Stellingen van ir. E.P. Carton behorende bij het proefschrift:
"Dynamic compaction of ceramics and composites".

1. De door R.R. Boade gevonden precursor waves in koper poeder wijzen niet op een HEL-waarde van het poeder, maar zijn het gevolg van het voorpersen.
   (R.R. Boade, J. Appl. Phys. 41 pp. 4542-4551)

2. De bewering dat tangentiële trekspanningen ontstaan door de zelf-reflectie van de initiële schokgolf in de cilindrische configuratie is onjuist.

3. Schokgolven in poeders zijn minder schokkend dan die in de vaste stof.

4. Daar waar de mens rechtop is gaan lopen, gaat ze thans veelal juist zwaar gebukt.

5. Bossen in Nederland tonen slechts een verkapte versie van de natuur.

6. Soms worden problemen inzichtelijker door deze globaal te beschouwen in plaats van in detail.

7. De huidige medische mogelijkheden brengen het begrip flexibele dead-line tot leven.

8. In tegenstelling tot een Nederlands gezegde zijn appels goed met peren te vergelijken.

9. Gezien het verleden van de staat Israël, is het vreemd dat het Israëlische woord "Shalom" (vrede) een van de bekendste Hebreeuwse woorden is.

10. Implosieve verdichting is een benaming die de lading beter dekt dan explosief verdichten.
Shock Compaction of Ceramics and Composites
Shock Compaction of Ceramics and Composites

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 voor Promoties aangewezen,
op maandag 2 februari 1998 te 13.30 uur,
door

Erik Peter CARTON

materiaalkundig ingenieur

geboren te Amstelveen
Dit proefschrift is goedgekeurd door de promotoren:
Prof. dr. J. Schoonman
Prof. ir. L. Katgerman

Samenstelling promotiecommissie:

Rector Magnificus, voorzitter
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Appendix A Flash X-ray photography
“Like any orderly process, an explosive shock can be investigated, its effects recorded, understood and used. The rapidity and violence of the explosion do not vitiate Newton’s laws, nor those of thermodynamics, chemistry, or quantum mechanics. They do however, force matter into new states quite different from those we customarily study...”.

G.E. Duvall (1968)
Chapter 1

INTRODUCTION

1.1 Powder compaction

Ceramics generally are chemically inert, hard, refractory, and have a relatively low density compared to metals. Therefore they form an interesting group of materials for high technology applications. The hardness and refractiveness exclude the possibility of processing them by casting, forging and machining, as is usual for metals and many polymers. Instead, technical ceramics are usually synthesized as powders and further processed by precompacting them in a green form and subsequently sintering at high temperature in an oven for their final compaction and consolidation. Usually, a high temperature process is required, since sintering is a diffusion controlled process. Grain growth and a shift of chemical composition to a more thermodynamically stable one are unavoidable during this process. Thus, materials consisting of meta-stable phases and very small particle sizes (nano-crystalline, highly alloyed, and amorphous powders) can not be processed using sintering without some loss of their initial, often unique, properties. Also materials that have a low self-diffusion coefficient or decompose at high temperatures cannot be processed in this way. For these materials as well as unintentionally reacting material mixtures, alternative compaction techniques should be used. One of these techniques is the shock or explosive compaction of powders, in which the compaction of the powder occurs within a shock wave.

1.2 Shock waves in nature

“The sight and sound of an explosion leaves an impression of such chaos and violence that it is hard to perceive that the underlying process is an orderly and, in fact, natural event which is routinely studied and which is technologically useful” [1].

The thunder following the flash of light produced by lightning and the entering of extraterrestrial objects at high speed in the earth-atmosphere are examples of naturally occurring shock waves in air. The latter may produce also shock waves on earth upon impact on its surface. Craters produced by impact of meteorites are more clearly visible at the surface of the moon, due to both our natural “satellite view”, and the absence of an atmosphere with inherent erosion. It took much longer to find evidence for the impact of meteorites on earth. The first terrestrial crater that was recognized to be caused by the impact of a meteorite was the one in Arizona (USA) in the beginning of the twentieth century [2]. Here, a nickel-iron meteorite with a diameter of about 30 meter hit the flat sandstone desert at a velocity between 6 to 10 kilometers per second, about 50,000 year ago. Upon impact, pressures of tens of gigapascal (hundreds of kilobar) which persisted only for a few milliseconds left a crater behind almost 200 meter deep and of more than a kilometer in diameter. Within and around that and other craters, the impact and shock compression process left behind shock-metamorphosed minerals like stishovite (a dense form of silicate) and unique forms of diamond (hexagonal diamond) obtained from graphite [1].
1.3 Explosives

The first explosive (black powder) has been developed in China about 1000 years ago [3]. Its use mainly involved fireworks and signals. About 1300 the Arabs had developed the first gun, a bamboo tube reinforced with iron, which used a charge of black powder to fire an arrow. The first described application in civil engineering was in the Malpas Tunnel of the Canal du Midi in France in 1679. By 1700 the use of black powder was widely accepted in mining. This rather late introduction has various reasons, such as high cost, lack of suitable drilling tools, and fear of roof collapse [4]. The use in coal mines, however, has been less successful, since black powder has a dangerous tendency to ignite coal gas (mostly methane) and coal dust, and many mine explosions occurred indeed. This lead to the search of alternative explosive materials, and in 1846 nitroglycerin or blasting oil was discovered in Italy, and in 1867 Nobel invented dynamite (from the Greek dynamis, “power”), a porous siliceous earth absorbing large quantities of nitroglycerin.

Apart from the military applications, nowadays there is a world wide massive use of explosives in mining and construction [5]. The development of new explosives having ever higher performance (i.e. a higher detonation velocity through a higher energy release rate) is shown to be limited by the vibration velocities of the interatomic bonds within the molecule that makes up the explosives (mostly C-H, O-H, and N-H bonds).

The vibrational barrier has been compared by Walker [6] with other natural barriers observed in technological developments, like the sound and thermal barrier. These barriers hindered the development of ever faster flying (supersonic) aircraft and rockets during and right after WW II, due to, respectively, the translational and vibrational velocities of O₂ and N₂ molecules in air, see Figure 1.

![Figure 1](image-url)

Figure 1. Barriers hindering technical development of super- and hypersonic flight and the development of explosives with higher detonation velocities [6].
1.4 Shock wave processing of materials

Given the natural occurrence of shock-induced material synthesis, it is not surprising that both static high-pressure and shock compression have been utilized for the synthesis of materials in the laboratory. The development in static high-pressure equipment (for example the diamond anvil cell (DAC)) have made it possible to test materials at a pressure up to 400 GPa [7], while by using shock waves pressures of up to 1000 GPa are possible. The shock wave and static compaction techniques are just the extremes of different, so called, dynamic compaction techniques that can be characterized by their strain rate occurring in the process [8]. A typical strain rate that occurs in shock compaction of powders is $10^3 \text{s}^{-1}$, which can be generated either by projectile impact or by the detonation of an explosive.

Shock compaction of powders is only one of the techniques that make use of explosives to process materials. Other examples of materials processing techniques that make use of the fast energy release provided by the detonation of an explosive are: shock synthesis, explosive forming of metal plates, explosive cutting, hardening, welding, and cladding [13]. In shock synthesis use is made of either a shock induced phase transition or a shock induced chemical reaction to obtain a new phase.

For all these techniques, except for the shock compaction of powders, examples of commercial applications can be given, although the scale at which they are used is small compared to the more conventional materials processing techniques. Commercial fabrication methods involve explosive welding of metal plates and the shock-synthesis of polycrystalline diamond. The first “sandwich” coins in the United States produced between 1967 and 1972 were made from explosively bonded metals [1]. The strength of the explosive welding technique is its ability to weld dissimilar metals like Al-Fe and Fe-Ti that are not weldable by conventional (high-temperature) welding technique due to the formation of brittle intermetallics.

In 1961 DeCarli and Jamieson [9] were the first to achieve the long sought goal of synthesis of diamond from graphite. Although static high pressure had been successfully used to synthesize diamond by this time, the shock synthesis was the first without a catalyst. The DuPont Company patent of 1968 provided the basis for the present large scale commercial operation of the process by that company [10]. The large scale involves about 3000 kg explosives in a container with an inner diameter of 1.22 meter and a length of 3 meter, in which in the center a second tube with a diameter of 11 cm is situated containing a graphite-copper powder mixture. About 62 % of the recovered graphite powder has been converted to polycrystalline diamond. In Japan the shock-induced phase-transition of hexagonal BN (hBN) to wurtzite phase BN has been applied commercially [11]. The hBN powder is mixed with cubic BN and metal powders and sintered under hydrostatic pressure of 5 GPa (HIP) to produce tools for the cutting of various steels.

The preceding examples make clear that commercial application of explosive processing of materials is possible in cases where the technique produces unique products or possibilities, unattainable with more conventional processes. Or oppositely, if the same products can be fabricated with another technique, there is no point in doing it by a process that requires shock waves. This is the reason why the shock compaction of powders is limited to those materials or material combinations that are difficult to process with the more conventional techniques of pressing and sintering. Examples of some of these materials are the strong covalently bonded ceramics, as well as the group of amorphous and nano-crystalline materials (rapidly solidified and mechanically alloyed powders). Unfortunately, these materials are generally characterized by a brittle fracture behavior and a very high hardness, what makes them also difficult to
consolidate by the shock compaction technique. So far, a dense, crack free and strong (well bonded) large object of the aforementioned materials has not been fabricated using shock compaction of powders. Especially the occurrence of macro-cracks in the compacts has prevented the commercial application of this technique.

1.5 Scope and outline of this thesis

This thesis is based on a number of publications describing some of the experimental work on the shock compaction of ceramic powders and composites.

The goal of this Ph.D. project is to improve the shock compaction technique for ceramics and composites. For a successful application of this technique in material science the understanding of the physics behind the generation, propagation, and interaction of shock and release waves in a powder is essential. The consolidation mechanisms and the importance of the many parameters that influence the process are not yet fully understood. The possibilities and limitations of the shock compaction process is explored through the fabrication of homogeneous materials that are free of (macro-) cracks and have a high relative density. This is obtained either by shock compaction alone, or by a subsequent process step. Furthermore, understanding of the process and its parameters will be increased through the development of measuring techniques during the shock compaction process.

In order to delimit the research area, the experimental work is restricted to the, so called, direct cylindrical explosive compaction method. In this type of configuration an explosive layer is in direct contact with a cylindrical container that is filled with the powder to be compacted. Furthermore, in all experiments the powder and pores between the powder particles (filled with air) are at room temperature and at atmospheric pressure prior to the shock compaction process.

