocity curve for 57.9% TMD UO$_2$ with the 72.5% TMD SiC data, shown in Fig. 7.9, shows a maximum error of 4.2%. The calculation of the shock wave velocity in 72.5% TMD SiC with the deformation curve of 81.4% TMD BeO and 57.9% TMD UO$_2$ shown in Fig. 7.10 gives an even better result than the calculation in Fig. 7.8.

The results of the calculations shown in Figs. 7.9 and 7.10 indicate the possibility of a $\Delta r(\sigma, \varepsilon)$-curve that would be applicable to all porous ceramic assemblies with $\varepsilon > 50$% TMD. In the model it was assumed that the deformation of the particles due to sintering or prepressing has the same effect on the contact area between the particles as the shock wave deformation. This is unlikely, because even with different static compaction techniques there is a difference in pore-structure. Pressing e.g. results in a different pore shape than sintering. In sintering the neckforming results in a different contact area, than occurs after pressing.

It is therefore reasonable to assume that the initial contact area and its deformation depend on the pretreatments (like pressing or sintering) applied to the material, before the shock wave is applied. This makes it hard to develop a general relation between the shock wave and initial deformation. The simple approximation presently used is applicable to all pretreatments.

The present model might be refined by a calculation of the initial deformation dependent on the pretreatment of the assembly. This refinement, however, would soon involve complex descriptions of porous assemblies and was, therefore, omitted for reasons of simplicity in the present model. Furthermore, this effect may not be to critical.

The particle size is likely to have an effect on the mechanisms, viz. fracture or plastic deformation at a given stress. If, however, plastic deformation is the most important mechanism the particle size probably has little effect. It is, therefore, assumed that the particle size has more effect on the energy dissipation effects in a shock wave than on the equilibrium properties.

Another simplification in the model was the principle of a head-on collision of two spheres. In an assembly the particle will not collide head on
in general. In our current model, however, we only consider the longitudinal velocities. The contribution of particle contacts under small angles to the longitudinal velocity apparently outweighs other contributions. The model might be further developed to contain an average contact angle which could be calculated from contact forces in a porous assembly\textsuperscript{11}.

7.7 CONCLUSIONS

The presented deformation model is successful in the calculation of shock wave velocities in several assemblies of BeO, SiC, and UO$_2$. The model can be used to predict the shock wave velocity as a function of the shock stress for a porous assembly at several densities, when solid material properties and the data for one density are known. Even a very simple approximation of the internal shock stress in the solid of the porous assembly gives an excellent correlation. The predictions are valid for densities above random loose packing density, which is about 50\% TMD.

The success of the predictions indicates that the used simplified presentation of a very complicated process gives a good approximation. The resultant shock wave in a porous substance or powder seems to be transmitted only after a certain deformation of the particles is reached. This requires a novel approach to shock waves in porous substances as compared to solids.

The results furthermore seem to indicate that the deformation curves are not dependent on the solid material. This means that there might be a generally applicable deformation curve for, e.g. ceramics, as calculated in this chapter.

7.8 REFERENCES

APPENDIX A: ISOTROPIC COMPACTION OF AN ARRAY OF SPHERES

If an array of spheres is isotropically compacted the density of the assembly after compaction can be related to the deformation of the spheres.

In Fig. 7.A1 an array of spheres is shown before and after compaction. The spheres do not rearrange but are deformed over a length $R\Delta l$. Because there is no rearrangement of the spheres the relative density of the inscribed spheres (with a radius of $(1-\Delta l)$ times the original radius) is the same as the relative density of the spheres in the original array. This fact can be used to find an equation for the deformation $\Delta l$ as a function of the relative density, $\varepsilon$.

The total volume, $V_0$ of a loosely packed assembly of $N$ spheres, with radius, $R$, can be found from:

$$V_0 = \frac{4\pi N R^3}{3 \varepsilon_0} \quad (7.A1)$$

in which $\varepsilon_0$ is the relative density of the loosely packed assembly compared to the solid material density.
Figure 7.A1: Schematic representation of the isotropic compaction of a loosely packed assembly. The inscribed spheres shown in the compacted assembly have the same relative density as the original loose packing. The radius of the inscribed spheres is \((1-\Delta l)R\).

If the assembly with volume, \(V\), is isotropically compressed and the spheres are deformed over a length of \(R\Delta l\), we find for the volume, \(V\), of the compressed assembly:

\[
V = \frac{4\pi N \ R^3 \ (1-\Delta l)^3}{3 \ \epsilon_0} \tag{7.A2}
\]

The relative density of the compressed assembly, \(\epsilon\), can be found from the total solid volume after compaction, which must be equal to the volume of the spheres in the original array, to obey mass conservation, and the new total volume, \(V\). This yields:
\[ \varepsilon = \frac{4\pi N R^3}{V} \] (7.A3)

Combination of Eqs. (7.A3) and (7.A2) gives an expression for \( \Delta l \) as a function of the relative densities:

\[ \Delta l = 1 - \left( \frac{\varepsilon_0}{\varepsilon} \right)^\frac{1}{3} \] (7.A4)

The density of a random loose packing of irregular particles varies between 45% TMD and 55% TMD. In the following \( \Delta l \) will be calculated with \( \varepsilon_0 = 50\% \) TMD. The maximum error of \( \pm 10\% \) in the relative density, leads to a maximum error of \( \pm 3.3\% \) in the initial deformation.

With a relative density for the loosely packed assembly of \( \varepsilon_0 = 50\% \) TMD and a maximum density of \( \varepsilon_i = 100\% \) TMD, the maximum value for \( \Delta l(\varepsilon_0 = 50\%, \varepsilon_i = 100\%) = 0.21 \). This maximum value does not apply to the sphere deformation in a shock wave. Because the deformation in the shock wave is not isotropic it is possible to find values for the shock wave deformation, \( \Delta r_0 > 0.21 \).
CHAPTER 8

Shock wave absorption in AlN powder in a cylindrical configuration

ABSTRACT

The absorption of a shock wave in several AlN powders was characterized with a shock wave absorption parameter. The absorption of the shock wave energy per unit area in 34 to 37% dense AlN powder with an average particle size of 5.5 μm (determined with a Fisher Sub-Sieve Sizer, FSSS) was found to vary between 11 to 14%/mm. In 36 to 37% dense AlN powder with an average (FSSS) particle size of 3.3 μm, the absorption was found to be 10%/mm. In 35% dense AlN powder with an average (FSSS) particle size of 1.5 μm the absorption was found to be 18 to 22%/mm.

The effect of the difference between the powders is discussed in relation to the calculated shock stresses in the assemblies, and its effect on the shock wave compaction of the powders.
8.1 INTRODUCTION

By applying a shock wave to a porous material its density can be increased up to more than 99% of its theoretical maximum density (TMD). This new densification method, the so-called dynamic compaction process, enables the densification of porous materials which are difficult to compact with conventional means such as sintering and pressing. Examples of these are single phase materials or composites which are thermodynamically instable at the high temperatures necessary for sintering. For these materials, such as the hydroxyapatite-based bone implants, or the nickel-aluminum-based aerospace composites, dynamic compaction is a promising alternative production process.

Due to the relatively short history of the process, and the wide range of materials which can be dynamically compacted, the optimal conditions for dynamic compaction need to be determined experimentally for each material. The present work is aimed at determining the optimal conditions for compaction in the cylindrical configuration. These optimal conditions are found between under-compaction, if too little shock wave energy is available for complete compaction, and over-compaction if too much shock wave energy at the center of the sample results in fracture.

To determine the optimal conditions for dynamic compaction in the cylindrical configuration, Prümmer (1987) introduced the $E/M$-method, which is still the most generally used method not based on computer simulations. Computer simulations can only be applied when the material properties are well-known, and, therefore, have little predictive value for new materials.

The $E/M$-method is an experimental approach ($E$ is the mass of the explosive, $M$ is the mass of the sample to be densified). It is basically a step-wise adjustment of two parameters, the detonation velocity of the explosive, and the amount of explosive in order to obtain a sample, which is as dense as possible. These two parameters determine the height and duration of the dynamic stress pulse, or shock wave. A disadvantage of the $E/M$-method is that its results only apply to one powder size distribution, and one sample size. In general several steps are necessary to obtain the optimal conditions for compaction, and these optimal conditions do not apply when e.g. the powder size distribution, or the solid properties are changed.

The aim of the present experimental technique is to find one parameter that can be obtained in one experiment, and fully characterizes the shock wave behaviour of a porous material. When this single parameter is known the optimal conditions for compaction can be calculated without further experiments. For this purpose we introduce a shock wave absorption parameter, $f$, which describes the relative absorption of shock wave energy per unit length. With this
absorption parameter it is possible to calculate the parameters which yield a compact that is as homogeneous as possible. It should also be possible to model up- and downscaling of the process. Furthermore, the absorption parameter is expected to be independent of the shape of the configuration. Therefore, when more complex shapes than the cylinder are to be compacted, it should be possible to predict shock wave 'dead' areas. Prümmer (1973)² used a model in which the absorption of the shock stress is proportional to the shock stress. Because the absorption of the shock wave by mechanisms like heating are energy-related, we prefer to use a model based on the absorption of shock wave energy and not of shock stress.

To model the shock wave absorption process all processes that affect the shock wave energy must be accounted for. Changes in the shock wave energy per unit surface area can be divided in having three different origins: (1) intrinsic, if shock wave energy is spent in e.g. compaction of a porous assembly by deformation and fracture of particles, (2) extrinsic, when shock wave energy is transmitted to the environment, e.g. at boundaries in so-called rarefaction waves (negative stress, or stretching waves), and (3) geometrical, when the same total amount of energy is transmitted through a larger or smaller surface.

In its present form the model is developed for a cylindrical configuration in which the shock wave travels from the sides of the cylinder to its center. In this configuration extrinsic effects do not occur, because there are no external boundaries. We must, therefore, incorporate geometrical changes, due to the decreasing surface when travelling towards the center of a cylinder, and intrinsic changes which are modelled with the absorption parameter \( f \).

The assumptions underlying the present model are;

1. The intrinsic absorption of shock wave energy in a porous material is proportional to the energy per unit surface,
2. The change in shock wave energy per unit area due to intrinsic absorption is independent of the changes due to geometrical effects,
3. The duration of the shock pulse is not changed due to intrinsic, or geometrical changes in the shock wave energy per unit area.

In the present form of the model it is assumed that the shock wave travels in the radial direction. Although, the shock wave has a component in the axial direction, for the practical situations considered here the radial component is predominant. The influence of this simplification on the value of \( f \) will be smaller than 15%.

In the following the change in the shock wave energy per unit area is divided into geometrical and intrinsic effects. These effects are then expressed as functions of the energy per unit area, \( e \). This results in an expression for the change in the energy per unit area as a function of the location of the shock
wave front.

By combining the energy and momentum conservation laws, and an equation of state for the porous assembly this expression can be rewritten to yield an equation for the mass displacement velocity as a function of the location of the shock wave front. When the conditions at the container wall are known, this function can be used to calculate the shock wave conditions, including the shock wave velocity, throughout the sample.

The time of arrival of the shock wave front is calculated by numerical integration of the shock wave velocity over the radius of the sample. This integration is fitted to the experimental data to obtain the absorption coefficient.

8.2 THE MODEL

The change in the shock wave energy per unit surface, $\frac{dE}{dx}$, is considered to consist of two parts; a geometrical effect, and an intrinsic absorption effect:

$$\frac{dE}{dx} = \left(\frac{dE}{dx}\right)_{geom} + \left(\frac{dE}{dx}\right)_{abs}$$  \hspace{1cm} (8.1)

As stated in assumption (2) the geometrical change is considered to be independent of absorption, and, therefore, the total amount of shock wave energy, $E_s$, is independent of the geometrical change, when $E_s$ is defined as:

$$E_s = S \ e$$  \hspace{1cm} (8.2)

with $S$ being the cross-sectional area of the shock wave. This means that:

$$\left(\frac{dE_s}{dx}\right)_{geom} = S \left(\frac{dE}{dx}\right)_{geom} + e \ \frac{dS}{dx} = 0$$  \hspace{1cm} (8.3)

The geometrical change in shock wave energy per unit surface, $e$, therefore becomes:

$$\left(\frac{dE}{dx}\right)_{geom} = - \frac{e}{S} \ \frac{dS}{dx}$$  \hspace{1cm} (8.4)

As stated in assumption (1) the intrinsic absorption of shock wave energy per unit surface is taken to be proportional to the amount of shock wave energy per unit surface:
\[ \frac{de}{dx}_{abs} = -f e \]  

(8.5)

with \( f \) being the absorption coefficient.