In the experimental work, mainly TiB$_2$ and B$_4$C have been used, since these materials represent the group of very hard and brittle strong covalently bonded ceramics. The Vickers hardness values of TiB$_2$ and B$_4$C are 25 and 30 GPa, respectively. The hardness of the latter is only surpassed by cubic BN and diamond. For TiB$_2$ powder, loaded to shock pressures between 17 and 27 GPa, the remaining strain in the powder particles has been determined to be only between 0.001 to 0.03 %, demonstrating the very limited plastic deformation possibilities of this material [12].

In Chapter 2 an introduction to the fundamentals of shock wave compaction is given. There is a large number of books concerning the general field of shock wave physics [13]. However, these books hardly deal with the implication of shock wave physics for shock waves in powders. Fortunately, several scientists that worked in the field of shock wave compaction for decades (which started in the late forties [14]), lately presented there life-time work in books [15]. Nevertheless, most information about the subject is scattered in the literature and in Chapter 2 the information available is presented in a condensed form.

The (direct) cylindrical configuration and its most important parameters are the subject of Chapter 3. The first section of this chapter explains the reason for choosing this type of configuration and the experimental procedures. The second section deals with cracking and other types of compact failure that are frequently observed in compacting powders in the cylindrical configuration. Here, several failure mechanisms are described and suggestions to prevent compact failure are given, supported by experimental results or computer simulations.

In Chapter 4 a new type of cylindrical configuration is introduced, that by using two explosive layers with different detonation velocity, generates an oblique detonation wave.
This configuration makes it possible to generate higher (though controlled) shock wave pressures in the powder, while still using an explosive with relatively low detonation velocity and a long pulse duration. The latter is beneficial since this kind of explosives is cheap and helps to prevent cracking.

In Chapter 5 the development of a temperature measuring technique for the cylindrical configuration is described. In order to obtain a very short response time, the powder to be compacted is used as the thermocouple.

Chapter 6 describes the fabrication of composite materials, both ceramic-polymer mixtures and a ceramic-metallic (cermet) mixture. Due to the short duration and rather low temperatures of the process, generally the components are unaffected by the compaction, apart from some deformation of the softer components. In the ceramic-metallic mixture a reaction was initiated locally within a special type of cracks.

In order to fabricate dense, crack free materials, two cermets have been fabricated by capillarity driven melt-infiltration of liquid aluminum in the pores of shock compacted ceramics (B₄C and TiB₂). The fabrication method and some material properties of the resulting cermets, BORCAL and TIBAL, respectively, are described in Chapter 7.

The work described in Chapter 8 demonstrates that it is also possible to form a product (or a green form) with the shock compaction process. Axi-symmetrical forms have been obtained using mandrels of PVC and aluminum. By using a polymer as mandrel material, a hole will remain in the compact, due to a shock-induced decomposition of the polymer. In the case of a shaped aluminum mandrel, nozzle inserts as well as complete rocket nozzles have been fabricated and tested in a test rocket solid fuel burner. Here, use was made of the melt-infiltration technique (described in Chapter 7) to free the inner surface of the nozzles. Finally, in Chapter 9 concluding remarks are presented.
References


Chapter 2

FUNDAMENTALS OF SHOCK WAVE COMPACTION

The necessary theoretical background for understanding the principles of shock wave compaction is described here. The most basic shock wave phenomena are explained using materials in the solid state. However, powders form an unique medium and their peculiarities towards shock wave propagation are the main subject of this chapter.

First, the propagation of elastic waves in several media is described, followed by the description of shock waves. The parameters describing the shock state are related through equations derived from the conservation of mass, momentum, and energy. These so called jump-relations, together with an empirically derived equation of state or Hugoniot of the material are needed for a full description of the shock state.

The importance of the shock impedance of media to reflection and refraction of shock waves, including detonation waves, is described. Also is shown how an equation of state, or Hugoniot, is determined and some of the usual ways to present it.

After this general introduction to shock wave physics, the theory describing the shock compaction of powders is presented. First, the mechanisms of the compaction process are described. The Hugoniot of a powder material is shown in relation to that of the material in its solid and porous states. Also some of the many models for the derivation of the Hugoniot of a powder from its solid state Hugoniot are described and compared. Furthermore, possible mechanisms of bonding or consolidation of the powder particles are presented.

Finally, the differences and resemblances between static and shock compaction of powders is discussed. This demonstrates the complexity of the phenomena occurring during the propagation of a shock wave through such heterogeneous media like powders.
2.1 ELASTIC WAVES

Mechanical energy is generally transported through a medium by elastic stress waves. The stresses remain below the yield strength of the medium in which, therefore, only elastic strain takes place. The stress is released in the same way as it was applied, indicating that elastic wave propagation is an isentropic process (dS = 0, in which S is the entropy). The speed of elastic waves (normally called sonic waves) depends on the stress situation within the medium, the density of the medium, and its elastic constants or moduli. Of all possible stress situations, two are the easiest to apply: uni-axial compression and pure shear stress. In the first, the (elastic) deviation is parallel to the wave propagation and is called a longitudinal sound wave, $c_l$. In the latter, the deviation is perpendicular to the wave propagation, and is called a transversal sound wave or shear wave, $c_s$. When the density, $\rho$, of the medium is known, the sound velocities can be calculated by using, respectively,

$$c_l = \sqrt{\left( \frac{G}{\rho} \right)},$$

(2.1)

and

$$c_s = \sqrt{\left[ (K + 4/3G)/\rho \right]},$$

(2.2)

in which G is the shear modulus and $K$ is the bulk modulus of the medium. From equations (2.1) and (2.2) it is clear that longitudinal sound waves always move faster then transversal sound waves in a medium. Since fluids do not have a shear strength only bulk sound waves are possible here, which are given by,

$$c_b = \sqrt{\left( K/\rho \right)}. $$

(2.3)

When the density of the medium is known, its elastic constants (moduli) and Poisson’s ratio can be calculated after measuring the longitudinal and transversal sound velocities, see Table I. The velocity of sound of a medium can conveniently be determined by measuring transit times or resonant frequencies of ultrasound through a medium with known length.

Table I: Relation between sound velocities, density and elastic moduli of materials.

<table>
<thead>
<tr>
<th>material parameter:</th>
<th>relation with density ($\rho$) and longitudinal and transverse sound velocities ($c_l$ and $c_t$):</th>
</tr>
</thead>
<tbody>
<tr>
<td>Poisson’s ratio ($\nu$)</td>
<td>$\nu = (c_t^2 - 2c_s^2)/2(c_t^2 - c_l^2)$</td>
</tr>
<tr>
<td>Bulk modulus ($K$)</td>
<td>$K = \rho (c_t^2 - 4/3c_l^2)$</td>
</tr>
<tr>
<td>Young’s Modulus ($E$)</td>
<td>$E = \rho c_t^2 [4 - 1/(1 - c_s^2/c_l^2)]$</td>
</tr>
<tr>
<td>Shear Modulus ($G$)</td>
<td>$G = \rho c_l^2$</td>
</tr>
</tbody>
</table>

From M.E. Kipp and D.E. Grady, SAND 89-1461, Sandia National Laboratories, 1989
Table II: Sound velocities and elastic moduli for different media.

<table>
<thead>
<tr>
<th>Material</th>
<th>G [GPa]</th>
<th>K [GPa]</th>
<th>Density [g/cm³]</th>
<th>Transverse sound velocity [m/s]</th>
<th>Longitudinal sound velocity [m/s]</th>
<th>Bulk sound velocity [m/s]</th>
</tr>
</thead>
<tbody>
<tr>
<td>Solids</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Aluminum</td>
<td>25</td>
<td>78</td>
<td>2.7</td>
<td>3040</td>
<td>6420</td>
<td>5375</td>
</tr>
<tr>
<td>Polyethylene</td>
<td>0.26</td>
<td>3.1</td>
<td>0.9</td>
<td>540</td>
<td>1950</td>
<td>1848</td>
</tr>
<tr>
<td>Boron carbide</td>
<td>199</td>
<td>230</td>
<td>2.517</td>
<td>8897</td>
<td>14140</td>
<td>9717</td>
</tr>
<tr>
<td>Titandiboride</td>
<td>237</td>
<td>216</td>
<td>4.509</td>
<td>7450</td>
<td>10850</td>
<td>6610</td>
</tr>
<tr>
<td>Liquids</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Water</td>
<td>-</td>
<td>2.2</td>
<td>0.998</td>
<td>-</td>
<td>1497</td>
<td>1497</td>
</tr>
<tr>
<td>Mercury</td>
<td>-</td>
<td>28.4</td>
<td>13.5</td>
<td>-</td>
<td>1450</td>
<td>1450</td>
</tr>
<tr>
<td>Gases</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Air</td>
<td>-</td>
<td></td>
<td>1.3×10⁻³</td>
<td>-</td>
<td>331</td>
<td>331</td>
</tr>
<tr>
<td>Neon</td>
<td>-</td>
<td></td>
<td>0.9×10⁻³</td>
<td>-</td>
<td>435</td>
<td>435</td>
</tr>
<tr>
<td>Powders</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Alumina⁵(50%)</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td>1220</td>
<td></td>
</tr>
<tr>
<td>Tungsten⁶(60%)</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td>550</td>
<td></td>
</tr>
</tbody>
</table>

Data obtained from CRC Handbook of Chemistry and Physics 76th edition, 1995
a) M.E. Kipp, D.E. Grady, and J.L. Wise, Shock wave and high strain rate phenomena in materials 1992, pp. 1083-1091
b) Jones, Blessing, and Robbins, Mat. Evaluation 1986, 859-62
c) O.V. Roman et al., 6th Int. Conf. on High Energy Rate Fabrication, Essen, 1977, 6.6.1-14

By applying an isotropic pressure on the medium, one can determine the elastic properties at various pressures, and hence the pressure dependency of the moduli.
In Table II sound velocities and elastic moduli are given for solids, gases, liquids, and powders.
2.2 SHOCK WAVES

A shock wave is a wave which produces an abrupt discontinuous, pressure jump in the medium. It propagates faster then the speed of sound of the medium. This results from the property of most materials to transmit sound at a speed, \( c = \sqrt{\left( \frac{\partial P}{\partial \rho} \right)_S} \), where \( S \) is entropy, where the slope of the \( P \) versus \( \rho \) curve increases with pressure beyond an initial practically linear region, see Fig. 1.