Substitution of Eqs. (8.4) and (8.5) into (8.1) yields:

\[ \frac{de}{dx} = -\frac{e}{S} \frac{dS}{dx} - f e \]  

(8.6)

The present experiments are performed in a cylindrical configuration. The surface, \( S \), of a cylinder with height, \( h \), and radius, \( r \), is found from:

\[ S = 2\pi r h \]  

(8.7)

The shock wave travels from the outside of the cylinder, with radius \( R \), inward, which means that:

\[ x = R - r \Rightarrow dx = -dr \]  

(8.8)

in which \( r \) is the radius of the cylinder formed by the shock wave front.

Combining Eqs. (8.7) and (8.8) gives:

\[ \frac{1}{S} \frac{dS}{dx} = -\frac{1}{r} \]  

(8.9)

Substitution of Eqs. (8.8) and (8.9) into (8.6) yields:

\[ \frac{de}{dr} = \left( -\frac{1}{r} + f \right) e \]  

(8.10)

Integration yields:

\[ \frac{e}{e_0} = \left( \frac{R}{r} \right) \exp[-f (R-r)] \]  

(8.11)

From the conservation laws a relation can be found between the mass displacement velocity, \( u \), and the energy per unit area, \( e \). An expression for the energy per unit surface, \( e \), can be found from energy conservation:

\[ e = \sigma u \Delta t \]  

(8.12)
in which \( \sigma \) is the shock stress, \( u \) is the mass displacement velocity, and \( \Delta t \) is the duration of the shock pulse. The shock stress can be expressed in the mass displacement velocity, \( u \), and the shock wave velocity, \( U \), using momentum conservation, which gives:

\[
\sigma = \rho_0 \, u \, U \tag{8.13}
\]

in which \( \rho_0 \) is the density of the assembly before arrival of the shock wave.
For porous AIN of about 40% TMD the shock wave velocity can be related in good approximation to the mass displacement velocity with (see Appendix A):

\[
U = S_p \, u \tag{8.14}
\]

with \( S_p = 1.3 \).
Combining Eqs. (8.12), (8.13), and (8.14) yields an expression for the energy per unit surface, as a function of shock pulse duration, \( \Delta t \), and mass displacement velocity, \( u \), only:

\[
e = \rho_0 \, S_p \, u^3 \, \Delta t \tag{8.15}
\]

Substitution of Eq. (8.15) into (8.11) gives:

\[
\frac{u^3 \, \Delta t}{u_0^3 \, \Delta t_0} = \left( \frac{R}{r} \right) \exp[-f \,(R-r)] \tag{8.16}
\]

With assumption (3) (\( \Delta t = \Delta t_0 \)) this equation can be rewritten to:

\[
u = u_0 \, \left\{ \left( \frac{R}{r} \right) \exp[-f \,(R-r)] \right\}^{\frac{1}{3}} \tag{8.17}
\]

The only parameter which must be known to calculate the mass displacement velocity in the assembly as a function of the radius with Eq. (8.17) is the mass displacement velocity at the wall of the cylinder, \( u_0 \), which can be calculated from the stress, \( \sigma_0 \), at the wall of the cylinder. This stress can be calculated from the detonation velocity of the explosive, and the density of the explosive as shown in Appendix B:
\[
\sigma_0 = \frac{1}{I_x} \frac{1}{4} \rho_x D^2
\]  

(8.18)

in which \(I_x\) and \(I_p\) are the shock wave impedance of the explosive and the powder, respectively, which are discussed in Appendix B.

By combining Eqs. (8.13) and (8.14) the mass displacement velocity at the wall, \(u_0\), can be determined from:

\[
u_0 = \sqrt{\frac{\sigma_0}{\rho_0 S_p}}
\]  

(8.19)

In the experiments the shock wave velocity in the powder is not measured, but the time, \(t(x)\), at which the shock wave arrives at point \(x\). If the influence of the obliquity of the shock front is neglected, conform to the assumptions made in the model, the time \(t(x)\) can be calculated from the shock wave velocity by integration:

\[
t(x) = \int_0^x \frac{1}{U} \, dx
\]  

(8.20)

In the present work we used a numerical integration of Eq. (8.20), which was fitted with the least squares approach to the experimental data to calculate the absorption parameter \(f\).

8.3 EXPERIMENTAL ASPECTS

In our experiments we used the cylindrical configuration shown in Fig. 8.1. The ceramic powder was placed in a aluminum tube with an inner and outer diameter of 30 mm and 35 mm, respectively, and a height of 120 mm. The top of the tube was closed with an aluminum plug with a thickness of 10 mm. The bottom of the tube was closed with a PVC plug of 10 mm thickness. Through pre-drilled holes in the bottom plug 9 Dynasen CA 1206 ionisation pins were inserted into the powder. The top of the ionisation pins was placed 10 mm above the top of the plug to prevent interference from shock reflections on the plug. The ionisation pins were placed in a cross-like pattern as shown in
Fig. 8.2. The pins were equally distributed over the radius of the sample.

The passage of the shock wave was recorded with a Krenz Electronics TRC 6070 transient recorder with a time resolution of 50 ns. The ionisation pins were connected to the transient recorder through a trigger unit (designed at TNO-PML), which was used to put a voltage difference of 100 V over the ionisation pins. The passage of the shock wave ionizes the air in the powder assembly, and this causes a short circuiting. Subsequently, the trigger unit gives a signal, which is registered by the transient recorder.

In the cylindrical configuration, which is shown in Fig. 8.1, the explosive is placed around the powder container. The explosive is held by a PVC envelope with an inner and outer diameter of 74 and 82 mm, respectively. The envelope has a height of 175 mm. The envelope is closed at the bottom with a 5 mm thick PVC plug. This plug fits around the powder container and centers it. The top of the envelope is closed with a 10 mm thick PVC cap. The detonation of the explosive is initiated with a detonator, which is placed at the center of the top cap. The detonation then travels downward to and alongside the powder container.
Figure 8.1: A schematic representation of the cylindrical configuration used for the shock wave absorption experiments.

Figure 8.2: Top-view of the bottom plug with the ionisation pins.
Two types of explosives were used: (a) AMPA2.1, which was mixed at the TNO Prins Maurits Laboratory (TNO-PML) and exists of 81.2% ammonium nitrate, 10% TNT, and 8.8% aluminium. At the diameter used it has a detonation velocity of 3.6 km/s.\(^3\) (b) Triamite, which is a commercially available explosive comprising 80% ammonium nitrate, 19.8% TNT, and 0.2% aluminum. Under the present conditions it has a detonation velocity of 3.0 km/s.\(^3\)

Three commercial grades of AlN powders were used, i.e. (a) Gimex Grade A, with an average particle size of \(D_{50}=5.5\) \(\mu\)m (determined with a Fisher Sub-Sieve Sizer, FSSS), (b) Gimex Grade A200, with an average (FSSS) particle size of \(D_{50}=3.3\) \(\mu\)m, and (c) Gimex Grade F, with an average (FSSS) particle size of \(D_{50}=1.5\) \(\mu\)m. The powder properties are shown in Table 8.1.

**Table 8.1:** Properties of the AlN powders from Gimex.

<table>
<thead>
<tr>
<th></th>
<th>Grade A</th>
<th>Grade A200</th>
<th>Grade F</th>
</tr>
</thead>
<tbody>
<tr>
<td>Mean (FSSS) particle</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>size (D_{50}) ((\mu)m)</td>
<td>5.5</td>
<td>3.3</td>
<td>1.5</td>
</tr>
<tr>
<td>Particle size range ((\mu)m)</td>
<td>3-8</td>
<td>1.4-10</td>
<td>0.2-5</td>
</tr>
<tr>
<td>Specific surface area (m(^2)/g)</td>
<td>1.5-3.0</td>
<td>3.7</td>
<td>3.5</td>
</tr>
<tr>
<td>Chemical composition (%)</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Al</td>
<td>&gt;65.0</td>
<td>65.0-67.0</td>
<td>...</td>
</tr>
<tr>
<td>N</td>
<td>&gt;31.5</td>
<td>32.0-34.0</td>
<td>33.2</td>
</tr>
<tr>
<td>C</td>
<td>&lt;0.08</td>
<td>0.05-0.15</td>
<td>0.05</td>
</tr>
<tr>
<td>O</td>
<td>&lt;1.5</td>
<td>0.8-1.5</td>
<td>0.10</td>
</tr>
<tr>
<td>other metals</td>
<td>&lt;0.25</td>
<td>0.1-0.2</td>
<td>&lt;0.1</td>
</tr>
</tbody>
</table>

158
Figure 8.3(a): Scanning electron micrograph (magnification $2.5 \times 10^3$) of AlN Gimex Grade A powder.

Figure 8.3(b): Scanning electron micrograph (magnification $2.5 \times 10^3$) of AlN Gimex Grade A200 powder.
Figure 8.3(c): Scanning electron micrograph (magnification \(2.5 \cdot 10^3\)) of AlN Gimex Grade F powder.

Scanning electron micrographs of the three powders are shown in Fig. 8.3(a)-8.3(c). From these figures it can be calculated that the Grade A200 [Fig. 8.3(b)] powder has a particle size that appears on the average to be larger than Grade A [Fig. 8.3(a)]. This is in contradiction with the FSSS powder size provided by Gimex. Despite the presence of larger particles [up to 8 \(\mu m\), see Fig. 8.3(c)] the average particle size of Grade F appears indeed to be smaller than those of Grades A and A200, due to the large fraction of smaller particles with a diameter < 1 \(\mu m\).

Further experimental conditions are shown in Table 8.2.

The conditions at the wall of the cylinder calculated with Eqs. (8.18) and (8.19) are shown in Table 8.3. The conditions which were chosen are those which are generally used at TNO-PML for the initial experiments on new materials. For AlN powders these conditions yield a final sample density of 80 to 92% TMD.
### Table 8.2: Experimental conditions

<table>
<thead>
<tr>
<th>Experiment No.</th>
<th>Powder type</th>
<th>Average particle size $D_{50}$ (μm)</th>
<th>Initial density powder ε (%TMD)</th>
<th>Density explosive $\rho_x$ ($10^3$ kg/m³)</th>
<th>Detonation velocity $D$ (km/s)</th>
</tr>
</thead>
<tbody>
<tr>
<td>P30</td>
<td>Grade A</td>
<td>5.5</td>
<td>37.0</td>
<td>1.02</td>
<td>3.6</td>
</tr>
<tr>
<td>P31</td>
<td>Grade A</td>
<td>5.5</td>
<td>34.1</td>
<td>1.03</td>
<td>3.6</td>
</tr>
<tr>
<td>R53</td>
<td>Grade A</td>
<td>5.5</td>
<td>34.4</td>
<td>1.12</td>
<td>3.0</td>
</tr>
<tr>
<td>P36</td>
<td>Grade F</td>
<td>1.5</td>
<td>37.4</td>
<td>1.01</td>
<td>3.6</td>
</tr>
<tr>
<td>R88</td>
<td>Grade F</td>
<td>1.5</td>
<td>36.0</td>
<td>0.99</td>
<td>3.0</td>
</tr>
<tr>
<td>P39</td>
<td>Grade A200</td>
<td>3.3</td>
<td>35.2</td>
<td>1.01</td>
<td>3.6</td>
</tr>
</tbody>
</table>

### Table 8.3: Conditions calculated for the inner wall of the cylinder.

<table>
<thead>
<tr>
<th>Experiment No.</th>
<th>Stress at wall $\sigma_0$ [Eq.(8.18)] (GPa)</th>
<th>Mass displacement velocity at wall $u_0$ [Eq.(8.19)] (km/s)</th>
<th>Shock wave velocity at wall $U_0$ [Eq.(8.14)] (km/s)</th>
</tr>
</thead>
<tbody>
<tr>
<td>P30</td>
<td>2.38</td>
<td>1.24</td>
<td>1.61</td>
</tr>
<tr>
<td>P31</td>
<td>2.34</td>
<td>1.28</td>
<td>1.67</td>
</tr>
<tr>
<td>R53</td>
<td>1.82</td>
<td>1.13</td>
<td>1.46</td>
</tr>
<tr>
<td>P36</td>
<td>2.37</td>
<td>1.23</td>
<td>1.60</td>
</tr>
<tr>
<td>R88</td>
<td>1.68</td>
<td>1.06</td>
<td>1.37</td>
</tr>
<tr>
<td>P39</td>
<td>2.33</td>
<td>1.26</td>
<td>1.64</td>
</tr>
</tbody>
</table>
8.4 RESULTS AND DISCUSSION

A. Grade A powder; average (FSSS) particle size 5.5 μm

1. AMPA2.1 explosive; detonation velocity 3.6 km/s

In Fig. 8.4 the results of experiments P30 and P31 are shown. The time, $t$, at which the shock was registered at the ionisation pins is plotted versus the distance, $r$, of the pin from the center of the sample. It is assumed that the shock wave is symmetrical around the center of the sample; the distance of the pins (see Fig. 8.2) can then be plotted versus one common axis.