A wave with an amplitude beyond this region therefore gradually steepens with travel until it becomes practically a discontinuity and, hence, a shock front. By contrast, a shock wave is immediately generated upon impact of a solid body or a detonation wave [1]. Shock compression is a thermodynamically irreversible process. The entropy increases across the shock front due to dissipative processes such as viscous flow and heat conduction. These processes are also responsible for limiting the maximum steepness of the shock front. Shock waves are compressive and accelerate the mass of the medium in the direction of wave propagation [2].

The pressure of the compressed medium will be reduced to ambient pressure by release waves (also called expansion, rarefaction or unloading waves). Release waves propagate with the speed of sound of the compressed medium and accelerate the particles of the material oppositely to the direction of wave propagation. The combination of a shock wave and a trailing rarefaction wave is called a shock pulse.

![Diagram showing pressure-relative density curves](image)

**Figure 1.** Pressure-relative density curves showing effect of pressure on sound speed \( c(\rho) \). The increase in slope with pressure, implying decreasing compressibility, corresponds to increasing sound speed [1].
2.2.1 The jump-relations

To determine the shock state, equations are needed that relate such parameters as pressure ($P$), internal energy ($E$), and specific volume ($V$) or density ($\rho$) behind the shock wave to the same quantities in front of the shock wave, in terms of the shock wave velocity ($U_s$) and the particle velocity ($u_p$) due to the shock wave. These equations will be derived using the laws of conservation of mass, momentum and energy across the shock front [2]. Two characteristics of shock waves should be clearly distinguished:

1. The shock wave velocity ($U_s$) is the pressure dependent velocity at which the disturbance propagates, and in both metals and ceramics it will be several kilometers per second.

2. The particle velocity ($u_p$) results from the velocity change (acceleration) imparted to the material (it is a mass velocity) by the passage of a shock wave. Its magnitude also depends on the strength of the shock wave and ranges from an infinitesimal value for sound waves, up to a few km/s for detonation and shock waves.

The interpretation and analysis of two- and three-dimensional shocks is very difficult. For simplicity, a steady plane shock wave, i.e. a one-dimensional shock wave for which the initial and final states of the medium are each in thermodynamic equilibrium, is considered. It propagates through the medium at velocity $U_s$, relative to an observer in the laboratory, see Fig. 2. It is assumed that the stress amplitudes produced by the shock wave are in excess of about 10 GPa, so that the shear strength of the material (for metals generally less than 1 GPa [3]) can be neglected and the material treated as a fluid subjected to an isotropic pressure $P$. This is known as the hydrodynamic approximation. The laws of conservation are applied on an area $A$, for a time period $\Delta t$, of this steady plane shock wave.

<table>
<thead>
<tr>
<th>Behind</th>
<th>Ahead</th>
</tr>
</thead>
<tbody>
<tr>
<td>Particle velocity</td>
<td>$u_p$</td>
</tr>
<tr>
<td>Pressure</td>
<td>$P$</td>
</tr>
<tr>
<td>Density</td>
<td>$\rho = 1/V$</td>
</tr>
<tr>
<td>Internal energy</td>
<td>$E$</td>
</tr>
<tr>
<td>Temperature</td>
<td>$T$</td>
</tr>
</tbody>
</table>

**Plane shock front**

Figure 2. Steady state shock front propagating into an undisturbed medium in laboratory coordinates [1].
A. Conservation of mass

Conservation of mass across the shock front requires that the mass intercepted by the wave front equals the mass left behind by the shock front:

\[ \rho_0 U_s A \Delta t = \rho (U_s - u_p) A \Delta t \quad \text{or,} \]
\[ \rho_0 U_s = \rho (U_s - u_p). \quad (2.4) \]

B. Conservation of momentum

The mass behind the shock front, initially at rest, is accelerated in the shock front to the particle velocity \( u_p \). Conservation of momentum requires that an impulse (force times its duration) that equals this change in momentum (mass times change in velocity) has been applied to the medium:

\[ (P - P_0) A \Delta t = (\rho_0 U_s A \Delta t) u_p \quad \text{or,} \]
\[ P - P_0 = \rho_0 U_s u_p. \quad (2.5) \]

The quantity \( \rho_0 U_s \) is called the shock impedance (\( Z \)) of the undisturbed material. In general it varies with shock pressure.

C. Conservation of energy

The conservation of energy requires that the work performed on the medium equals the increase in kinetic and specific internal energy of the medium:

\[ (P - P_0) A u_p \Delta t = \frac{1}{2} \rho_0 U_s A \Delta t u_p^2 + \rho_0 U_s A \Delta t (E - E_0), \quad \text{or} \]
\[ E - E_0 = \frac{1}{2} (P - P_0) (V_0 - V), \quad (2.6) \]

where \( V = 1/\rho \).

Equations (2.4) to (2.6) are called the jump relations or Rankine-Hugoniot relations and are generally applied in shock wave physics. Although they have been derived for a plane wave front, they also hold locally for the flow components normal to a curved shock front. The jump relations have been derived on the basis of the hydrodynamic approximation in which the medium is treated as a perfect fluid (zero viscosity) subjected to an isotropic pressure \( P \). At lower pressures, where this approximation is invalid, \( P \) must be replaced by \( \sigma_x \), the \( x \)-component of stress acting normal to the shock front.

Solving equations (2.4) and (2.5) simultaneously yields the particularly useful forms:

\[ u_p = \sqrt{[(P - P_0)(V_0 - V)]}, \quad (2.7) \]
and
\[ U_s = V_0 \sqrt{[(P - P_0) / (V_0 - V)]}, \quad (2.8) \]
from which the relative compression of a material during shock compression can be derived,

\[(V_0 - V)/V_0 = \Delta V/V_0 = u_p/U_s.\] 

(2.9)

The three jump relations contain five parameters \(E, \rho, P, U_s,\) and \(u_p,\) therefore the shock state is not completely determined by them. One more relation, an equation of state of the medium, is required before specification of one parameter (characterizing the shock strength) enables calculation of the other four.

### 2.2.2 Equation of state (Hugoniot)

The equation of state or Hugoniot characterizes the particular material in which the shock is propagating. In general it must be determined experimentally. If the initial conditions \(P_0\) and \(V_0\) are specified, then equations (2.4) and (2.5) relate the four parameters, \(U_s, u_p, P\) and \(V.\)

Measurement of any two, usually \(U_s\) and \(u_p,\) permits calculation of the others.

The shock wave velocity, \(U_s,\) can be readily determined from the measured shock transit time across a plate of known thickness. The particle velocity, \(u_p,\) may be determined by measuring the free-surface velocity, \(u_{fs},\) of the plate. It will be shown later that the measured free-surface velocity approximates \(2u_p.\)

Such data have been collected for hundreds of solids and liquids [4]. In the absence of shock-induced phase transitions, it is found that the shock and particle velocities are related over a wide pressure range by a simple, linear empirical relation [2];

\[U_s = C + s u_p,\] 

(2.10)

where to a close approximation \(C = \sqrt{\langle K/\rho_0 \rangle}\) is the bulk sound velocity derived from the bulk modulus of elasticity \(K\) (equation 2.3). To a fair approximation [1, 2],

\[s = (\Gamma + 1)/2\] 

(2.11)

for many metals, where \(\Gamma\) is the Grüneisen parameter [2] defined by:

\[\Gamma = V(\partial P/\partial E)_V = \beta V K/c_v = C^2 \beta / c_v,\] 

(2.12)

in which \(\beta\) is the volume thermal expansivity, and \(c_v\) is the specific heat at constant volume. In Table III values of \(C\) and \(s\) for several materials are presented.

The Hugoniot curve defines the equilibrium states of a material which are achieved by shock compression from one initial condition. It should be emphasized that the Hugoniot curve does not describe the state points through which the material passes during shock compression; rather, it defines only the locus of possible final equilibrium states.

Substitution of equation (2.10) into equations (2.7) and (2.8) gives analytic functions for principal Hugoniot curves (corresponding to ambient initial conditions) which relate pairs of shock parameters. Three of these representations are illustrated in Fig. 3 for solid aluminum (AA2024), copper, and sodium [5].
Table III: Hugoniot parameters of materials

<table>
<thead>
<tr>
<th>Material</th>
<th>$P_{\text{max}}$ [GPa]</th>
<th>$C$ [km/s]</th>
<th>$s$ [-]</th>
</tr>
</thead>
<tbody>
<tr>
<td>Al</td>
<td>207</td>
<td>5.333</td>
<td>1.356</td>
</tr>
<tr>
<td>W</td>
<td>540</td>
<td>4.015</td>
<td>1.252</td>
</tr>
<tr>
<td>Fe</td>
<td>12.8</td>
<td>4.63</td>
<td>1.33</td>
</tr>
<tr>
<td>U</td>
<td>480</td>
<td>2.51</td>
<td>1.51</td>
</tr>
<tr>
<td>NaCl</td>
<td>87</td>
<td>3.385</td>
<td>1.38</td>
</tr>
<tr>
<td>KCl</td>
<td>72</td>
<td>2.15</td>
<td>1.54</td>
</tr>
<tr>
<td>MgO</td>
<td>122</td>
<td>6.60</td>
<td>1.37</td>
</tr>
<tr>
<td>Al$_2$O$_3$</td>
<td>145</td>
<td>7.93</td>
<td>1.50</td>
</tr>
<tr>
<td>TiO$_2$</td>
<td>123</td>
<td>2.926</td>
<td>1.865</td>
</tr>
<tr>
<td>B$_4$C$^a$</td>
<td>20 (HEL)</td>
<td>14</td>
<td>1.0</td>
</tr>
<tr>
<td>B$_4$C$^b$</td>
<td>&gt; 20</td>
<td>6.95</td>
<td>1.38</td>
</tr>
<tr>
<td>TiB$_2$$^b$</td>
<td>60</td>
<td>8.622</td>
<td>0.795</td>
</tr>
<tr>
<td>Teflon</td>
<td>59</td>
<td>1.865</td>
<td>1.712</td>
</tr>
<tr>
<td>PMMA</td>
<td>2</td>
<td>2.95</td>
<td>0.85</td>
</tr>
<tr>
<td>PMMA</td>
<td>2-19</td>
<td>2.510</td>
<td>1.545</td>
</tr>
<tr>
<td>H$_2$O</td>
<td>60</td>
<td>1.65</td>
<td>1.92</td>
</tr>
<tr>
<td>H$_2$O (Ice)</td>
<td>122</td>
<td>3.111</td>
<td>1.160</td>
</tr>
</tbody>
</table>

Data from S.S. Batsanov, Chapter 1 in Effects of explosions on materials, Springer-Verlag, New York, 1994
a) D.E. Grady, J. de Physique IV (4), C8-385-391 (1994).