![Graph](image)

**Figure 8.4:** The time at which the shock was recorded at the ionisation pins is plotted versus the distance of the pin from the center of the samples P30 and P31. The fit to the data is included.

Because the time registration starts with the first pin that is triggered, and this pin is not always exactly at the same distance from the center, the experiments do not have a common reference. Using one pin as a common reference to which the time registration is calibrated introduces a large error over the entire data range if there is a large random error in the time registration or positioning. To be able to compare experiments, however, a common
reference is necessary. Because the results show an approximately linear relation between \( t \) and \( r \), the average experimental values of \( t \) and \( r \) were used as a reference for the experiments.

In Fig. 8.4 the best fits with Eq. (8.20) are also shown for both experiments. These fits were also calibrated to the average experimental values of \( t \) and \( r \). In other words; a fitted curve passes through the average experimental values of \( t \) and \( r \).

The results show a high reproducibility. The theoretical curve obtained with Eq. (8.20) fits the experimental data with an average deviation of only 3% for both experiments. The absorption coefficients for experiments P30 and P31 found from these fits are 1.7 \( R^{-1} \) and 1.9 \( R^{-1} \) respectively. Since the radius \( R \) is 15 mm, the absorption coefficients are 11 and 13\%/mm, respectively. This means that over a length of 1 mm about 12\% of the shock wave energy per unit area is absorbed in the powders.

2. Triamite explosive; detonation velocity 3.0 km/s

In experiment R53 the same powder was used as in P30 and P31, but a different explosive was applied to generate the shock wave. In Fig. 8.5 the results are shown, together with the curve fitted with Eq. (8.20). The scatter in the experimental data is larger than in the first two experiments. No apparent relation could be found between the pairs of data that appear to be parallel to the fitted curve and the positioning of the pins. The positioning of the pins (see Fig. 8.2) is such that the pairs do not belong to one of the sections of the cross.

The deviation in the fit for this experiment is 7\%. The absorption coefficient is 2.1 \( R^{-1} \) or 14\%/mm.
3. *Comparison of the results for the two explosives*

In Fig. 8.6 the experimental results and fits are shown for P30 and R53 together. In this figure it can be seen that the difference in detonation velocity, which is a measure for the shock stress (see Appendix B), has a significant effect on the $t(r)$ curves. The absorption coefficients found in the experiments with the different explosives are, however, nearly the same. This indicates that the absorption coefficient is indeed only dependent on the powder properties as was assumed in the model. To demonstrate that the difference in the two curves in Fig. 8.6 is not due to the difference in absorption factors, but mainly to the difference in conditions at the wall, the curves for $f=11\%$/mm and $f=14\%$/mm (using the conditions of R53) are compared in Fig. 8.7. In this case only a small difference is seen at the center of the sample.
Figure 8.6: Experimental results and fit of experiment P30 compared with those of R53.

Figure 8.7: The effect of the absorption coefficient on the $t(r)$ curve for the conditions used in experiment R53.
When the absorption coefficient and the conditions at the wall (Table 8.3) are known the shock wave velocity in the powder can be calculated with Eqs. (8.14) and (8.17). These calculated shock wave velocities for P30, P31, and R53 are shown in Fig. 8.8. It can be seen that the shock wave velocity increases strongly near the center of the sample due to the sharp decrease in the area through which the shock wave is transmitted. This effect is even stronger for the shock stress, which can be calculated with Eq. (8.13). In Fig. 8.9 the shock stress, calculated for the three experiments, is shown as a function of the radius. In compaction experiments this effect can result in a so-called Mach-stem; due to interference of the shock waves in the center of the sample a stem is created with extremely high shock stresses. These high stresses counteract the shock wave that travels inward, and can result in a shock wave that travels outwards from the center (and downwards) moving material from the center outwards, creating a hole in the sample. This is known as over-compaction.

When the recovered samples of P30 and P31 are studied (Figs. 8.10 and 8.11) it can be seen that even the small difference in the stress curves (Fig. 8.9) found for these two experiments can have an effect on compaction. The sample with the lowest stress (P31) shows more cracks in the center. These cracks occur after initial compaction. They are more severe in the compact with the lowest stresses. In sample R53 the stress was much lower than in samples P30 and P31, and in the cross-section of the recovered sample (Fig. 8.12) it can be seen that even more cracks occur.
Figure 8.8: The calculated shock wave velocity for the experiments P30, P31, and R53.

Figure 8.9: The calculated shock stress for the experiments P30, P31, and R53.
Figure 8.10: Cross-section of recovered sample P30.

Figure 8.11: Cross-section of recovered sample P31.
B. Grade F powder; average (FSSS) particle size 1.5 μm

In Fig. 8.13 the experimental results, and the best fits obtained with Eq. (8.20) are shown for the experiments P36 and R88. For P36 that was performed with the AMPA2.1 explosive (detonation velocity 3.6 km/s) the fit shows an average deviation of 8%. The absorption coefficient for experiment P36 is 2.7 $R^1$ or 18%/mm. This value is significantly higher than was found for the Grade A powder (11-14%/mm) with a larger average grain size, according to FSSS and SEM analyses.

For experiment R88 that was performed with the Triamite explosive (detonation velocity 3.0 km/s) the fit shows an average deviation of 11%, and an absorption coefficient of 3.3 $R^1$ or 22%/mm. This value is also significantly higher than was found for the Grade A powder.

The absorption coefficients found in these experiments with different explosives are, again, comparable. This indicates that also for the Grade F powder the absorption coefficient is indeed mainly dependent on the powder properties, as assumed in the model.

169
C. Grade A200 powder; average (FSSS) particle size 3.3 μm

In Fig. 8.14 the experimental results, along with the best fit obtained with Eq. (8.20) is shown for P39, performed with Triamite explosive. The fit shows an average deviation of 6%. The absorption coefficient is 1.5 $R^{-1}$, or 10%/mm. This value is somewhat lower than was found for the Grade A powder (11-14%/mm). As was mentioned earlier, the average FSSS grain sizes that were given by Gimex suggested that Grade A powder has a larger average grain size. SEM analysis [Fig. 8.3(a) and 8.3(b)], however, showed this to be unlikely.
Figure 8.14: Experimental results and fit of experiment P39.

Table 8.4: Absorption parameters of the fitted curves and the average deviation from experimental data.

<table>
<thead>
<tr>
<th>Experiment No.</th>
<th>Absorption coefficient $f$ (%/mm)</th>
<th>Average deviation from data (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>P30</td>
<td>11</td>
<td>3.2</td>
</tr>
<tr>
<td>P31</td>
<td>13</td>
<td>3.1</td>
</tr>
<tr>
<td>R53</td>
<td>14</td>
<td>7.4</td>
</tr>
<tr>
<td>P36</td>
<td>18</td>
<td>7.9</td>
</tr>
<tr>
<td>R88</td>
<td>22</td>
<td>11</td>
</tr>
<tr>
<td>P39</td>
<td>10</td>
<td>6.0</td>
</tr>
</tbody>
</table>
D. The effect of the explosive on the $t(r)$ curves

The absorption coefficients for all experiments are shown in Table 8.4. The effect of the explosive on the compaction experiment is discernible in the conditions at the wall of the cylinder. The calculated stress at the wall is 1.7-1.8 GPa in the experiments with a detonation velocity of 3.0 km/s, and 2.3-2.4 GPa for those with $D=3.6$ km/s. When Fig. 8.6 is compared with Fig. 8.13, it can be seen that the effect of the detonation velocities is comparable for two powders with a different average particle size. In both these figures the absorption coefficient is nearly independent of the detonation velocity for both curves (11 and 14%/mm in Fig. 8.6, and 18 and 22%/mm in Fig. 8.13). The decrease in shock wave velocity in both figures can, therefore, be attributed to the difference in detonation velocity.

E. The effect of the average powder size on the absorption

In Fig. 8.15 the fitted curves are shown for three experiments (P30, P36, and P39) with three different average powder sizes. These experiments were all performed with AMPA2.1 ($D=3.6$ km/s). It can be seen that, although the difference in the curves for Grade A (average particle size 5.5 µm), and Grade A200 (average particle size 3.3 µm) is small, the difference between the $t(r)$ curve of Grade F (average particle size 1.5 µm) and Grade A or A200 is comparable to the effect of a different detonation velocity, as was found in Figs. 8.6 and 8.13. This effect is also visible in Fig. 8.16 in which two experiments (R53 and R88) are shown with Grade A and F powders which were performed with Triamite ($D=3.0$ km/s). The effect of the decreased averaged powder size (5.5 µm to 1.5 µm) in this figure is comparable to the effect found for AMPA2.1 (Fig. 8.15). This means that the choice of powder is as important for successful compaction as the choice of explosive.
**Figure 8.15:** The fitted $t(r)$ curves for the experiments with AMPA2.1 ($D=3.6 \text{ km/s}$).

**Figure 8.16:** The fitted $t(r)$ curves for the experiments with Triamite ($D=3.0 \text{ km/s}$).
The importance of this effect becomes clear when the velocity curves are drawn for these experiments. In Fig. 8.17 the velocities in the experiments with AMPA2.1 are shown, and in Fig. 8.18 those with Triamite. In both figures it can be seen that the increase of shock wave velocity in the center is strongest for the powders with the larger average particle sizes. In these figures the effect of the average particle size is comparable for both detonation velocities.

![Diagram](image)

**Figure 8.17:** The calculated shock wave velocities for the experiments with AMPA2.1 ($D=3.6$ km/s).

174
Figure 8.18: The calculated shock wave velocities for the experiments with Triamite \((D=3.0 \text{ km/s})\).

Figure 8.19: The calculated shock stresses for the experiments with AMPA2.1 \((D=3.6 \text{ km/s})\).
Figure 8.20: The calculated shock stresses for the experiments with Triamite ($D=3.0 \text{ km/s}$).

When the results are used to plot the shock stress versus the diameter, using Eq. (8.13), shown in Figs. 8.19 and 8.20, it can be seen that for the powders with a large average particle size and corresponding low absorption coefficient, the increase in shock stress in the center of the sample is much larger than for those with a smaller particle size and a high absorption coefficient. Comparing these figures with Fig. 8.9 shows that also for the shock stress the average particle size is as important as the detonation velocity of the explosive.

It is interesting to note that when a cross-section of sample P39, in which a shock stress was calculated that was somewhat higher than found in experiment R53, is studied (Fig. 8.21), it is found that there are much fewer cracks, although the coloration of the center suggests that the sample has a porous core.
The absorption coefficient is largest for Grade F powder with the smallest average grain size, and smallest for Grade A200 powder. When the particle sizes deduced from the SEM micrographs of the powders [Fig. 8.3(a) to (c)] are used, this means that the absorption coefficient increases with decreasing particle size. This stronger absorption for smaller powders is also found in the literature for compaction experiments on Al₂O₃. This is probably due to the larger number of particles the shock wave passes over the same distance in a powder with a small average particle size compared to a powder with a larger average particle size, because shock wave energy is most likely to be lost due to boundary effects during shock wave transfer from particle to particle. A larger number of particles per distance travelled results in an increased energy dissipation due to these boundary effects such as friction, plastic deformation, and heating.
8.5 CONCLUSIONS

The conditions of the presented experiments resulted in a nearly constant shock wave velocity throughout the sample. This resulted in an approximately linear relation between the time of arrival and the location of the shock wave in the sample. The use of the linear approximation for the calibration of the fit to the experimental data is, therefore, valid.

The absorption coefficient proved to be insensitive to the type of explosive in several tests with two different explosives. The detonation velocities under the presented experimental conditions of these explosives are 3.0 and 3.6 km/s.

Experiments on 34-37% dense AlN powder assemblies showed a strong average powder size dependency of the absorption coefficient. The absorption of the shock wave energy per unit area in Gimex Grade A powder with an average (FSSS) particle size of 5.5 µm was found to vary between 11 and 14%/mm. In Gimex Grade A200 powder with an average (FSSS) particle size of 3.3 µm the absorption was found to be 10%/mm. Contrary to the FSSS analysis, scanning electron microscopy of this Grade A200 powder showed a larger average particle size for Grade A200 powder compared to Grade A. In Gimex Grade F powder with an average (FSSS) particle size of 1.5 µm the absorption was found to be 18 to 22%/mm.

The shock wave absorption in powders with a smaller average particle size appears to be much larger than found in larger powders under similar conditions. Such a difference has a strong effect on the optimal conditions for dynamic compaction.

The results for AlN powders demonstrate that the absorption coefficient can be used as a modelling parameter for the study of shock waves in powders. Powders can be characterized in first approximation with only this single parameter. With the absorption coefficient the conditions during compaction, such as the shock stress, can be evaluated. The structure of the recovered compacts is in agreement with the shock stress curves which could be calculated with the absorption coefficient. With the introduced model the presented experimental technique can be used for an in-situ analysis of the compaction process, that can be related to the compaction results.