Figure 3. Hugoniot of Al-alloy (2024), copper and sodium in three planes [5].

These geometric interpretations of the shock front jump relations are very useful. From equation (2.8) it is evident that the line with slope $\Delta P/\Delta V$, which connects the initial state to the final shock state on the P-V Hugoniot curve, determines the shock velocity. This so called Rayleigh line, is shown in Fig. 3 for a shock state in copper. Since the Hugoniot curve is concave upward for normal materials it is obvious that the shock wave velocity increases as the pressure increases.

Equation (2.6) shows that the increase in specific internal energy ($E-E_0$) resulting from shock compression of a material is given by the area below the Rayleigh line. In the case of a shock pulse only part of this internal energy is recoverable when the pressure is released by the
trailing release (rarefaction) wave. The release isentrope may be calculated from the Hugoniot by means of the Mie-Grüneisen equation of state, obtained by integrating equation (2.12) [1]:

$$P_S - P_H = \Gamma (E_S - E_H) / V,$$

(2.13)

where the subscripts H and S denote states lying on the Hugoniot curve and the isentrope, respectively. Even for operations with explosives in direct contact with a material, the pressures generated in (solid) ceramics and metals are sufficiently low that the isentrope will differ little from the Hugoniot. Upon expansion, internal energy in the amount $E_F - E = \int_{P_0}^{P} PdV$ (which derives form the first and second laws of thermodynamics, $dE = TdS - PdV$, since $dS = 0$ along an isentrope) is recoverable. The subscript F denotes the state on the isentrope at ambient (final) condition. Thus, the shaded area between the Rayleigh line and the release isentrope is a measure of the waste energy dissipated in the material after passage of a shock pulse, and can be detected as a temperature rise. Using the specific heat of the material the temperature rise can be calculated. Shock temperatures and residual temperatures after unloading are shown for several materials in Figure 4, as functions of shock pressure [1]. Because of the high compressibility of gases, porous and powder materials, entropy changes in the shock wave process are much greater there. The Hugoniot and isentrope of these media differ much more and consequently the dissipated energy after passage of the shock pulse is considerable.

![Figure 4. Dependence of shock temperatures (solid lines) and residual temperatures (dashed lines) on shock pressure for solids [1].](image-url)
2.2.3 Shock wave interactions

Different materials have different shock impedances, \( Z = \rho_0 U_s \), which strongly influence the transmission of a plane shock or detonation wave from one material to another. For steady shock waves in solids and liquids, simple graphical solution procedures are possible. For times very near the instant of interaction all shock waves may be considered to be approximately steady. Interactions are best treated in the pressure-particle velocity plane because;

1. The pressure (P) or particle velocity \( (u_p) \) is usually specified as initial or boundary condition on certain surfaces.

2. The pressure and particle velocity are continuous at material interfaces; otherwise mixing or cavitation would occur.

The slope of the line connecting the origin and the relevant point on the \( P-u_p \) Hugoniot curve determines the magnitude of the shock impedance \( Z \) at pressure \( P \), see Figure 3(c).

Since this slope is only weakly increasing with pressure, the shock impedance of the material can be approximated by its value at ambient conditions as:

\[
Z = \rho_0 U_s = \rho_0 C_0, \quad (2.14)
\]

where \( C_0 \) is the bulk sound velocity of the material at ambient conditions.

Substituting \( C_0 = \sqrt{K/\rho_0} \) in equation (2.14) shows that the shock impedance of a material is determined by its density and compressibility:

Table IV: Materials (acoustic) impedances calculated from sound velocity and density.

<table>
<thead>
<tr>
<th>Material</th>
<th>Density [g/cm(^3)]</th>
<th>Longitudinal sound velocity [km/s]</th>
<th>Impedance ( Z ) (10^6) [kg.m(^{-2})s(^{-1})]</th>
</tr>
</thead>
<tbody>
<tr>
<td>Carbon steel</td>
<td>7.85</td>
<td>5.94</td>
<td>46.6</td>
</tr>
<tr>
<td>Stainless steel (304L)</td>
<td>7.9</td>
<td>5.64</td>
<td>44.6</td>
</tr>
<tr>
<td>Aluminum (1100)</td>
<td>2.71</td>
<td>6.35</td>
<td>17.2</td>
</tr>
<tr>
<td>Copper (110)</td>
<td>8.9</td>
<td>4.70</td>
<td>41.8</td>
</tr>
<tr>
<td>Lead</td>
<td>11.34</td>
<td>2.16</td>
<td>24.5</td>
</tr>
<tr>
<td>Nickel</td>
<td>8.8</td>
<td>5.63</td>
<td>49.5</td>
</tr>
<tr>
<td>Tungsten</td>
<td>19.25</td>
<td>5.18</td>
<td>99.8</td>
</tr>
<tr>
<td>Air</td>
<td>0.00129</td>
<td>0.331</td>
<td>0.0004</td>
</tr>
<tr>
<td>Water</td>
<td>1.0</td>
<td>1.49</td>
<td>1.49</td>
</tr>
<tr>
<td>Ice</td>
<td>0.9</td>
<td>3.98</td>
<td>3.6</td>
</tr>
<tr>
<td>Teflon</td>
<td>2.2</td>
<td>1.35</td>
<td>3.0</td>
</tr>
<tr>
<td>PMMA</td>
<td>1.18</td>
<td>2.67</td>
<td>3.2</td>
</tr>
<tr>
<td>Quartz (natural)</td>
<td>2.65</td>
<td>5.73</td>
<td>15.2</td>
</tr>
<tr>
<td>WC</td>
<td>10-15</td>
<td>6.66</td>
<td>67-99</td>
</tr>
<tr>
<td>BaC</td>
<td>2.52</td>
<td>14.14</td>
<td>35.6</td>
</tr>
<tr>
<td>TiB(_3)</td>
<td>4.52</td>
<td>10.85</td>
<td>49.0</td>
</tr>
</tbody>
</table>

Data from ASM Metals Handbook, 9th ed., Vol 9, American Society of Metals, 1984
Here, $Z$ has the unit [kg m$^{-2}$ s$^{-1}$]. For several materials values of $Z$, as calculated from equation (2.14), are given in Table IV.

Reflection and refraction of shock waves occur due to mismatches in impedance of different materials. In the P-u plane, the pressure increase of a shock wave must lie on the Hugoniot curve. Similarly a pressure decrease (rarefaction) must lie on an isentrope passing through the initial state. Interface continuity corresponds to the intersection of two such curves. Curves of positive slope correspond to waves propagating in the positive x-direction, while reflection characteristics have negative slopes and correspond to negative-going waves.

The reflection characteristic is simply the mirror image of the curve with positive slope, taken in a vertical line through the appropriate initial state [6]. Considering negligible entropy changes (solids and liquids at not too high shock wave pressure), the isentrope differs very little from the Hugoniot, and the principal Hugoniot may be used to approximate all Hugoniot curves and isentropes in the P-u plane [1].

**Example 1: Transmission of a shock wave into a medium of higher shock impedance**

The solution in the P-u plane and the wave profiles before and after the interaction are shown in Fig. 5. An incident plane shock $S_i$ of pressure $P_i$ and particle velocity $u_i$ moves into a medium L (left) of relatively low shock impedance and transforms this medium from pressure $P_0$ ($<P_i$) and zero particle velocity to the state ($P_1, u_1$). The slope of the straight line connecting the state (0,0) to ($P_1, u_1$) is seen to be the shock impedance $\rho_0 U_i$. When the incident shock encounters material R (right) of higher relative shock impedance, $\rho_{0R} U_i > \rho_0 U_i$, a transmitted shock $S_t$ moves into medium R, transforming it from the undisturbed state (0,0) to state ($P_2, u_2$). Reflected back into medium L, which is now at state ($P_1, u_1$) is a reflected shock $S_R$ which reduces the particle velocity to $u_2$ and increases the pressure to $P_2$. As an example, a 24 GPa shock in aluminum is transmitted into iron as a 34 GPa shock while a 10 GPa shock is reflected back into the aluminum.

![Figure 5](image.png)

Figure 5. Transmission of a plane shock wave into a material of higher impedance. The figure shows the solution in the P-u plane and the wave profiles before and after interaction [1].
Example 2: Transmission of a shock wave into a medium of lower shock impedance

The solution in the P-u plane and the wave profiles before and after the interaction are shown in Fig. 6. In this case, the amplitude of the transmitted shock $S_t$ is less than that of the incident shock $S_i$. A rarefaction $R_r$ is reflected back into material $L$, thereby reducing the pressure to $P_2$ and increasing the particle velocity to $u_2$. Here, the reflection characteristic $R_r$ is a release wave (following the isentrope) since the pressure is reduced by the interaction. For example a 24 GPa shock in aluminum is transmitted into polyethylene (PE) as a 9.5 GPa shock while a 14.5 GPa rarefaction wave is reflected.

![P-u diagram showing transmission of shock wave](image)

Figure 6. Transmission of a plane shock wave into a material of lower impedance [1].

Example 3: Shock wave induced in a medium by a detonation wave

Figure 7 shows a P-u diagram with Hugoniot curves for a variety of materials, and reflection characteristics for several explosives. The dots on the reflection characteristics indicate the steady, so called Chapman-Jouget, detonation pressure and particle velocity. The intersections of material Hugoniots with the explosive reflection characteristics give the shock-strengths produced in materials by normally incident detonation waves. For example, a plane detonation wave in TNT normally incident on an aluminum interface produces a shock pressure of about 24 GPa at the interface. Since the C-J pressure is less than this, a shock wave is reflected back into the explosive gases. On the other hand, in water TNT produces a shock pressure of about 13 GPa, which is lower than the C-J pressure, and a rarefaction wave is reflected.

Table V: Interface pressures for normal and grazing detonation of Composition B explosive in contact with various materials [1].

<table>
<thead>
<tr>
<th>Material</th>
<th>Shock Pressure [GPa]</th>
<th>Shock Pressure [GPa]</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Normal</td>
<td>Grazing</td>
</tr>
<tr>
<td>Copper</td>
<td>48.6</td>
<td>20.5</td>
</tr>
<tr>
<td>Iron</td>
<td>47.5</td>
<td>19.6</td>
</tr>
<tr>
<td>Aluminum</td>
<td>36.0</td>
<td>18.9</td>
</tr>
<tr>
<td>PMMA (Plexiglas)</td>
<td>22.0</td>
<td>10.5</td>
</tr>
<tr>
<td>Water</td>
<td>19.5</td>
<td>12.1</td>
</tr>
</tbody>
</table>
In many shock compaction, hardening and welding operations of materials the incident detonation wave is not normal but parallel to the material surface. This grazing detonation wave produces a lower shock-strength in the material compared to normal incidence, as can be seen in Table V.

![Graph showing shock wave pressure induced in various materials by normally incident plane detonation waves](image)

**Figure 7.** Shock wave pressure induced in various materials by normally incident plane detonation waves [1].

**Example 4: Interaction of shock wave with a free surface**

This is the limit of example 2, and corresponds to the impedance of material R being vanishingly small (air). When a shock wave encounters a free surface, the material is suddenly free to expand to zero (atmospheric) pressure by means of a rarefaction wave, as shown in Fig. 8. The incident shock had initially accelerated the particles to a velocity $u_1$, and upon expansion they are further accelerated by an amount nearly equal to $u_1$. Thus, for materials of high relative density, the free surface velocity $u_R$ equals approximately $2u_1$, and the pressure at the surface remains zero. This is the basis for experimentally obtaining the particle velocity in many Hugoniot measurements [6].

![Diagram of shock wave interaction with a free surface](image)

**Figure 8.** Interaction of a plane shock wave with a free surface [1].
2.3 SHOCK COMPACTATION OF POWDERS

A powder can be considered as a composite material since it is a mixture of a solid and a gas. The solid phase consists of many individual particles, usually with different forms and a distribution of sizes, embedded in a continuous gas phase. The density of a (ceramic or metallic) powder can be varied over a wide range, typically between 30 and 80 percent of theoretical maximum density (TMD) of the solid. This is a complicating factor, since the physical properties of a powder are a function of the relative density. While the bulk modulus in solids ranges from about 1 to about 10^3 GPa, that of a powder can be as low as 1 MPa [7]. Consequently the sound velocity of a powder is very low compared to the solid phase, as can be seen in Table II. This means that the shock impedance of a powder will be very low and it will be very difficult to introduce a high shock wave pressure in it. The shock wave velocity in a powder appears to be more strongly related to the properties of the powder assembly than it is to the properties of the bulk material being compacted. One of the most influencing factors appears to be the starting density of the assembly, which is related to the coordination number and shape of the particles, the particle size and the size distribution.

Due to the intrinsic heterogeneous nature of a powder and the short time span of the shock compression process, a full understanding of the extremely complex nature of events occurring on a particulate scale has not been obtained so far. Also the large number of variables that control the process is a complicating factor. One of the difficulties in attempting to understand the particulate nature of the shock compaction process has been the inability to monitor it on a particulate scale. On this scale the powder structure cannot be treated as a continuum under shock pressures. Nevertheless, the shock compaction process is generally described by macroscopic parameters like the measured powder density, shock wave velocity and particle velocity. Since it is usually assumed that the thermodynamic equilibrium state is achieved in the shock compressed matter behind the shock front, also the jump relations are applicable for shock waves in powders.

2.3.1 Compaction mechanisms

As was shown earlier, behind the shock front of a shock wave, the medium, here a powder, is transferred to another state with a higher pressure, density and particle velocity. This means that the compaction process of the powder must occur within the very short shock rise time of the shock wave. Pressure measurements performed during compaction experiments have shown that the rise time of shock waves in powders is of the order of 10 to 100 ns [8]. This means that the width of the shock front of a shock wave which travels with a velocity of 2 km/s (=2 mm/μs) is of the order of 20 to 200 μm. For comparison, in solids the shock rise time is of the order of 10 ps and the shock wave velocity is several kilometers per second, resulting in a width of the shock front of the order of 100 nm. Thus compared to solids, the shock compaction zone in a powder, as shown in Figure 9, is composed of a zone of significant width in which the powder structure is transformed into a denser one, or ultimately into a solid, under the action of a pressure pulse from the explosive energy source. Through post-compaction microscopic examination of the compacted powder it is possible to reconstruct the sequence of particulate events that have occurred.
Within the compaction zone several investigators [9, 10, 11, 12] have identified the presence of three mechanistic regions of densification or void elimination, which are also shown in Fig. 9. This is similar to densification behavior observed in the static pressing of powders [13], see Fig. 10.
These three stages of compaction are not totally sequential but may overlap each other and, under certain circumstances, may even be absent, e.g., with a powder like lead, stages one and three are of little significance, whilst with hard powders such as ceramics stage two is of minor importance [14].

The first region is one in which the arriving shock front imparts the initial velocity to the powder particles quickly rearranging them to the most favorable position for the least resistance for further movement; this occurs within the first one or two particle diameters of the compaction zone. The highest relative velocity between particles is achieved in this region with significant densification occurring at relatively low pressures. There is minimal particle deformation and heat generation with little or no potential for interparticle bonding. In this stage the void content will be reduced up to 30-40 percent by volume at which the particles form a rigid matrix.

As the pressure increases, the densification passes into the second region, particle yield. The point contacts between particles rapidly grow into areas of contact which increase in size as densification continues. The particles must yield and begin to exhibit significant deformation with increasing consolidation. This is the region in which frictional and deformational heat is generated in the outer layers of the powder particles. This creates localized thermal softening or even melting of the particles surfaces. As a result most of the flow of material into the void spaces, takes place in these thermally softened outer surface layers and not in the bulk volume of the particles. The width of this region is considerably greater than the first region, and the largest amount of deformational strain is introduced into the powder particles here [11]. Further, the relative velocity between the particles continually decreases through the width of the region until all of the particles are moving at a uniform mass or particle velocity at the beginning of the third region.

The third and final region is one in which further densification occurs through particle fracture and/or bulk deformation. In this stage very high pressures are required with little increase in void elimination realized. The deformation is no longer dependent on localized material flow, but occurs through the bulk of the compacted material.

Continued densification in this region results in particle fracture. When possible, densification is to be avoided in the latter region as it is normally accompanied by significant cracking and may even lead to a loss or reversal of densification.

Restacking and rearrangement of particles is an universal densification mechanism occurring in all powders during compaction. However, for powders that have a high starting density, 60-70%TMD obtained for example by a static precompaction or optimized particle size distribution, further densification occurs directly in the other two regions.

In which region main densification takes place, depends largely on the mechanical properties of the material during the stress state, strain-rate and temperature (distribution) present. For materials which possess high ductility, as in metals like copper and aluminum, large plastic strains are possible, permitting void collapse. The plastic strain concentrates on the particle surface. This is an effective way to reduce the void volume within a powder, thus this region is where the main densification takes place.

On the other hand, strong covalently bonded materials like some ceramics do not possess much ductility. All material strain is elastic, and upon further straining the material will fracture without much plastic deformation. So, main densification, apart from particle rearrangement, will take place in region three. Most materials are somewhere in between of both extremes and densification will occur in all regions. For example, the ceramics with an ionic type of bonding, like MgO and Al₂O₃, show considerable plastic deformation during
shock compaction. This is indicated by a considerable broadening of the x-ray diffraction lines compared to those of the starting material [15, 16]. From the measured microstrain they calculated that the stored strain energy resulting from explosive shocking can reach values equal to the total surface energies of these powders. Another reason for the broadening of x-ray diffraction lines is a decrease in crystallite size (coherently diffracting domains). Through specialized computational procedures the crystallite size and lattice strain contributions of line broadening can be separated because of their different diffraction angle dependencies. It was found that in the case of ionic materials, microstrain was increased, while in the case of covalent materials the main effect was a decrease in crystallite size [17]. For TiN powder, judging from its electronegativity a material with intermediate properties between ionic and covalent, Sawaoka et al. [18] found the main effect of shock treatment was an increase in microstrain similar to ionic materials.

2.3.2 Powder Hugoniot

The shock wave media can be divided in solids, liquids, gases and plasma’s. Each of these media can consist of any material or mixture of materials. In this paragraph we restrict ourselves to solids. The shock wave behavior of this medium (described with a Hugoniot) is strongly influenced by its porosity and whether the medium is a porous solid material or a powder (assembly of loose particles). As a starting point the Hugoniot of the non-porous solid is described. Then porosity is introduced in the material, first as closed porosity, creating a porous material, then the material is introduced in a particulate form, creating a powder. In this way, the relation and differences between the Hugoniot’s of the material in different forms will be demonstrated.

A. Hugoniot of a dense solid

For each initial condition the Hugoniot of a material can be determined. The principal Hugoniot is obtained when the standard conditions are taken as the initial condition. Steady plane shock waves are generally introduced by the perpendicular impact of a flat projectile accelerated by a gas-gun. A gas-gun is a vacuum tube in which a projectile is accelerated by the sudden expansion of a precompacted light gas (Helium or Hydrogen). In the plane shock wave that results from the impact of the projectile (flyer) with the target (subject), the acceleration and strain of the materials occurs in only one direction, which is parallel to the shock wave velocity, see Fig. 2. The uni-axial strain creates a three dimensional stress state within the material. This stress state can be described as a hydrodynamic compressive stress on which a deviatoric stress is superimposed.

When the shock pressure is very high, the deviatoric stress will exceed the shear strength of the material by far and the material will flow (plastic deformation). From the moment the material starts to flow, the Hugoniot will be parallel to the hydrostatic compression curve of the material, with a constant offset as long as the shear stress is not a function of strain or pressure. This is the hydrodynamic approximation that was adopted in chapter 2.2.

When the shock pressure is not so high, the shear strength of the material will prevent it from flowing and an elastic response is obtained. The shock wave pressure (uniaxial strain) at which the material starts to flow is designated as the Hugoniot Elastic Limit (HEL), see Table VI. It is clear that the HEL of a material depends on its yield strength as is obtained from uniaxial stress experiments [19]. In intermediate shock conditions the shock wave will be divided in a fast running elastic precursor, that brings the material to the HEL stress condition,
Table VI: Hugoniot elastic limits of materials.

<table>
<thead>
<tr>
<th>Material</th>
<th>Hugoniot elastic limit [GPa]</th>
</tr>
</thead>
<tbody>
<tr>
<td>B₄C</td>
<td>19</td>
</tr>
<tr>
<td>ZrO₂</td>
<td>16</td>
</tr>
<tr>
<td>SiC</td>
<td>15.5</td>
</tr>
<tr>
<td>AlN</td>
<td>8</td>
</tr>
<tr>
<td>TiB₂</td>
<td>7</td>
</tr>
<tr>
<td>Al₂O₃</td>
<td>6</td>
</tr>
<tr>
<td>Al₄ and W</td>
<td>0.5 and 4</td>
</tr>
</tbody>
</table>

Data from D. Grady, Metals Materials and Processes, 3(4), pp. 233-42 (1992)
a) S.S. Batsanov, in Effects of explosions on materials, Springer-Verlag, New York, 1994, pp. 26

and a slower plastic shock wave bringing the material to its final shock state. This can be made clear by looking at the Hugoniot of a material with considerable strength in the P-V plane.