Future studies might incorporate the axial component of the shock wave, although the resulting increase in accuracy (estimated to be smaller than 15%) in the determination of the absorption coefficient, $f$, is not likely to be of influence on the value of the presented experimental technique as a tool for in-situ analysis.
8.5 REFERENCES

5. Chapter 7 of this work.
6. Chapter 6 of this work.

APPENDIX A: CALCULATION OF THE SHOCK WAVE VELOCITY IN POROUS AISI

In Chapter 7 a method was developed to relate the shock wave behavior of a porous assembly to the shock wave behavior of a solid. In this method the powder is modelled as an assembly of spheres. These spheres have solid state material properties. The stress in the solid phase, $\sigma_s$, is calculated from the stress on the assembly $\sigma_a$ using:

$$\sigma_s = \frac{\sigma_a}{\epsilon}$$  (8.A1)

With this method the shock wave velocity in a porous assembly, $U(\sigma_s)$, can be calculated from the mass displacement and the shock wave velocity in the solid phase [$u_s(\sigma_s)$ and $U_s(\sigma_s)$, respectively] with the use of a deformation curve, $\Delta r_0(\sigma_s)$, which is a measure of the deformation of the spheres due to the passage of the shock wave:

$$U(\sigma_s) = \frac{1}{\frac{1}{U_s(\sigma_s)} + \frac{1}{\frac{\Delta r_0(\sigma_s)}{(1-\Delta l)}} \frac{1}{2 u_s(\sigma_s)}}$$  (8.A2)
in which \( \Delta l \) is the initial deformation of the spheres due to pre-pressing or sintering of the assembly, before applying the shock wave. In the case of a powder assembly at tapdensity the initial deformation \( \Delta l \) is zero.

For the powders at tapdensity used in the present experiments Eq. (8.A2), therefore, becomes:

\[
U(\sigma_s) = \frac{1}{1 + \frac{\Delta r_0(\sigma_s)}{U_s(\sigma_s) + 2u_s(\sigma_s)}} \tag{8.A3}
\]

By combining Eq. (8.13) with (8.A1) it is found that:

\[
\rho_0 U(\sigma_s) u(\sigma_s) = \epsilon \rho_{0,s} U_s(\sigma_s) u_s(\sigma_s) \tag{8.A4}
\]

in which \( \rho_{0,s} \) is the theoretical maximum density of the solid. Combining the fact that \( \rho_0 = \epsilon \rho_{0,s} \), and Eqs. (8.A3) and (8.A4) yields an expression for the mass displacement velocity of the powder:

\[
u(\sigma_s) = \left[ 1 + \frac{\Delta r_0(\sigma_s)}{2u_s(\sigma_s)} \right] u_s(\sigma_s) \tag{8.A5}
\]

It was found that the deformation curves which represent the deformation of the powder due to the shock wave as a function of the stress in the solid phase \( \sigma_s \), were mutually exchangeable for ceramics, the most important assembly property being the relative density. To obtain a deformation curve for the AlN powders in the present experiments the deformation curve for 39% TMD UO\(_2\) was calculated. The Hugoniot for solid and 39% TMD UO\(_2\) are shown in Fig. 8.A1. The deformation curve for 39% TMD UO\(_2\) is shown in Fig. 8.A2.
Figure 8.A1: Hugoniot of solid and 39% dense UO₂.

Figure 8.A2: Deformation curve of 39% TMD UO₂.
Using this deformation curve a Hugoniot was calculated with Eqs. (8.A3) and (8.A5) for 39% TMD AlN, as shown in Fig. 8.A3. For this a solid Hugoniot for AlN (see Fig. 8.A3) was used with an intercept; $C_{0,s} = 7.906$ km/s and a slope; $S_s = 1.357.$ Furthermore, $\rho_{0,s} = 3.26 \times 10^3$ kg/m$^3$ was used for the solid density of AlN. The calculated Hugoniot for 39% TMD AlN was approximated with:

$$U(\sigma_a) = 1.3 \ u(\sigma_a)$$  \hspace{1cm} (8.A6)

This is a reasonable approximation of the calculated curve as can be seen in Fig. 8.A3. Equation (8.A6) was used for the 34 to 37% dense AlN powders in the present experiments.

![Graph showing Hugoniot curves](image)

**Figure 8.A3:** Solid AlN Hugoniot, calculated powder Hugoniot for 40% TMD AlN, and an approximation for the powder Hugoniot ($U=1.3u$).
APPENDIX B: CALCULATION OF THE STRESS AT THE CONTAINER WALL

The stress at the container wall is calculated from a mechanical balance. In the present calculations the aluminum container is neglected, and the balance is determined as if direct contact exists between the explosive and the ceramic powder. This is based on the assumption that the energy loss in the aluminum container due to e.g. reflections is negligible, because of the small thickness of the container wall compared to the shock length. A first order approximation is used in which the shock wave impedance, $I$, is independent of $u$:

$$\sigma = \rho_0 \ U \ u \approx I \ u \quad (8.\text{B1})$$

First an expression is derived for the stress in the porous ceramic assembly for a perpendicularly incoming stress wave. In Fig. 8.B1 the effect of a perpendicular shock wave impact on the imaginary boundary between the ceramic powder and the explosive is shown.

**Figure 8.B1:** Schematic representation of the shock reflection on the imaginary boundary between the explosive and the ceramic powder (the aluminum tube in-between is neglected).
For the stress at the boundary in the explosive after reflection, $\sigma_b$, it is found that:

$$\sigma_b - \sigma_x = I_x u_b$$  \hspace{1cm} (8.B2)

in which $\sigma_x$ is the detonation stress of the explosive, $I_x$ the impedance of the explosive, and $u_b$ the mass displacement velocity of the explosive after the shock wave is reflected on the boundary. For the stress at the boundary in the porous ceramic assembly, $\sigma_0$, it is found that:

$$\sigma_0 = I_p u_0$$  \hspace{1cm} (8.B3)

in which $I_p$ is the impedance of the porous ceramic assembly, and $u_0$ the mass displacement velocity in the assembly at the boundary.

Mechanical balance dictates that:

$$\sigma_b = \sigma_0, \quad \text{and} \quad u_x - u_b = u_0$$  \hspace{1cm} (8.B4)

with $u_x$ being the mass displacement velocity in the detonation.

From the balance in Eq. (8.B4) and Eqs. (8.B2) and (8.B3) it is found that:

$$\sigma_0 = \frac{\sigma_x + I_x u_x I_p}{I_x + I_p}$$  \hspace{1cm} (8.B5)

Using the above derivation for a perpendicularly incoming shock wave now an expression for a shock wave is deduced, which makes an angle $\alpha$ with the boundary surface. Due to the angle, the mass displacement velocity in the detonation wave in the direction of the boundary, $u_{x,h}$ is reduced to:

$$u_{x,h} = u_x \cos \alpha$$  \hspace{1cm} (8.B6)

Substitution of Eq. (8.B6) into Eq. (8.B5) yields after some rewriting:

$$\sigma_0 = \frac{1 + \cos \alpha}{1 + \frac{I_x}{I_p}} \sigma_x$$  \hspace{1cm} (8.B7)

In the cylindrical configuration the detonation wave travels along the outer container wall downwards. This indicates an angle of $\alpha = \pi/2$, which means that $\cos \alpha = 0$. 

184
Using the classical expression for the detonation stress in a explosive:

\[ \sigma_x = \frac{1}{1+\Gamma_x} \rho_x D^2 \]  \hspace{1cm} (8.B8)

with \( \Gamma_x \) being the Grüneisen coefficient of the explosive. For the ammonium nitrate based explosives in the present experiments \( \Gamma_x = 3 \) was used. Substitution in Eq. (8.B7) yields:

\[ \sigma_0 = \frac{1}{1 + \frac{I_x}{I_p}} \left( \frac{1}{4} \right) \rho_x D^2 \]  \hspace{1cm} (8.B9)

The impedance of the detonated explosive (gaseous phase) is:

\[ I_x = \rho_x D \]  \hspace{1cm} (8.B10)

in which \( \rho_x \) is the density of the explosive before detonation, and \( D \) the detonation velocity. The impedance of the ceramic assembly, \( I_p \), can be approximated by multiplying the impedance of the solid ceramic, \( I_c \), with the fraction, \( \varepsilon \), of the surface that is occupied by the solid phase:

\[ I_p = \varepsilon I_c \]  \hspace{1cm} (8.B11)

with:

\[ I_c = \rho_{0,s} C_{0,s} \]  \hspace{1cm} (8.B12)

in which \( \rho_{0,s} \) and \( C_{0,s} \) are the maximum density and the bulk sound velocity of the solid phase, respectively.
CHAPTER 9

Shock wave absorption in Si₃N₄ and ZrO₂ powders in a cylindrical configuration

ABSTRACT

The absorption of a shock wave in ZrO₂ and Si₃N₄ powders was characterized with a shock wave absorption parameter. The absorption of the shock wave energy per unit area in Si₃N₄ powders with an average particle size of 0.6 and 4.8 μm was found to be about 5%/mm and 10%/mm, respectively. The effect of the absorption coefficient on the compaction is shown.

In ZrO₂ powders with an average particle size of 0.65 and 3.5 μm the absorption coefficient was found to be much larger, 19 and 12%/mm, respectively, while the effect of the particle size on the absorption was exactly the opposite to what was found for Si₃N₄.

The difference between ZrO₂ and Si₃N₄ is discussed in relation to the calculated shock stresses in the assemblies.
9.1 INTRODUCTION

By applying a shock wave to a porous material its density can be increased up to more than 99% of its theoretical maximum density (TMD). This new densification method, which is referred to as the dynamic compaction process, enables us to densify porous materials which are difficult to densify with conventional means such as sintering and pressing. Examples are single-phase materials or composites which are thermodynamically instable at the high temperatures usually required for sintering. For these materials, such as hydroxyapatite-based biomaterials, or nickel-aluminum-based composites for aerospace applications, dynamic compaction is a promising densification process.

Due to the relatively short history of the process, and the wide scope of materials to which it is applicable, the optimal conditions for dynamic compaction need necessarily be determined experimentally for each material. The present work is aimed at determining the optimal conditions for compaction in the cylindrical configuration. These optimal conditions are found between undercompaction when too little shock wave energy is available for complete compaction, and overcompaction when too much shock wave energy at the center of the sample results in fracture.

To determine the optimal conditions for dynamic compaction with the use of explosives, Prümer (1987) introduced the $E/M$-method, which is still the most generally used method not based on computer simulations. Computer simulations can only be applied, if the material properties are well-known, and, therefore, have little predictive value, when it comes to new materials.

The $E/M$-method is an experimental approach ($E$ is the mass of the explosive, $M$ is the mass of the sample to be densified). It is basically a step-wise adjustment of two parameters, i.e. the detonation velocity of the explosive, and the amount of explosive, to obtain a sample, which is as dense as possible. These two parameters determine the height and duration of the dynamic stress pulse, or shock wave. A disadvantage of the $E/M$ method is that its result only applies to one powder size distribution, and one sample size. In general, several steps are necessary to obtain the optimal conditions for compaction, and these optimal conditions do not apply when e.g. the powder size distribution, or the solid properties are changed.

The aim of the present model is to find one parameter that can be obtained in one experiment, and fully characterizes the shock wave behavior of a porous material. If this single parameter is known, the optimal conditions for compaction can be calculated without further experiments. For this purpose we introduce a shock wave absorption parameter, $f$, which describes the relative absorption of shock wave energy per unit length. With this absorption parameter
it is possible to calculate the parameters which yield a compact that is as homogeneous as possible. It should also be possible to model up- and downscaling of the process. Furthermore, the absorption parameter is expected to be independent of the shape of the configuration. Therefore, when more complex shapes than the cylinder are to be compacted, it should be possible to predict shock wave 'dead' areas. Prümmer (1973)² used a model in which the absorption of the shock stress is proportional to the shock stress. Because the absorption of the shock wave by mechanisms like heating are energy-related we prefer to use a model based on the absorption of shock wave energy and not of shock stress.

To model the shock wave absorption process all processes which affect the shock wave energy must be accounted for. Changes in the shock wave energy per unit surface can be divided in having three different origins: (1) intrinsic, when shock wave energy is spent in e.g. compaction of a porous assembly by deformation of particles, (2) extrinsic, when shock wave energy is transmitted to the environment, e.g. at boundaries in so-called rarefaction waves (negative stress, or stretching waves), and (3) geometrical, when the same total amount of energy is transmitted through a larger or smaller surface.

In its present form the model is developed for a cylindrical configuration in which the shock wave travels from the sides of the cylinder to its center. In this configuration extrinsic effects do not occur, because there are no external boundaries. We must, therefore, incorporate geometrical changes, due to the decreasing surface when travelling towards the center of a cylinder, and intrinsic changes which are modelled with the absorption parameter $f$.

The assumptions underlying the present model are;

(1) The intrinsic absorption of shock wave energy in a porous material is proportional to the energy per unit surface,
(2) The change in shock wave energy per unit area due to intrinsic absorption is independent of the changes due to geometrical effects,
(3) The duration of the shock pulse is not changed due to intrinsic, or geometrical changes in the shock wave energy per unit area.

In the present form of the model it is assumed that the shock wave travels in the radial direction. Although, the shock wave has a component in the axial direction, for the practical situations considered here, the radial component is predominant. The influence of this simplification on the value of $f$ will be smaller than 15%.

In the following the change in the shock wave energy per unit area is divided into geometrical and intrinsic effects. These effects are then expressed as functions of the energy per unit area, $e$. This results in an expression for the change in the energy per unit area as a function of the location of the shock
wave front.

By combining the energy and momentum conservation laws, and an equation of state for the porous assembly this expression can be rewritten to yield an equation for the mass displacement velocity as a function of the location of the shock wave front. When the conditions at the container wall are known, this function can be used to calculate the shock wave conditions, including the shock wave velocity, throughout the sample.

The time of arrival of the shock wave front is calculated by numerical integration of the shock wave velocity over the radius of the sample. This integration is fitted to the experimental data to obtain the absorption coefficient.

9.2 THE MODEL

The change in the shock wave energy per unit surface, \( \frac{de}{dx} \), is considered to consist of two parts; a geometrical effect, and an intrinsic absorption effect:

\[
\frac{de}{dx} = \left( \frac{de}{dx} \right)_{\text{geom}} + \left( \frac{de}{dx} \right)_{\text{abs}}
\]  

(9.1)

Earlier on \(^2\) we derived an equation for the absorption in a cylindrical configuration, i.e.

\[
\frac{e}{e_0} = \left( \frac{R}{r} \right) \exp[-f(R-r)]
\]  

(9.2)

in which \( e_0 \) is the shock wave energy per unit surface at the wall of the cylinder, \( R \) is the radius of the cylinder, \( r \) the actual radius of the shock front, and \( f \) the absorption coefficient.

From the conservation laws a relation can be found between the mass displacement velocity, \( u \), and the energy per unit area, \( e \). An expression for the energy per unit surface, \( e \), can be found from energy conservation:

\[
e = \sigma u \Delta t
\]  

(9.3)

in which \( \sigma \) is the shock stress, \( u \) is the mass displacement velocity, and \( \Delta t \) is the duration of the shock pulse. The shock stress can be expressed in the mass displacement velocity, \( u \), and the shock wave velocity, \( U \), using momentum conservation, which gives:
\[ \sigma = \rho_0 u U \] \hspace{1cm} (9.4)

in which \( \rho_0 \) is the density of the assembly before arrival of the shock wave.

With the use of a model for porous assemblies\(^4\) equations of state were determined for the porous assemblies of ZrO\(_2\) and Si\(_3\)N\(_4\) in the presented experiments (see Appendix A). To facilitate the calculations a linear approximation of these equations of state was used in the present calculations:

\[ U = C_{0,p} + S_p u \] \hspace{1cm} (9.5)

in which \( C_{0,p} \) and \( S_p \) are the intercept, and the slope of the equation of state of the powder. For the porous assemblies the parameters of these equations are shown in Table 9.1. In Chapter 8 on 40\% dense AlN assemblies, an equation of state was used with \( C_{0,p} = 0 \). For the assemblies in this Chapter the intercept is not negligible, and the solution becomes somewhat more complex.

Table 9.1: Equation of state parameters for porous assemblies.

<table>
<thead>
<tr>
<th>Ceramic material</th>
<th>Density (% TMD)</th>
<th>Intercept, ( C_{0,p} ) (km/s)</th>
<th>Slope ( S )</th>
</tr>
</thead>
<tbody>
<tr>
<td>Si(_3)N(_4)</td>
<td>50</td>
<td>1.0</td>
<td>1.4</td>
</tr>
<tr>
<td>ZrO(_2)</td>
<td>40</td>
<td>0.1</td>
<td>1.6</td>
</tr>
<tr>
<td>ZrO(_2)</td>
<td>50</td>
<td>0.6</td>
<td>1.6</td>
</tr>
</tbody>
</table>

With the assumption that the pulse duration does not change during the process (\( \Delta t = \Delta t_0 \)) a combination of Eqs. (9.2)-(9.5) yields:

\[ \frac{C_{0,p}u^2 + S_p u^3}{C_{0,p}u_0^2 + S_p u_0^3} = \left( \frac{R}{r} \right) \exp[-f(R-r)] \] \hspace{1cm} (9.6)

in which \( u_0 \) is the mass displacement velocity of the powder at the wall of the cylinder. Solving Eq. (9.6) gives one physical solution:
\[ u(r) = g(r)^\frac{1}{3} + \frac{C_{0,p}^2}{9 \cdot S_p^2 \cdot g(r)^\frac{1}{3}} \cdot \frac{C_{0,p}}{3S_p} \]  

(9.7)

with:

\[ g(r) = \frac{F(r)}{2S_p} - \left( \frac{C_{0,p}}{3S_p} \right)^3 + \sqrt{\frac{F(r)}{2S_p}} \cdot \frac{F(r)}{2S_p} \cdot \left( \frac{C_{0,p}}{3S_p} \right)^3 \]  

(9.8)

and:

\[ F(r) = [C_{0,p} u_0^2 + S_p u_0^2] \cdot \left( \frac{R}{r} \right) \cdot \exp[-f(R-r)] \]  

(9.9)

The only parameter which must be known to calculate the mass displacement velocity in the assembly as a function of the radius with Eq. (9.19) is the mass displacement velocity at the wall of the cylinder, \( u_0 \), which can be calculated from the stress, \( \sigma_0 \), at the wall of the cylinder. This can be calculated from the detonation velocity of the explosive, and the density of the explosive as shown in Chapter 8:

\[ \sigma_0 = \frac{1}{4} \cdot \frac{1}{I_x} \cdot \frac{I_p}{D^2} \]  

(9.10)

in which \( I_x \) and \( I_p \) are the shock wave impedance of the explosive and the powder, respectively, calculated as in Chapter 8.

By combining Eqs. (9.4) and (9.7) the mass displacement velocity at the wall, \( u_0 \), can be determined from:

\[ u_0 = -\frac{C_{0,p}}{2S_p} + \sqrt{\left[ \frac{C_{0,p}^2}{2S_p} + \frac{\sigma_0}{\epsilon \cdot \rho_0 S_p} \right]} \]  

(9.11)

In the experiments the shock wave velocity in the powder is not measured, but the time, \( t(x) \), at which the shock wave arrives at point \( x \). If the influence of the obliquity of the shock front is neglected, then the time \( t(x) \) can be calculated from the shock
wave velocity by integration:

\[ t(x) = \int_0^x \frac{1}{U} \, dx \]  \hspace{1cm} (9.12)

In the present work a numerical integration of Eq. (9.12) is used, which was fitted with the least squares approach to the experimental data in order to calculate the absorption parameter \( f \).

9.3 EXPERIMENTAL ASPECTS

In our experiments the cylindrical configuration shown in Fig. 9.1 was used. The ceramic powder was placed in a aluminum tube with an inner and outer diameter of 30 mm and 35 mm, respectively, and a height of 120 mm. The top of the tube was closed with an aluminum plug with a thickness of 10 mm. The bottom of the tube was closed with a PVC plug of 10 mm thickness. Through predrilled holes in the bottom plug 9 Dynasen CA 1206 ionisation pins were inserted into the powder. The top of the ionisation pins was placed 10 mm above the top of the plug to prevent interference from shock reflections on the plug. The ionisation pins were placed in a cross-like pattern as shown in Fig. 9.2. The pins were equally distributed over the radius of the sample.

The passage of the shock wave was recorded with a Krenz Electronics TRC 6070 transient recorder with a time resolution of 0.05 \( \mu \)s. The ionisation pins were connected to the transient recorder through a trigger unit (designed at PML-TNO laboratory), which was used to put a voltage difference of 100 V over the ionisation pins. The passage of the shock wave ionizes the air in the powder assembly and this causes a short circuit. When a short circuit occurs over the ionisation pins, the trigger unit gives a signal, which is registered by the transient recorder.

In the cylindrical configuration, which is shown in Fig. 9.1, the explosive is placed around the powder container. The explosive is held by a PVC envelope with an inner and outer diameter of respectively 74 and 82 mm. The envelope has a height of 175 mm. The envelope is closed at the bottom with a 5 mm thick PVC plug. This plug fits around the powder container and centers it. The top of the envelope is closed with a 10 mm thick PVC cap. The detonation of the explosive is initiated with a detonator, which is placed at the center of the top cap. The detonation then travels downward to and alongside the powder container.
Figure 9.1: A schematic representation of the cylindrical configuration used for the shock wave absorption experiments.

Figure 9.2: Top-view of the bottom plug with the ionisation pins.
Two types of explosive were used: (a) AMPA2.1, which was developed at the PML-TNO laboratory and exists of 81.2% ammonium nitrate, 10% TNT, and 8.8% aluminium. At the diameter used in the present experiments it has a detonation velocity of, $D=3.6 \text{ km/s}$.

(b) Triamite, which is a commercially available explosive that exists of 80% ammonium nitrate, 19.8% TNT, and 0.2% aluminum. At the diameter used in the present experiments it has a detonation velocity of, $D=3.0 \text{ km/s}$.

Two grades of Si$_3$N$_4$ powders were used: (a) a commercial grade, Gimex Grade LC 12-S with an average (Laser Diffraction) particle size of $D_{50}=0.6 \mu\text{m}$, and a powder with an average (Laser Diffraction) particle size of $D_{50}=4.8 \mu\text{m}$ that will be referred to as batch 2, and two commercial grades of ZrO$_2$ powders: (a) Gimex Grade Z-100, with an average (Laser Diffraction) particle size of $D_{50}=0.65 \mu\text{m}$, (b) Gimex Grade 200, with an average (Laser Diffraction) particle size of $D_{50}=3.5 \mu\text{m}$. The powder properties are shown in Tables 9.2 and 9.3. Scanning electron micrographs of the four powders are shown in Figs. 9.3(a)-9.3(d).

<table>
<thead>
<tr>
<th></th>
<th>Grade Z-100</th>
<th>Grade 200</th>
</tr>
</thead>
<tbody>
<tr>
<td>Mean particle size $D_{50}$ (µm)</td>
<td>0.65</td>
<td>3.5</td>
</tr>
<tr>
<td>HfO$_2$ impurity (wt%)</td>
<td>1.7</td>
<td>2</td>
</tr>
</tbody>
</table>
Figure 9.3(a): Scanning electron micrograph (magnification $10^4$) of ZrO$_2$ Gimex Grade Z-100 powder.

Figure 9.3(b): Scanning electron micrograph (magnification $10^4$) of ZrO$_2$ Gimex Grade 200 powder.
Figure 9.3(c): Scanning electron micrograph (magnification $10^4$) of Si$_3$N$_4$ Gimex Grade LC 12-S powder.

Figure 9.3(d): Scanning electron micrograph (magnification $10^4$) of Si$_3$N$_4$ powder of batch 2.
Table 9.3: Properties of Gimex Si₃N₄ powders.

<table>
<thead>
<tr>
<th></th>
<th>Grade LC 12-S</th>
<th>Batch 2</th>
</tr>
</thead>
<tbody>
<tr>
<td>Mean particle size $D_{50}$ (µm) (Laser Diffraction)</td>
<td>0.6</td>
<td>4.8</td>
</tr>
<tr>
<td>Particle size range (µm) (Laser Diffraction)</td>
<td>0.3-1.5</td>
<td>4.5-5</td>
</tr>
<tr>
<td>Specific surface area (m²/g) (BET)</td>
<td>18-21</td>
<td>...</td>
</tr>
</tbody>
</table>

For the Si₃N₄ powders experiments were performed with both Triamite ($D=3.0$ km/s) and AMPA2.1 ($D=3.6$ km/s). Because the results for the Si₃N₄ powders showed little effect of the detonation velocity on the absorption coefficient only experiments with Triamite were performed for the ZrO₂ powders.

The experimental conditions of a number of typical experiments, which will be used as examples, are shown in Table 9.4. The conditions at the wall of the cylinder as calculated with Eqs. (9.10) and (9.11) are shown in Table 9.5.

Table 9.4: Experimental conditions.