As an example the principal Hugoniot of boroncarbide (B₄C) is given in Fig. 11. Boroncarbide is a strong covalent bonded ceramic with one of the highest HEL’s recorded, see Table VI. Although it has a high HEL, it loses its strength at further compression (strain softening) as can be seen from the reducing offset from the materials hydrostatic compression curve (hydrostat), which is also indicated in Fig. 11. From equation (2.5) it is known that the shock wave velocity is given by the slope of its Rayleigh line in the P-V plane. For pressures up to the HEL this slope is constant and steep, indicating that the elastic wave has a high velocity in the material. The initial condition for any plastic wave will be the HEL of the material. The Rayleigh line for plastic shock waves is the line connecting the HEL with the Hugoniot point corresponding to the final shock pressure. The slope of the latter is smaller than that of the elastic waves indicating a lower speed. The elastic shock is outrunning the plastic shock wave. At very high pressures the plastic shock will have a higher velocity than the elastic shock wave and only one shock will travel through the material.

![Figure 11. Principal Hugoniot and hydrostat of solid B₄C in the P-V plane.](image)

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B. Hugoniot's of porous solids

The introduction of porosity influences the mechanical properties of the material. The material loses its rigidity as well as strength and the density will be reduced. The amount of porosity in porous materials can vary widely from almost no pores to foams with up to 95% of pore volume. The influence of porosity on the Hugoniot of a material is demonstrated in Fig. 12, in which, qualitatively, Hugoniot's of B₄C with different amounts of porosity are shown. It is shown that the Hugoniot shifts towards larger specific volumes, and the HEL of the material and its slope in the P-V plane are reduced with increased porosity. Brar et. al. in [20] compared measured and calculated HEL values for B₄C samples with different amounts of porosity. The calculated values, obtained with the assumption that the volume change between the initial state and the HEL state is the same for the fully dense specimen and for any porous specimen, show good agreement with the measured values. With this assumption also the decrease in propagation velocity of the elastic precursor with increasing porosity is clear. This velocity is given by the slope of the elastic part of the Hugoniot, and here a decreasing HEL is divided by a constant change in specific volume. The decrease in HEL in porous material is caused by a reduction in strength of the material. As can be seen in Fig. 12, the reduction of the HEL is rather strong with increasing porosity. This is probably the main reason why so many different HEL values for one material can be found in the literature. In ceramics, pore free material is hard to obtain without sintering aids. Specially the ones with the highest HEL values are hard to sinter to full density due to their covalent type of bonding.

At shock wave pressure above the HEL, two shock waves will travel through the specimen. The first is the elastic precursor traveling with its porosity dependent velocity, bringing the material to the HEL state, followed by a second or plastic shock wave traveling with a pressure dependent velocity, bringing the material to its final shock state. In the latter shock wave plastic flow and rearrangement of fragments due to micro-cracking will reduce the pore volume in an irreversible manner. The greater volume change, compared to the fully dense material at the same shock strength, results in a larger change in internal energy (equation 2.6). This means that the porous material obtains a higher temperature and hence, due to its thermal expansion, a larger specific volume.

This is the reason why the Hugoniot of the porous material always remains at the right of the Hugoniot of the fully dense material in the P-V plane, as is shown in Fig. 12.

![Figure 12. Qualitative representation of Hugonoiots of porous B₄C at various starting densities.](image-url)
C. Hugoniot's of powders

From the Hugoniot of a porous material to a powder Hugoniot is rather straightforward. The amount of porosity (relative pore volume) within a powder can vary as widely as in porous materials. In practice, however, a relative density between 30 and 80 percent of theoretical maximum density (TMD) is observed as starting density for powders. In contrast to a porous material, a powder generally does not possess strength compared to the shock wave pressure, since the individual particles can slide over each other. This means that the Hugoniot of a powder does not show an elastic part (HEL). Since the compressibility of a powder is very high compared to that of the solid or porous material, sound and shock wave velocities are rather low, see Table II. In Fig. 13 the Hugoniot of B$_4$C powder with a starting density of 65 \%TMD is given. The low shock wave velocities are clear if one compares the slopes of Rayleigh lines of a shock wave in the solid and powder material. Due to the high (irreversible) compressibility, see equation (2.7), the material obtains a rather high particle velocity, while the shock wave pressure is modest. In Fig. 14 Hugoniot's of powders are shown in the $U_s$-$u_p$-plane.

From the intercept with the $u_p=0$ line, it can be seen that the bulk sound velocity of a powder is very low. While the linear relation between $U_s$ and $u_p$, as observed in the Hugoniot of solids (equation 2.10), for powders is lost.

For a given shock wave velocity $U_s$, the particle velocity is much higher in a powder. The slope of the line connecting the origin with a point on the Hugoniot in the $P$-$u_p$ plane, represents the shock impedance of the powder (see Fig. 3c). This slope and hence the shock impedance is much smaller for a powder compared to the solid.

![Diagram](image_url)

Figure 13. Qualitative representation of B$_4$C powder Hugoniot (65 \%TMD starting density).
2.3.3 Powder Hugoniot models

The determination of a Hugoniot requires many experiments. In the case of powders a different Hugoniot should be determined for each starting density. It is therefore not surprising that models have been developed that relate the Hugoniot of a powder to the Hugoniot of the solid material. Many of these models make use of the simple, linear empirical relation between $U_S$ and $u_p$ obtained for most solids (equation 2.10). When no Hugoniot for the solid is available, models are available that can calculate the linear shock wave equation of state for solids for other material properties like the Grünenisen coefficient, the bond dissociation energy, and atomic lattice distances [21, 22].

The numerous studies and modeling of shock compression of metal and ceramic powders have shown that, within the assumptions made for the jump-relations, it is possible to define shock conditions like for example pressure, specific volume and particle velocity in a consistent manner for powders in spite of their obvious heterogeneity. Local conditions on the scale of a particle diameter are certainly heterogeneous, but with the present knowledge it is not possible to define these conditions quantitatively. Because of the unknown relationships between bulk and local conditions, it is best to recognize that the term "pressure" specifies a macroscopic condition and the use of the terminology "mean bulk temperature" is to be preferred to describe macroscopic values of temperature.

![Figure 14. Measured Hugoniots ($U_S$-$u_p$ plane) of iron at various starting densities.](from R.A. Graham, High Pressure Science and Technology 1993, pp. 3-12).
A. Plate-gap model

In the early sixties a very simple one-dimensional model was developed by Thouvenin [23]. A schematic presentation of the model is shown in Fig. 15. Here, the powder is assumed to be an array of plates of the same dimensions (d) and equidistant leading to equal gaps (l) between the plates. The fraction of gaps, \( \lambda = l / (l + d) \), equals the porosity of the powder, which is determined from \( \lambda = 1 - (\rho_0 / \rho_s) \). Here, \( \rho_0 \) is the density of the powder, and \( \rho_s \) is the density of the solid (at theoretical maximal density).

![Figure 15. Schematic representation of a shock wave propagating a powder according to the plate-gap model.](image)

A shock wave in this medium must travel for fraction 1-\( \lambda \) through the solid plates, which is assumed to occur with the same speed as in the solid (\( U_s = C + u_p \)). The fraction it travels through the gaps is assumed to proceed with the free surface velocity of the material. This free surface velocity was considered to be \( u_p \) by Touvenin, but later adjusted to twice the particle velocity of the solid phase (2\( u_p \)) by Sawaoka [24]. The shock wave velocity of the powder, \( U \), can be calculated by the relationship:

\[
1 / U = (1 - \lambda) / U_s + \lambda / 2 u_p, \tag{2.16}
\]

where \( U_s \) and \( u_p \) designate the shock parameters of the solid. The average particle velocity within the powder, \( u \), can be determined as:

\[
1 / u = (1 - \lambda) / U_s + \lambda / 2 u_p. \tag{2.17}
\]

Rearranging terms in equations (2.16) and (2.17) gives,

\[
U = 2 u_p U_s / (2 u_p (1 - \lambda) + \lambda U_s), \tag{2.18}
\]

and

\[
u = 2 u_p / (2 - \lambda). \tag{2.19}\]
Figure 16 shows that this simple model gives surprisingly good results. It incorporates the large influence of the starting density on the Hugoniot of a powder, relates the powder Hugoniot to the (linear) Hugoniot of the solid phase, gives the powder a low shock impedance and approaches the Hugoniot of the solid at very high pressures (high $u_p$).

**B. Particle deformation model**

Equation (2.16) resembles the outcome of a model developed by Booger [25], which is based upon the plastic deformation of touching spherical particles:

$$\frac{1}{U} = \frac{1}{U_s} + \frac{(\Delta r_0 - \Delta l)}{(1 - \Delta l)(1 - 2u_p)}$$ (2.20)

Here, $\Delta r_0$ and $\Delta l$ are dimensionless parameters that are a measure of the deformation of the particles. $\Delta r_0$ is the deformation of the spheres in the shock wave and $\Delta l$ is the deformation prior to shock loading according to their precompaction in order to account for powder densities above 50% of theoretical maximum. The deformation of the particles due to the shock wave ($\Delta r = \Delta r_0 - \Delta l$), introduces a delay time for shock propagation, since the deformation is assumed to occur with a velocity of twice the particle velocity of the solid phase. The amount of deformation (value of $\Delta r$) depends on the stress (pressure) of the shock wave. This relationship appears to be an assembly property and is nearly independent of the powder material; it is mainly a function of the starting density of the powder. Therefore with this model the unknown Hugoniot of a powder with a certain relative density can be calculated from its solid Hugoniot and from the known Hugoniot of another material with the same relative density.
An interesting aspect of this model is that it attempts to relate the macroscopic shock wave parameters of the powder to processes at the particle level. On the other hand it is unclear why such important aspects, like starting density of the powder and the rearrangement of particles, are so ill defined and excluded, respectively. The observed general increase in deformation or delay time with decreasing relative powder density is not because the particle deformation is material independent or an assembly property, but because particle rearrangement is the general compaction mechanism in powders. This model is, however, purely based on particle deformation. Examples given for more ductile materials like metals and polymers would therefore have been more appropriate. The examples given are, however, for ceramics which generally have a brittle mechanical behavior and micro-cracking together with the rearrangement of particle fragments is the main compaction mechanism.