<table>
<thead>
<tr>
<th>Experiment No.</th>
<th>Powder type</th>
<th>Average particle size $D_{50}$ (µm)</th>
<th>Initial density powder, ε (%TMD)</th>
<th>Density explosive $\rho_x$ (10³ kg/m³)</th>
<th>Detonation velocity $D$ (km/s)</th>
</tr>
</thead>
<tbody>
<tr>
<td>A15</td>
<td>Si₃N₄ LC 12-S</td>
<td>0.6</td>
<td>50</td>
<td>1.03</td>
<td>3.0</td>
</tr>
<tr>
<td>A18</td>
<td>Si₃N₄ LC 12-S</td>
<td>0.6</td>
<td>50</td>
<td>1.07</td>
<td>3.6</td>
</tr>
<tr>
<td>A24</td>
<td>Si₃N₄ batch 2</td>
<td>4.8</td>
<td>50</td>
<td>1.05</td>
<td>3.0</td>
</tr>
<tr>
<td>A27</td>
<td>Si₃N₄ batch 2</td>
<td>4.8</td>
<td>50</td>
<td>0.99</td>
<td>3.6</td>
</tr>
<tr>
<td>R107</td>
<td>ZrO₂ Z-100</td>
<td>0.65</td>
<td>50</td>
<td>1.10</td>
<td>3.0</td>
</tr>
<tr>
<td>P55</td>
<td>ZrO₂ 200</td>
<td>3.5</td>
<td>40</td>
<td>1.05</td>
<td>3.0</td>
</tr>
</tbody>
</table>
Table 9.5: Conditions calculated for the inner wall of the cylinder.

<table>
<thead>
<tr>
<th>Experiment No.</th>
<th>Stress at wall [Eq.(9.4)] $\sigma_0$ (GPa)</th>
<th>Mass displacement velocity at wall [Eq.(9.11)] $u_0$ (km/s)</th>
<th>Shock wave velocity at wall [Eq. (9.5)] $U_0$ (km/s)</th>
</tr>
</thead>
<tbody>
<tr>
<td>A15</td>
<td>1.7</td>
<td>0.58</td>
<td>1.8</td>
</tr>
<tr>
<td>A18</td>
<td>2.4</td>
<td>0.73</td>
<td>2.0</td>
</tr>
<tr>
<td>A24</td>
<td>1.8</td>
<td>0.56</td>
<td>1.8</td>
</tr>
<tr>
<td>A27</td>
<td>2.3</td>
<td>0.68</td>
<td>2.0</td>
</tr>
<tr>
<td>R107</td>
<td>2.0</td>
<td>0.52</td>
<td>1.4</td>
</tr>
<tr>
<td>P55</td>
<td>1.9</td>
<td>0.69</td>
<td>1.2</td>
</tr>
</tbody>
</table>

9.4 RESULTS FOR Si$_3$N$_4$ POWDERS

In Figs. 9.4 and 9.5 typical results are shown for two experiments with Si$_3$N$_4$ Grade LC 12-S powder with an average particle size of 0.6 $\mu$m. The first experiment was performed with Triamite ($D=3.0$ km/s), and the second with AMPA2.1 ($D=3.6$ km/s). In these figures the time, $t$, at which the shock was registered at the ionisation pins is plotted versus the distance, $r$, of the pin from the center of the sample. For this, it is assumed that the shock wave is symmetrical around the center of the sample, and that, therefore, the distance of the pins, shown in Fig. 9.2, can be plotted versus one common axis.
Figure 9.4: Registration of the shock pulse in dynamic compaction experiment A15, and a fit using Eq. (9.12). The average particle size of the Si$_3$N$_4$ powder was 0.6 μm.

Figure 9.5: Registration of the shock pulse in dynamic compaction experiment A18, and a fit using Eq. (9.12). The average particle size of the Si$_3$N$_4$ powder was 0.6 μm.
Because the time registration starts with the first pin that is triggered, and this pin is not always exactly at the same distance from the center, the experiments do not have a common reference. Using one pin as a common reference to calibrate the time registration too would introduce a large error over the entire data range, if there is a large random error in the time registration or positioning. To be able to compare experiments, however, a common reference is required.

Because the results show an approximately linear relation between $t$ and $r$, the average experimental values of $t$ and $r$ were used as a reference for the experiments. Averaging over $t$ and $r$ introduces an error in the calibration, if the relation between $t$ and $r$ is not linear. This error, however, is considered to be small compared to the random errors that would be introduced if only one pin were used as a reference.

In Figs. 9.4 and 9.5 the fitted curves using Eq. (9.12) are also shown. The absorption coefficients found for these two experiments were 0.6 $R^{-1}$ and 0.7 $R^{-1}$, from this value and the radius of the sample, the absorption per millimetre can be calculated by dividing by the radius (15 mm), which gives an absorption coefficient of 4%/mm and 5%/mm respectively.

In Figs. 9.6 and 9.7 typical results are shown for the same kind of experiments with Si$_2$N$_4$ batch 2 powder with an average particle size of 4.8 μm. The absorption coefficients found from the fits, which are also included are 1.2 $R^{-1}$ and 1.5 $R^{-1}$, or 8%/mm and 10%/mm, respectively.

In both series of experiments the absorption coefficient is somewhat higher for the measurements with AMPA2.1 with the highest detonation velocity. The difference, however, is small.
Figure 9.6: Registration of the shock pulse in dynamic compaction experiment A24, and a fit using Eq. (9.12). The average particle size of the $\text{Si}_3\text{N}_4$ powder was 4.8 $\mu$m.

Figure 9.7: Registration of the shock pulse in dynamic compaction experiment A27, and a fit using Eq. (9.12). The average particle size of the $\text{Si}_3\text{N}_4$ powder was 4.8 $\mu$m.
It should be observed that low absorption coefficients of about 7%/mm and less are inherently less accurate than higher absorption coefficients, because the high average shock wave velocities in these experiments result in a decreased accuracy of the data. This is, because they result in smaller time-differences, while the time-resolution remains unchanged. This means an increased relative error. Calculations showed that the effect of a 10% change in the absorption coefficient for experiment A24 (f=8%/mm) is comparable to a 25% change in f for experiment A15 (f=4%/mm). The average deviation of the fit is apparently less sensitive to the absorption coefficient for higher values of the absorption coefficient.

In Figs. 9.8 and 9.9 cross-sections are shown for the samples obtained in the experiments A15 & A24 performed with Triamite. The presence of cracks in the center of the sample of experiment A15, and more important their absence in the sample of experiment A24 indicates that the absorption coefficient has a direct relation to the compaction result.

Figure 9.8: Cross-section of the densified sample of experiment A15. The cracks in the center are probably due to high stresses in the center during compaction.
Figure 9.9: Cross-section of the densified sample of experiment A24. The sample shows a homogenous surface without cracks with only a few small superficial flaws.

In Fig. 9.10 the shock wave velocity, $U$, and the shock wave stress, $\sigma$, calculated with Eqs. (9.7) and (9.5), and Eqs. (9.7) and (9.4), respectively, using the conditions shown in Table 9.5, are shown for the experiments with the fine powder (0.6 $\mu$m). In Fig. 9.11 the shock wave velocity and shock stress are presented for the experiments with the coarse powder (4.8 $\mu$m). It can be seen that the shock wave velocity as well as the shock stress increase towards the center of the sample. This is due to the sharp decrease in the surface area through which the shock is transmitted.
Figure 9.10: The shock wave velocity, $U$, and shock stress, $\sigma$, calculated from the fit for experiments A15 and A18.

Figure 9.11: The shock wave velocity, $U$, and shock stress, $\sigma$, calculated from the fit for experiments A24 and A27.
In these figures the effect of a difference in absorption is easily recognizable. The increase of the shock wave velocity towards the center is less for the powder with the high absorption coefficient (Fig. 9.11). This effect is even stronger for the shock stress, and can also be seen in the earlier shown cross-sections (Figs. 9.8 and 9.9). High stresses in the center are generally associated with overcompaction, and the cracks in the sample of experiment A15 are likely the result of the high stresses in the center, shown in Fig. 9.10. In contrast with this, the cross-section of the densified sample of experiment A24 (Fig. 9.9) shows that the density of this compact is almost homogenous, as would be expected from the large almost horizontal tract in the stress curve for this sample (Fig. 9.11).

The results show that the shock wave absorption increases with the average particle size. Results of earlier experiments on AlN indicated the opposite. For these experiments the absorption decreased with increasing particle size. An explanation for this might be found in different absorption mechanisms that occur in AlN and Si$_3$N$_4$. If the shock wave absorption occurs mainly by dissipation during plastic deformation as is expected in the relatively ductile AlN, an increase in the number of particles per unit length would increase absorption. Absorption would then decrease if the particle sizes were enlarged, because there would be less particles per unit length. If the absorption were to be due mainly to particle fracture, a larger particle size would increase the absorption, because larger particles can be fractured easier.

9.5 RESULTS FOR ZrO$_2$ POWDERS

In Fig. 9.12 typical results are shown for an experiment with ZrO$_2$ Grade Z-100 powder with an average particle size of 0.65 μm, the experiment was performed with Triamite ($D=3.0$ km/s). In this figure the curve that was fitted with Eq. (9.12) is also shown. The absorption coefficient found for this experiment is 2.9 $R^{-1}$, or 19%/mm.
Figure 9.12: Registration of the shock pulse in dynamic compaction experiment R107, and a fit using Eq. (9.12). The average particle size of the ZrO₂ powder was 0.65 μm.

Figure 9.13: Registration of the shock pulse in dynamic compaction experiment P55, and a fit using Eq. (9.12). The average particle size of the ZrO₂ powder was 3.5 μm.
In Fig. 9.13 typical results are shown for the same kind of experiment with ZrO₂ Grade 200 powder with an average particle size of 3.5 μm. The absorption coefficient found from the fit, that is also shown is 1.8 R⁻¹, or 12%/mm.

No experiments were performed with AMPA2.1, because earlier results for AlN₃ and the results for Si₃N₄ proved that the detonation velocity has little effect on the absorption coefficient.

In Fig. 9.14 the shock wave velocity, \( U \), and the shock wave stress, \( \sigma \), as calculated with Eqs. (9.7) and (9.5) and Eqs. (9.7) and (9.4), respectively, using the conditions shown in Table 9.5, are shown for the experiments with both types of ZrO₂ powders. It can be seen that for ZrO₂ the shock wave velocity as well as the shock stress also increase towards the center of the sample.

![Diagram showing shock wave velocity and stress](image)

**Figure 9.14:** The shock wave velocity, \( U \), and shock stress, \( \sigma \), calculated from the fit for experiments R107 and P55.

In this figure the effect of a difference in absorption is easily recognizable. The increase of the shock wave velocity towards the center is much less for the fine powder with the high absorption coefficient (viz. curves...
for experiment R107 in Fig. 9.14). This effect is even stronger for the shock stress.

At the moment the effect of the initial powder density on the absorption coefficient is not fully understood. It is assumed to affect only the stress at the wall, and to have only minor influence on the absorption coefficient.

An interesting feature is observed when the SEM micrographs are studied. Although the average (Laser Diffraction) powder sizes are 0.65 and 3.5 μm for the ZrO₂ powders, the SEM micrographs [Figs. 9.3(a) and 9.3(b)] reveal that the larger-sized powder consists of a partially sintered fraction of the smaller-sized powder type. The lower absorption coefficient for the partially sintered powder suggests that this sintering beforehand decreases the absorption of shock wave energy.

This concurs with the earlier experiments on AlN³, in which it was found that a larger average particle size results in a decreased absorption. The effects suggest that the absorption process in AlN and ZrO₂ are determined by the number of particles per unit length. A likely explanation for this is that most shock wave energy is dissipated in the transmission of the shock wave from particle to particle, during plastic deformation.

9.6 DISCUSSION

The absorption coefficients of all the typical experiments are shown in Table 9.6. It appears that particle size effects such as were found in earlier experiments on AlN³, and in the dynamic compaction experiments on Al₂O₃ by Prümmer (1977)⁶ are found also for the ZrO₂ powders, but not for the Si₃N₄ powders. In the AlN and the ZrO₂ powders the absorption decreases with increasing particle size.

This can be explained by the fact that the absorption of shock wave energy in the powders of these relatively ductile materials occurs due to plastic deformation of the particles. Most plastic deformation occurs at the particle boundaries and, therefore, the number of particles per unit length determines the absorption. A smaller particle size means more boundaries and, therefore, a higher absorption.
Table 9.6: Absorption parameters of the fitted curves.

<table>
<thead>
<tr>
<th>Experiment No.</th>
<th>Absorption coefficient (f) ((R^{-1}))</th>
<th>Absorption coefficient (f) (%/mm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>A15</td>
<td>0.6</td>
<td>4</td>
</tr>
<tr>
<td>A18</td>
<td>0.7</td>
<td>5</td>
</tr>
<tr>
<td>A24</td>
<td>1.2</td>
<td>8</td>
</tr>
<tr>
<td>A27</td>
<td>1.5</td>
<td>10</td>
</tr>
<tr>
<td>R107</td>
<td>2.9</td>
<td>19</td>
</tr>
<tr>
<td>P55</td>
<td>1.8</td>
<td>12</td>
</tr>
</tbody>
</table>

The effect found in Si₃N₄ is exactly the opposite, the absorption increases with the particle size. A possible explanation for this might be that a different absorption mechanism occurs in Si₃N₄. If the main shock wave energy absorption occurs due to fracture a larger particle size increases absorption, because larger particles have more defects and are, therefore, easier to crack.

When the shock stress curves for the experiments with Triamite (\(D=3.0\) km/s) and the 0.6 \(\mu\)m Si₃N₄ and 0.65 \(\mu\)m ZrO₂ powders are compared (i.e. experiments A15 and R107 in Figs. 9.10 and 9.14, respectively) the effects of the material properties are evident. The shock stress curve in the fine Si₃N₄ powder steadily rises, while in the fine ZrO₂ powder a strong decline is observed. This large difference can be seen also in the absorption coefficients, being 4%/mm for the fine Si₃N₄ powder, and 19%/mm for the fine ZrO₂ powder. The absorption coefficient appears to be a useful tool in the evaluation of a powder for dynamic compaction. This was also shown in the comparison of the cross-sections (viz. Figs. 9.8 and 9.9), and the shock stress curves (viz. Figs. 9.10 and 9.11) of experiments A15 and A24, where a more homogenous compact was obtained for the powder with the higher absorption coefficient.

The absorption coefficient found for ZrO₂ with an average particle size of 3.5 \(\mu\)m was about 12%/mm. The absorption coefficients found for Si₃N₄ with an average particle size of 4.8 \(\mu\)m are in the range of 8 to 10%/mm. Earlier it was found for AlN powders with an average particle size of 5.5 \(\mu\)m that the absorption coefficient was in the range of 11 to 14%/mm. Therefore, although
the absorption coefficient increases with particle size for the Si₃N₄ powders, even for the powders with the larger particle sizes the absorption in Si₃N₄ powders is less than in AlN or ZrO₂ powders, while the values for AlN and ZrO₂ powders are more alike.

9.7 CONCLUSIONS

The absorption coefficient can be used as a modelling parameter for the study of shock waves in powders. Powders can be characterized in first approximation with only this one parameter. The conditions during compaction, such as the shock stress, can be calculated with the absorption coefficient. The structure of the densified Si₃N₄ compacts is in agreement with the shock stress curves that could be calculated with the absorption coefficient. When the absorption coefficient and the Hugoniot of a powder are known the optimal conditions for homogenous dynamic compaction can be determined without further experiments.

The absorption of the shock wave energy per unit area in Si₃N₄ powders with an average particle size of 0.6 and 4.8 μm was found to be about 5%/mm and 10%/mm, respectively. In ZrO₂ powders with an average particle size of 0.65 and 3.5 μm the absorption coefficient was found to be much larger, 19 and 12%/mm, respectively, while the effect of the particle size on the absorption was exactly the opposite to what was found for Si₃N₄. Such a difference has a strong effect on the optimal conditions for dynamic compaction.

From the experiments with ZrO₂ powders it appears that partial sintering of a powder decreases the shock wave absorption.

9.8 REFERENCES

3 Chapter 8 of this work.
4 Chapter 7 of this work.
5 A. M. Maas, internal TNO report (unpublished).
7 Chapter 6 of this work.
APPENDIX A: CALCULATION OF THE SHOCK WAVE VELOCITY IN POROUS ZrO₂ AND Si₃N₄

1. Theory

In Chapter 8 a method was developed to relate the shock wave behaviour of a porous assembly to the shock wave behaviour of a solid. In this method the powder is modelled as an assembly of spheres. These spheres have solid-state material properties. The stress in the solid phase, \( \sigma_s \), is calculated from the stress on the assembly \( \sigma_a \), and the relative density of the assembly, \( \varepsilon \), with:

\[
\sigma_s = \frac{\sigma_a}{\varepsilon} \quad (9.1)
\]

With this method the shock wave velocity in a porous assembly, \( U_s \), can be calculated from the mass displacement and the shock wave velocity in the solid phase [\( u_s(\sigma_s) \) and \( U_s(\sigma_s) \), respectively] with a deformation curve, \( \Delta r_0(\sigma_s) \), which is a measure of the deformation of the spheres due to the passage of the shock wave:

\[
U(\sigma_s) = \frac{1}{\frac{1}{U(\sigma_s)} + \frac{[\Delta r_0(\sigma_s)-\Delta l]}{(1-\Delta l)}} \quad (9.2)
\]

in which \( \Delta l \) is the initial deformation of the spheres due to prepressing, or sintering of the assembly, before applying a shock wave. The initial deformation can be calculated with:

\[
\Delta l = 1 - \left( \frac{\varepsilon_0}{\varepsilon} \right)^{\frac{1}{3}} \quad (9.3)
\]

in which \( \varepsilon_0 \) is the tap density of the powder in the assembly.
By combining Eq. (9.4) with (9.41) it is found that:

\[ \rho_0 \ U(\sigma_o) \ u(\sigma_s) = \varepsilon \ \rho_{0,s} \ U(\sigma_s) \ u(\sigma_s) \]  \hspace{1cm} (9.A4)

in which \( \rho_{0,s} \) is the theoretical maximum density of the solid. Combining the relation \( \rho_0=\varepsilon \ \rho_{0,s} \), and Eqs. (9.42) and (9.A4) yields an expression for the mass displacement velocity of the powder:

\[ u(\sigma_o) = \left[ 1 + \frac{\left[ \Delta r_0(\sigma_s) - \Delta l \right]}{2(1-\Delta l)} \frac{U_s(\sigma_s)}{u_s(\sigma_s)} \right] u_s(\sigma_s) \]  \hspace{1cm} (9.A5)

It was found that the deformation curves for ceramics were mutually exchangeable, the most important assembly property being the relative density.\(^4\) To obtain a deformation curve for the ZrO\(_2\) and Si\(_3\)N\(_4\) powders in the present experiments the deformation curve for 39\% TMD UO\(_2\) was calculated. The Hugoniots for solid and 39\% TMD UO\(_2\) are shown in Fig. 8.A1. The deformation curve for 39\% TMD UO\(_2\) is shown in Fig. 8.A2. For the calculations here it will be assumed that for the tap density of the ceramics \( \varepsilon_0=39\% \) TMD holds.
Figure 8.A1: Hugoniots of solid and 39% dense UO₂.

Figure 8.A2: Deformation curve of 39% TMD UO₂.
2. Hugoniot for porous ZrO$_2$ assemblies

For the determination of the equation of state of the porous ZrO$_2$ assemblies a Hugoniot for 100% TMD ZrO$_2$ was used, that was calculated from infrared and X-ray data (see Fig. 9.A1). This solid Hugoniot has an intercept $C_{0,s} = 5.40 \text{ km/s}$, and a slope $S_s = 0.956$. Furthermore, $\rho_{0,s} = 5.6 \times 10^3 \text{ kg/m}^3$ was used for the solid density of ZrO$_2$.

No data were available for 100% TMD ZrO$_2$. Therefore, it was not possible to verify the Hugoniot for solid ZrO$_2$ directly. However, data were available for 81% TMD ZrO$_2$, and with the use of the deformation curve of 81% TMD BeO, and Eqs. (9.A2) and (9.A5) these data could be used to verify the solid Hugoniot and the Eqs. (9.A2) and (9.A5) simultaneously. In Fig. 9.A1 the Hugoniot for 100% TMD and 81% TMD ZrO$_2$ are shown. The calculated Hugoniot for 81% ZrO$_2$ shows an average deviation of 3.5 % from the experimental data (see Fig. 9.A1). It is, therefore, concluded that Eqs. (9.A2) and (9.A5) in combination with a deformation curve, and the theoretical solid Hugoniot for ZrO$_2$ can be used to determine the Hugoniot for porous ZrO$_2$ assemblies.

![Hugoniot diagram](image)

**Figure 9.A1:** Calculated Hugoniot for 100% TMD ZrO$_2$, and for 81% TMD ZrO$_2$, compared with data from Marsh$^8$ for 81% TMD ZrO$_2$.  

215
Using the deformation curve for 39% TMD UO₂ (see Fig. 8.A2) a Hugoniot was calculated with Eqs. (9.A2) and (9.A5) for 40% TMD ZrO₂, as shown in Fig. 9.A2. The Hugoniot for 40% TMD ZrO₂ was approximated with:

$$ U = 0.1 + 1.6 \, u $$  \hspace{1cm} (9.A6)

This is a reasonable approximation of the calculated curve as can be seen in Fig. 9.A2. Equation (9.A6) was used for the powder in experiment P55.

![Graph showing Hugoniot curves for 40% and 50% TMD ZrO₂](image)

**Figure 9.A2:** Calculated and approximated Hugoniot for 40% TMD, and 50% TMD ZrO₂.

The Hugoniot for 50% TMD ZrO₂ (see Fig. 9.A2) was calculated analogous to the Hugoniot for 40% TMD ZrO₂. This curve could be approximated with:

$$ U = 0.6 + 1.6 \, u $$  \hspace{1cm} (9.A7)

Equation (9.A7) was used for the powder in experiment R107.
3. Hugoniot for porous $\text{Si}_3\text{N}_4$ assemblies

For the determination of the equation of state of the porous $\text{Si}_3\text{N}_4$ assemblies a Hugoniot for 100% TMD $\text{Si}_3\text{N}_4$ was used that was calculated from infrared and X-ray data (see Fig. 9.A3).\(^7\) This solid Hugoniot has an intercept $C_{0,s} = 5.09 \text{ km/s}$ and a slope $S_s = 1.33$. Furthermore, $\rho_{0,s} = 3.44 \times 10^3 \text{ kg/m}^3$ was used for the solid density of $\text{Si}_3\text{N}_4$.

Using the deformation curve for 39% TMD UO$_2$ (see Fig. 8.A2) a Hugoniot was calculated with Eqs. (9.A2) and (9.A5) for 50% TMD $\text{Si}_3\text{N}_4$ as shown in Fig. 9.A3.

![Hugoniot diagram for 100% and 50% TMD $\text{Si}_3\text{N}_4$.](image)

**Figure 9.A3:** Hugoniots for 100% TMD and 50% TMD $\text{Si}_3\text{N}_4$.

The Hugoniot for 50% TMD $\text{Si}_3\text{N}_4$ was approximated with:

$$U = 1.0 + 1.4 \, u \quad (9.A8)$$

This is a reasonable approximation of the calculated curve as can be seen in Fig. 9.A3. Equation (9.A6) was used for the powders in experiments A15, A18, A24, and A27.
DYNAMIC COMPACTION OF CERAMICS

P. Booger

SUMMARY

Dynamic compaction is a relatively new and promising densification method for ceramics. By applying a shock wave to a porous material its density can be increased up to more than 99% of its theoretical maximum density (TMD). Ceramics which are difficult to sinter can be densified without additives. Due to the unique processing conditions it is also possible to compact single phase materials or composites which are thermodynamically instable at the high temperatures necessary for sintering. Furthermore, it is possible to obtain thermodynamically unstable phases, like the cubic phase of BN and the hexagonal phase of diamond.

Several explosives are studied for application in dynamic compaction.

To improve the commercial applicability of the process an experimental technique is proposed that determines the key-properties of a ceramic powder in one experiment. With the results of this one experiment the conditions for optimal compaction of this powder can be calculated.

The technique is based on shock wave properties of solid and porous ceramic assemblies. Because the determination of these properties requires complicated and time-consuming labour, while only a limited amount of literature data is available, two models are proposed for the calculation of these properties. These models are also ment to improve the theoretical understanding of the effects of a shock wave in a solid or powder.

First a theoretical shock wave equation of state for inorganic solids is derived based on the Morse potential function, known from classical infrared spectroscopy. Using this potential function and an interstitial-electron model, a linear relation between the shock wave velocity and the mass displacement velocity can be found analogous to the common empirical relation, but with parameters derived from easily accessible non-shock-wave data. Model calculations for the example materials silver and copper are within 5% average error of the experimental data.

The linear equation is applicable in two ways; (1) with data from infrared and X-ray measurements, and (2) with the experimental sound velocity and the bond dissociation energy. The equation is applicable to a wide range of inorganic materials. It is used to calculate the shock wave state of 35 different
metals. With the first method the model calculations are within 1 to 10% accuracy for metals, which have an electron configuration in the gaseous atomic state with non-filled orbitals, and/or a dissociation energy of 40 kJ mol⁻¹ or higher. With the second method the calculations are within 2 to 24% accuracy for those metals.