Another drawback of the model is the requirement of reference Hugoniot data, which could be difficult to obtain and limiting the application of the model to the pressure range of the reference Hugoniot data. The reference Hugoniot data with densities above 80 %TMD in [25] are not from powders, but from porous materials.

C. Mie-Grüneisen method

Some models make use of the Mie-Grüneisen equation of state (equation 2.13) to develop the Hugoniot of a powder from the Hugoniot of the solid material. \( P \) and \( E \), which are the pressure and internal energy for the porous material, are related to the solid Hugoniot pressure \( (P_H) \) and internal energy \( (E_H) \) at the same specific volume \( V \):

\[
P = P_H + \Gamma (E - E_H)/V,
\]

(2.21)

where \( \Gamma \) is the Grüneisen parameter at the specific volume \( V \).

The ratio \( \Gamma/V \) is assumed to be a constant:

\[
\Gamma/V = \Gamma_0/V_0 = \text{constant}.
\]

(2.22)

This approximation is often employed in shock data analysis and is usually reasonable [26]. This means that the \( (P, V, E) \) state of a material can be related to another reference state, such as a point on the Hugoniot. \( \Gamma_0 \) and \( V_0 \) are the Grüneisen parameter (equation 2.12) and specific volume at zero pressure, respectively. From the Rankine-Hugoniot equations (2.4-2.6) and the equation of state of the solid material (equation 2.10), the following relationship can be derived:

\[
P_H = C^2 (V_0 - V)/(V_0 - s (V_0 - V))^2.
\]

(2.23)

This equation describes the solid \( (P,V) \)-Hugoniot. Using equations (2.21) and (2.22) and again the Rankine-Hugoniot relations, we can obtain the shock pressure \( P \), shock velocity \( U_s \), and the particle velocity \( u_p \) for the powder material:

\[
P = P_H [2 - \rho_0 \Gamma_0 (V_0 - V)]/[2 - \rho_0 \Gamma_0 (V_00 - V)],
\]

(2.24)

\[
U_s = V_{00} [ (P - P_0)/(V_{00} - V)]^{1/4},
\]

(2.25)

\[
u_p = [(P - P_0) (V_{00} - V)]^{1/4},
\]

(2.26)
in which the starting specific volume of the powder is designated $V_{00}$, in order to distinguish it from the specific volume of the solid at zero pressure $V_0$.

Also Dijken [27] makes use of the Mie-Grüneisen equation of state in order to calculate the extra increase in internal energy in a shock compacted powder compared to the solid phase. One of his assumptions is that the compaction of a powder occurs at zero pressure, quasi-statically and without any energy consumption up to full solid density. The assumptions restrict his model to soft, ductile materials like Al, Cu, and Fe. For these materials the model indeed is shown to work well.

D. P-α model

In the P-α model, developed by Herrmann in 1968 [28], $\alpha$ is defined as the ratio of the specific volume of the porous (and powder) material, $V$, at a given stress and energy state to the specific volume of the corresponding solid material at the same stress and energy, $V_s$:

$$\alpha = \frac{V}{V_s}$$

(2.27)

The parameter $\alpha$ allows a convenient separation of the volume change due to compression of the material from that due to pore collapse. In the model it is assumed that the function that relates pressure to specific volume and specific internal energy for the material in the porous state is the same as that which relates these quantities for the material in its nonporous state.

$$P = f(V_s, E) = f(V/\alpha, E)$$

(2.28)

The P-α model gives the pressure in the porous material as a function of specific volume, specific internal energy, and porosity. The form of this function is determined by the pressure-specific volume-specific internal energy (PVE) equation of state for the solid material, which is calculated using the Mie-Grüneisen method.

This description of the dynamic compaction behavior is not complete, since the porosity $\alpha$ appears in the PVE equation, which must therefore be supplemented by a pore-collapse relation to describe the behavior of $\alpha$. As an example, Fig. 17 shows the P-α relation obtained for powder with an starting density of 68 %TMD.

For this pore collapse relation some algebraic relation is fitted to an experimentally determined Hugoniot, of particular porosity, in the partially compacted region. Polynomial functions for the P(α)-relation are adequate for most porous materials. The P-α relation requires the definition of a stress point $P_\alpha$, which is the stress where compaction of the porous material to a voidless state is essentially complete. Graham later called this rather poorly defined parameter the crush strength of the powder material. Later, a dynamic model of pore collapse was developed by Carroll and Holt to incorporate rate-dependency [29], viscosity and work hardening [30].

The strength of this model is that it allows, in a simple mathematical form, a detailed description of the irreversible compaction at low pressures and that it reduces to the correct Hugoniot at high pressures [31]. Once the pore compaction curve is determined at one initial porosity, the model predicts the response at other initial porosities. The model is widely used in numerical work on shock propagation in porous media. Drawback is that it , as any empirical model, needs experimental results. To predict the P-α relation mechanistic models are needed based on the actual internal mechanisms of particle deformation and fracture.
2.3.4 Powder consolidation

The general behavior of powder Hugoniot's compared to the solid behavior is shown in Fig. 18. Graham [32] pointed out that the "crush-up" to solid density for a metal is typically significantly less than for a ceramic. The crush strength varies in metals from 0.6 GPa for a soft aluminum alloy to 6.5 GPa for tungsten, while this value is thought to vary from 5 to 20 GPa for ceramics, depending on the initial sample density and on materials properties [33]. For materials like ceramics in which the crush strength is high, it is to be expected that the crush-up behavior will dominate the compression of typical porous ceramic compacts for many shock-loading processes.

Figure 18. Pressure-density plot showing difference in "crush up strength" between metals and ceramics [32].
The P-α model is very useful for modeling the powder crush-up behavior. For high pressures compared to the materials crush strength, the Plate-gap model, in which the powder is compressed to solid density at zero shock pressure can also provide a basis for modeling shock compaction.

The disappearance of voids in a powder, is not synonymous with bonding or welding of particles. An understanding of bonding requires new concepts. Bonding of particles can be attributed to a variety of mechanisms such as mechanical interlocking, electrostatic forces, and interfacial forces [31]. But here the term “bonding” is used in a monolithic material to mean the bonding that involves the transfer of atoms across contact interfaces and the reconstruction of their bonds. There are, in this context, two important requirements for the process of bonding to take place:

- transport of atoms, and
- reduction of surface energy resulting from the formation of interfacial bonds.

The first process is typically controlled by temperature, but the presence of defects such as vacancies and dislocations will substantially augment it. The second requirement is sensitive to the nature of chemical bonding of atoms. Therefore, the joining of covalently bonded materials such as diamond and SiC is difficult because of their special requirements in atomic spacing and bond angles. By contrast, the rearrangement of metallic bonds is not so restricted as that of covalent bonds. The conditions for ionic materials lie between those of metals and covalent materials. With metals it is known that if their surfaces are clean and free of foreign atoms, light contact is sufficient to establish bonds even at room temperatures. But with covalent materials high temperatures are required to disrupt strong atomic bonds and initiate mass diffusion.

Since powders are normally covered with layers of oxides and other contaminants, the formation of bonds between particles requires high temperatures or mechanical removal of the contaminant layers by fracture or plastic deformation. This is the reason that there exists generally speaking two ways in which particle bonding or consolidation is considered: plastic deformation, and melting.

A. Plastic deformation

In roll welding of metals clean surfaces are created during the expansion of the surface during the plastic deformation accompanying the decrease in layer thickness of the metals. For bonding to occur in roll welding of metals, typically surface expansions of over 100 % are required. This is much more plastic deformation than calculations show occurs due to pore collapse in shock compaction of powders. Thus, more intensely heterogeneous, localized deformations seem to be required to explain bonding under shock compression.

Morris [34] proposed four possible mechanisms of preferential surface deformation for metals, shown schematically in Fig. 19. They are: (1) jetting, (2) jet trapping, (3) frictional sliding, and (4) point deformation. Jetting is a phenomenon that occurs due to momentum conservation during the oblique impact of two materials. A small amount of material from the surface of the two materials is thrown away in the form of an escaping jet. This is the mechanism that is responsible for the cleaning of the surfaces in explosive welding. The jet has a very high velocity since it precedes the contact point of the impacting materials. In powders this jet does not have a long traveling distance, since it will meet powder particles on its way. Here the jet will get trapped and loose its, so called, micro-kinetic energy [35]. It is
clear that at the contact points between the particles locally high stresses occur. Here, the material will deform or even break, while the sliding of the particles or fragments under the applied stress will generate high stresses in the surface areas due to friction. However, these surface deformation mechanisms have not been related to bonding in a quantitative form. Since plastic deformation only occurs at pressures beyond the Hugoniot elastic limit, a simple requirement for it would be a shock wave pressure above the HEL of the material [36]. It is however likely that due to the many contact points within a powder, this pressure will locally already be surpassed at much lower shock wave pressures.

Another indication for the resistance of a material against deformation due to pressure is its hardness. The micro-indentation made by a diamond crystal (Hardness Vickers or Knoop) produces locally a high pressure, while this region is confined by the bulk of the material. This stress situation is somewhat analogous to that observed during shock compaction of materials. It is known that very high compressive stresses can produce significant plastic deformation resulting in high dislocation densities in otherwise brittle ceramic materials [37].

Experimentally an “engineering correlation” was found between the hardness of a material and the shock pressure required for its consolidation [38]. Both metals and ceramics were shown to lay on a single line, as is shown in Fig. 20. Also correlations between the required shock pressure and the materials yield strength or cohesive energy density have been published [39]. Determination of the required pressure by the HEL or hardness of the material does not incorporate the influence that porosity has on the consolidation process. To be able to do this Ferreira and Meyers [39] have developed a model based on the energy required for: void collapse, melting and the generation and movement of dislocations. This total energy was equalized to the shock energy or increase in internal energy of the material (equation 2.6). This makes it possible to incorporate the starting density of the powder \( \rho_0 \) \( (= 1/V_0) \). The required pressure for shock compaction of different powder materials was calculated at several distentions \( \alpha = V_0/\rho_0 \), with the hardness ranging from 1.2 GPa to 98 GPa. The calculated pressure-distention-hardness relations are shown in Fig. 21. These results show that
Figure 20. "Engineering" correlation between hardness and pressure required for shock consolidation [38].

Figure 21. Pressure required for shock consolidation versus hardness for various distentions [39].

as porosity, and hence distention, increases, a lower shock wave pressure is required to consolidate the material. Based on the analogy with explosive welding of metal plates, Shertser [40] followed an approach based on the idea that microkinetic energy is the main parameter determining the possibility for bonding between particles. He proposed an expression for the minimum pressure $P_b$ to obtain bonding, taking into account not only the hardness of the material and its distention $\alpha$, but also the influence of an oxygen layer on the particles surfaces.

$$P_b = k^2 H_0/(\alpha-1),$$

(2.29)

where $k$ depends on oxide layer thickness $\delta_o$. 

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Fig. 22 shows schematically how the surface of a normal solid looks like. An oxygen layer has formed as a result of the interaction with air, and normally also some contaminants like grease adhere at the surface. For powders, which have a much larger surface area compared to solid materials, this region is extremely important since this is where the inter-particle bonding must take place. It is therefore strange that this is the only model that incorporates the existence of the oxygen layer and the role its thickness plays in the required shock pressure. Later, Shertser [41] proposed a mechanism responsible for cleaning the particles surfaces during shock compaction. Due to the high pressure that occurs when a particle impacts another particle the surface starts to flow hydrodynamically. Under influence of its surface tension, the oxygen layer flows to form small spheres which have less surface area. This provides a fresh clean surface in intense contact, which will bond like in the roll welding process.

![Diagram of films on a metal surface](image_url)

Figure 22. Schematic view of films on a metal surface (not to scale).
[from E. Rabinowicz, Friction and wear of materials, John Wiley & Sons, Inc., New York, p. 82]

![Diagram of energy comparison](image_url)

Figure 23. Comparison of the dissipated energies by a shock wave in solid versus porous material [1].
B. Melting and resolidification

From the jump-relation obtained by energy conservation (equation 2.6) the increase in internal energy of the shocked material can be determined. In case the material is shocked to a pressure $P$, the increase in internal energy is much more for a powder than for the solid, due to the much larger volume change in the former. This is qualitatively shown in Fig. 23. Furthermore, since the pressure release occurs along an isentrope, which lies close to the materials Hugoniot for solids, the solid looses much of its internal energy increase upon pressure release ($dE = PdV$). The powder, however, is compacted irreversibly and looses only a small fraction of its internal energy increase upon unloading.

Neglecting the initial pressure $P_0$ (normally 1 bar or $10^5$ Pa) compared to the shock wave pressure $P$ (in the order of tens of kbar or $10^9$ Pa), the increase in internal energy amounts to:

$$\Delta E = \frac{1}{2} P \Delta V.$$  \hfill (2.30)

Although this internal energy increase is used for different processes like defect generation (dislocations, vacancies, twinning) and the creation of fresh surfaces by fracture, by far most of the energy is used for heating the material.

Assuming all energy is used to heat the material, the upper bound for the temperature increase (assuming homogeneous temperature distribution) can be calculated by:

$$\Delta T = \Delta E/C_p,$$  \hfill (2.31)

in which $C_p$ is the materials average specific heat in the regime $T_0<T<T_m$, where $T_0$ denotes room temperature, and $T_m$ is the melting temperature of the material. In Fig. 4 and 24 the calculated increase in temperature is shown for solids and powders, respectively.

![Figure 24. The mean bulk temperature is strongly affected by the powder density. Most of the increase in temperature occurs within the lower pressure initial shock wave in the sample [32].](image.png)
Although it is clear that the temperature increase, at one shock wave pressure, in powders is much greater than in solids, for most metals and ceramics it is still insufficient for the complete melting of the material. Here again, a heterogeneous distribution of the dissipated energy is required. Most of the energy dissipating mechanisms occur at the surface areas of the particles (friction, micro-kinetic energy, void collapse), so it is likely that most of the energy will be dissipated there. Indeed, indications for melting of at least parts of shock compacted material has been found. In most cases the determination if melting and resolidification occurred is done microscopically on preserved samples after shock compaction. Frequently interparticle regions with a very fine dendritic structure and even amorphous regions are found [42]. These regions indicate that the particle surfaces have melted and subsequently cooled at a very high cooling rate. Graham et al. [43] used a direct measuring technique to proof shock-induced melting in powder compacts. An electrochemical cell was composed of powders. The electrolyte was a KCl-LiCl eutectic pressed at different starting densities. The cell remained inactive until the powder was melted either under shock pressure or release of pressure. Partial melting was clearly indicated in time-resolved electrochemical voltage measurements and the degree of melt was shown to be sensitive to the starting density of the powder which, together with the pressure of the initial shock wave, controls the increase in temperature.

Schwartz et al. [44] have developed a model in which surface melting is assumed a priori. The melted fraction is calculated based on the ratio of the energy required to melt a unit of mass of the material and the total dissipated energy behind the shock front. Then, the window of processing parameters is discussed in terms of the minimum melt fraction, and the minimum duration of the shock state, $t_d$, to assure resolidification of the melt before pressure release occurs. The upper bound for the mass fraction of melted material, $L_u$, is:

$$L_u = \Delta E/[C_p(T_m - T_0) - H_m],$$  \hspace{1cm} (2.32)

in which $H_m$ is the heat of fusion, and $T_0$ and $T_m$ are room temperature and the melting temperature, respectively. The lower bound, $L_d$, according to Vreeland et al. [45] is the melt fraction calculated under thermal equilibrium conditions when the input shock energy exceeds that required to form melt, and is given by:

$$L_d = (\Delta E - C_p(T_m - T_0))/ H_m$$ \hspace{1cm} (2.33)

Resolidification of the melt fraction, that is assumed to surround all particles, requires a minimum shock duration, $t_d$:

$$t_d > t_s + t_e.$$ \hspace{1cm} (2.34)

Here, $t_s$ is the time for solidification of melted layers and $t_e$ is the time to conduct the excess heat in the molten layer into the cooler interior of the particles.

Furthermore, there are several models that have attempted to account for thermal histories of heterogeneous energy deposition through the surface of the particles [46, 47]. None of those models was related to the question of consolidation. The maximum temperature achieved at the particle surfaces depends on the rate of energy deposition, and the rate of heat conduction.
into the interior of the particles. The rate of energy deposition is determined by the rise time of the shock wave, $\tau$, taken as:

$$\tau = \frac{2R}{U_s},$$  \hspace{1cm} (2.35)

where $R$ is the radius of the spherical particles, and $U_s$ is the shock wave velocity.

Gourdie [47] developed an energy deposition model and introduced an constant energy flux at the particle surface during the shock rise time:

$$F = f \frac{E}{\tau A},$$  \hspace{1cm} (2.36)

where $f$ is the fraction of energy deposited at the powder surface, $E$ is the specific energy behind the shock, and $A$ is the measured surface area per unit mass of the powder. Gourdie assumed $f$ to be close to 1, but later Vreeland et al. [45] calculated $f$ to be close to 0.5 from experimental results using melted fractions that they observed in recovered samples. A decrease in the shock rise time will allow less heat to be conducted away from the powder surface, and this will increase the interface temperature. In Fig. 25 a calculated temperature profile versus distance from the particle surface (depth) is given for a steel powder with an initial density of 3.8 g/cm$^3$ (48 %TMD) shock compacted at 4.8 GPa at different times.

![Figure 25. Result of calculations of the temperature distribution in a shocked iron powder particle at various times [W.H. Gourdie, Progress in Mat. Sci. 30, 39-80 (1986)].](image_url)

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Kondo [48] defined a skin around each particle with a mass fraction $\gamma$ defined by:

$$\gamma = 1 - (1 - \delta/R)^3 \frac{V_{00}}{V_0}$$  \hspace{1cm} (2.37)

where $\delta$ is the thickness of the skin, and $V_{00}$ and $V_0$ are the specific volumes of the powder and the solid at a specific pressure, respectively. The internal energy is represented as:

$$E^* = \gamma E_0 + (1 - \gamma) E_H$$  \hspace{1cm} (2.38)

in which $E^*$, $E_0$, and $E_H$ are the specific energy of the powder, the skin and the core, respectively. It is assumed in the skin model that the core is shock compressed like a solid without being influenced by the initial porous state. In Fig. 26 a schematic representation of the skin model is shown. It clearly demonstrates the inhomogeneous temperature distribution occurring in the powder compact during and directly after passing of the shock front.

### 2.4 STATIC VERSUS SHOCK COMPACTION

The first step in most material fabricating powder technologies, involves the quasi-static compaction of the starting powders. The so-called green form obtained this way is further processed by processes like sintering (for example liquid phase or reaction sintering, and hot isostatic pressing, HIP) or infiltration (for example by chemical vapor infiltration (CVI), or the capillary infiltration by a liquid). The success of these fabrication technologies depends largely on the density and homogeneity in density distribution of the powder compact obtained in the initial compaction process. Shock compaction of powders is not an exception and also here a static precompaction is the first processing step. The starting density of the powder obtained here determines largely the compaction behavior during the shock compaction and hence the quality of the resulting compact.

Another reason for discussing static compaction here, is to show the different phenomena that occur in shock wave compaction compared to static compaction.
The quasi-static and shock wave compaction are just the extremes of many different techniques that are applied to densify powders. Clyens and Johnson have given an overview of the different dynamic compaction techniques arranged by the strain rate that occurs in the compaction processes [14].

2.4.1 Static compaction

Of all possible methods used for static compaction, here only uniaxial compression is considered. This is done for two reasons: first, because it is probably the most simple way to generate pressure and second, because this is the generally applied method for the (pre)compaction of powders. In the uniaxial compression method, the powder is situated in a die, and an axial compressive stress is applied by a plunger. The latter is normally actuated by some hydraulic system. The plunger is moving very slowly into the die, so the mass or particle velocity of the powder is close to zero (quasi-static compaction). Figure 27 shows the compaction and pressure release behavior of two TiB$_2$ powders of different starting density in the P-$\rho$ plane [49]. With increasing density the resistance to compaction increases (decreasing compressibility of the powder). Since elastic waves transport the pressure with the speed of sound through the medium (Table I and II), the compressive stress is applied over the total volume of the powder sample. This means that there is mechanical equilibrium between the normal stress on the plunger and bottom of the powder (near the bottom of the die). In the ideal case this would lead to a homogeneous pressure distribution, and hence a homogeneous densification of the powder. However, inter-particle and particle-wall friction are responsible for a reduction in stress and density in the vertical direction and along the die wall. Figure 28 shows both the normal stress and density distribution (from radiography) along the radius for both the top (plunger) and the bottom of an uniaxially compressed Fe$_2$O$_3$ powder [50]. This clearly illustrates the level of inhomogeneity that may occur in this compaction process. A lubricant or a reduction in wall roughness may be used to obtain a more homogeneous density distribution.

![