The shock wave equation of state is also applied to calculate the shock wave behaviour of AlN, Al₂O₃, B, B₄C, BeO, SiC, Si₃N₄, TiB₂, TiO₂, and UO₂. With the first method, calculations have been performed for Al₂O₃, B, BeO, and TiO₂. The results are within 5% accuracy, as long as no phase transformation occurs. With the second method calculations have been performed for AlN, Al₂O₃, B, B₄C, BeO, SiC, Si₃N₄, TiB₂, and UO₂, for which the accuracy varies between 4 and 10%, as long as no phase transformation occurs.

Furthermore, it is proposed that the slope of the shock wave equation of state after a phase transformation can be determined by approximation using theory and experimental evidence, and an example is given for B₄C how to estimate the intercept after a phase transformation.

Secondly a model is proposed in which the propagation of shock waves in ceramic particle assemblies is described with simple shock wave mechanics. With this model shock wave velocities in particle assemblies of BeO, SiC, and UO₂ have been predicted within 9% accuracy from measurements at a different density and solid material properties.

Furthermore, assembly properties of several BeO, SiC, and UO₂ porous assemblies are compared. The results indicate that it is possible to discriminate between material effects and assembly effects. This yields the possibility of calculating the shock wave velocity in a porous ceramic assembly using generally applicable assembly properties, as well as the solid material properties of the ceramic.

The experimental technique is based on a shock wave absorption parameter, which is used to characterize the absorption of a shock wave in a porous assembly.

First the shock wave absorption of several AlN powders is studied. The absorption of the shock wave energy per unit area decreases from about 20%/mm for a powder with an average particle size of 1.5 μm to about 10%/mm for a powder with an average particle size of 6-10 μm. The increase of the absorption coefficient with decreasing average particle size in the AlN powders is discussed in relation to the calculated shock stresses in the assemblies and its effect on the shock wave compaction of the powders.

To study the effect of different solid material properties the experimental technique has also been applied to Si₃N₄ and ZrO₂ powders. The absorption of
the shock wave energy per unit area in Si₃N₄ powders with an average particle size of 0.6 and 4.8 µm was found to be about 5%/mm and 10%/mm, respectively. The effect of the average particle size is opposite to the effect found for AlN. The effect of the absorption coefficient on the compaction is shown. In ZrO₂ powders with an average particle size of 0.65 and 3.5 µm the absorption coefficient was found to be much larger, about 20 and 10%/mm, respectively. For ZrO₂ the effect of the average particle size is the same as found for AlN.

The difference between ZrO₂ and Si₃N₄ is discussed in relation to the calculated shock stresses in the assemblies.

The results of the experimental technique show that the effect of an extrinsic parameter, like the average particle size, on the shock wave absorption can be in the same order of magnitude as the effect of an intrinsic parameter, like the shock wave properties of the solid ceramic.

The calculations with the absorption model show a direct correlation with the quality of the compact. It is shown that a homogenous shock wave velocity or stress distribution in the compact corresponds with a homogenous compact. The proposed shock wave absorption coefficient can be used to determine the conditions for a homogenous shock wave velocity distribution and corresponding optimal compaction.
DYNAMISCH VERDICHTEN VAN KERAMIEK

P. Boogerd

SAMENVATTING

Dynamisch verdichten is een relatief nieuwe en veelbelovende verdichtingsmethode voor keramiek. Door een schokgolf door een poreus materiaal te laten lopen kan men de dichtheid ervan verhogen tot meer dan 99% van de theoretisch maximale dichtheid (TMD). Keramische materialen, die moeilijk te sinteren zijn, kunnen worden verdicht zonder hulpmiddelen. Door de unieke omstandigheden, waaronder het proces wordt uitgevoerd, is het ook mogelijk om eenfasige materialen of composieten te verdichten, die thermodynamisch instabiel zijn bij de hoge temperaturen, die nodig zijn voor sinteren. Verder is het mogelijk om thermodynamisch onstabiele fasen, zoals de kubische fase van BN en de hexagonale fase van diamant, te verkrijgen.

Verscheidene explosieven zijn bestudeerd met betrekking tot hun toepasbaarheid voor dynamisch verdichten.

Om de commerciële toepasbaarheid van het proces te verbeteren wordt een experimentele techniek voorgesteld, die de belangrijkste eigenschappen van een keramisch poeder bepaalt met één experiment. Met de resultaten van dit ene experiment kunnen de omstandigheden voor optimale verdichting van dit poeder berekend worden.

De techniek is gebaseerd op de schokgolfeigenschappen van vaste en poreuze keramische materialen. Omdat de bepaling van deze eigenschappen gecompliceerd en bewerkelijk is, terwijl ook maar een kleine hoeveelheid gegevens in de literatuur beschikbaar is, worden twee modellen voorgesteld voor de berekening van deze eigenschappen. Deze modellen zijn ook bedoeld om het theoretisch begrip van de effecten van een schokgolf op een vaste stof of een poeder te vergroten.

Als eerste wordt een theoretische toestandsvergelijking afgeleid voor anorganische vaste stoffen, die gebaseerd is op de potentiaalfunctie van Morse, bekend uit de klassieke infraroodspectroscopie. Door gebruik te maken van deze potentiaalfunctie en een tussenrooster-electronmodel kan een lineaire relatie gevonden worden tussen de schokgolfsnelheid en de massaverplaatsingssnelheid, analoog aan de gebruikelijke empirische relatie, maar met parameters die afgeleid worden van makkelijk toegankelijke gegevens, die kunnen worden.
bepaald zonder schokgolfmetingen. De berekeningen met het model voor de voorbeeldmaterialen zilver en koper vallen binnen een gemiddelde fout van 5% van de experimentele gegevens.

De lineaire vergelijking is op twee manieren toepasbaar; (1) met gegevens uit infrarood- en röntgendiffractiometingen en (2) met de experimentele geluidsnelheid en de bindingsdissociatie-energie. De vergelijking is toepasbaar op een breed scala van anorganische materialen. Zij wordt gebruikt om de schokgolfstoestand van 35 verschillende metalen te berekenen. Met de eerste methodie hebben de berekeningen een nauwkeurigheid van 1 tot 10% voor metalen, die een electronenconfiguratie hebben in gasvormige atomaire toestand met ongevulde orbitalen en/of een dissociatieenergie van 40 kJ mol⁻¹ of hoger. Met de tweede methode hebben de berekeningen een nauwkeurigheid van 2 tot 24% voor deze metalen.

De schokgolfstoestandsvergelijking is ook gebruikt om het schokgolfgedrag van AlN, Al₂O₃, B, B₄C, BeO, SiC, Si₃N₄, TiB₂, TiO₂, en UO₂ te berekenen. Met de eerste methode zijn berekeningen uitgevoerd voor Al₂O₃, B, BeO en TiO₂, de resultaten vallen binnen een nauwkeurigheid van 5%, zolang er geen fasenovergang plaatsvindt. Met de tweede methode zijn berekeningen uitgevoerd voor AlN, Al₂O₃, B, B₄C, BeO, SiC, Si₃N₄, TiB₂, en UO₂, waarbij de nauwkeurigheid varieert tussen 4 en 10%, zolang er geen fasenovergang plaatsvindt.

Verder wordt er voorgesteld dat de helling van de schokgolfstoestandsvergelijking na een fasenovergang bij benadering bepaald kan worden door gebruik te maken van theorie en experimenteel bewijs en wordt er een voorbeeld gegeven voor B₄C voor het schatten van het snijpunt met de schokgolfnelheid-as na een fasenovergang.

Als tweede wordt een model voorgesteld waarmee de voortplanting van schokgolven in keramische poederstapelingen wordt beschreven met behulp van eenvoudige schokgolfmechanica. Met dit model zijn de schokgolfnelheden in verscheidene BeO, SiC en UO₂ poederstapelingen voorspeld binnen een nauwkeurigheid van 9% aan de hand van metingen bij een andere dichtheid en de materiaaleigenschappen van de vaste stof.

Verder zijn de eigenschappen van verscheidene BeO, SiC en UO₂ poederstapelingen vergeleken. De resultaten duiden erop dat het mogelijk is onderscheid te maken tussen materiaaleffecten en stapelingseffecten. Dit biedt de mogelijkheid om de schokgolfnelheid in een poreus keramisch materiaal te berekenen door gebruik te maken van algemeen toepasbare poederstapelingseigenschappen en de eigenschappen van de keramische vaste stof.

De experimentele techniek is gebaseerd op een schokgolfabsorptieparameter, die wordt gebruikt om de absorptie van een schokgolf in een poreus
materiaal te karakteriseren.

Als eerste is de schokgolfabsorptie van een aantal AlN poeders bestudeerd. De absorptie van de schokgolfenergie per eenheid van oppervlak neemt af van ongeveer 20%/mm voor een poeder met een gemiddelde deeltjesgrootte van 1,5 μm tot ongeveer 10%/mm voor een poeder met een gemiddelde deeltjesgrootte van 6-10 μm. De toename van de absorptiecoëfficiënt met afnemende deeltjesgrootte in de AlN poeders wordt besproken in relatie tot de berekende schokdrukken in de poederstapelingen en het gevolg daarvan voor het schokgolfverdichten van de poeders.

Om het effect van verschillende vaste-stof-materiaaleigenschappen te bestuderen is de experimentele techniek ook toegepast op Si₃N₄ en ZrO₂ poeders. Voor de absorptie van de schokgolfenergie per eenheid van oppervlak in Si₃N₄ poeders met gemiddelde deeltjesgrootten van 0,6 μm en 4,8 μm werden waarden gevonden van, respectievelijk, ongeveer 5%/mm en 10%/mm. Het effect van de gemiddelde deeltjesgrootte is tegengesteld aan het effect dat gevonden werd voor AlN. Het effect van de absorptiecoëfficiënt op de verdichting wordt getoond. Voor ZrO₂ poeders met gemiddelde deeltjesgrootten van 0,65 μm en 3,5 μm werden veel hogere waarden voor de absorptiecoëfficiënt gevonden van, respectievelijk, ongeveer 20%/mm en 10%/mm. Voor ZrO₂ is het effect van de gemiddelde deeltjesgrootte hetzelfde als het effect dat gevonden werd voor AlN.

Het verschil tussen ZrO₂ en Si₃N₄ wordt besproken met betrekking tot de berekende schokdrukken in de poeders.

De resultaten van de experimentele techniek tonen aan dat het effect van een extrinsieke parameter, zoals de gemiddelde deeltjesgrootte op de schokgolfabsorptie van dezelfde orde van grootte kan zijn als het effect van intrinsieke parameters, zoals de schokgolf eigenschappen van het vaste keramiek.

De berekeningen met het absorptiemodel tonen een directe correlatie met de kwaliteit van het verdichte materiaal. Er wordt getoond dat een homogene schokgolfsnelheids- of schokgolfdrukverdeling in het materiaal overeenkomt met een homogeen verdicht materiaal. De voorgestelde schokgolfabsorptiecoëfficiënt kan gebruikt worden om de omstandigheden voor een homogene schokgolfsnelheidsverdeling en de daarmee samenhangende optimale verdichting te bepalen.
NAWOORD

Aan dit promotie onderzoek hebben velen een bijdrage geleverd. Een aantal van hen wil ik in het bijzonder bedanken.

Voor hun begeleiding en in mij gestelde vertrouwen ben ik mijn promotor prof. dr. J. Schoonman en Albert van der Steen zeer erkentelijk.

Tijdens het onderzoek heeft Amanda Maas een onmisbare bijdrage aan het experimenteel werk op het PML geleverd, waarin zij, onder andere, werd bijgestaan door de afstudeerders Ad Janssens, Caspar van Papendrecht en Guy Meddens. Voor de ondersteuning van dit werk stonden de medewerkers van de werkplaatsen van het PML altijd klaar en met name het technische advies van Jan Mulder en zijn collega's was altijd zeer welkom.

Een aanzienlijk deel van de theorie is in samenwerking met Ries Verbeek ontwikkeld. Zonder Ed de Jong, Durandus Dijken, Hans Scholtz en Marianne Stuivinga zouden de discussies op het PML nooit zo verhelderend zijn geweest. De bijdrage van Hans Klop was onmisbaar voor de totstandkoming van dit proefschrift.


Ook buiten het PML en de Technische Universiteit Delft heeft een aantal mensen een bijdrage geleverd. Nico Broug was steeds een inspirerende bron met evenwichtige suggesties en Jan Meerhof leverde suggesties uit een wiskundige hoek. Voor inspiratie op momenten van desoriëntatie wil ik ook Muriëla de Graaff en Nienke Smits van Burgst hartelijk bedanken.

227
CURRICULUM VITAE


Van 1 november 1989 tot 1 november 1993 was hij als wetenschappelijk medewerker in dienst van het TNO-Prins Maurits Laboratorium te Rijswijk. Gedurende deze periode voerde hij een onderzoek uit naar het dynamisch verdichten van keramiek. In 1994 sloot hij het onderzoek af. Een gedeelte van dit onderzoek is beschreven in dit proefschrift.

LIST OF PUBLICATIONS


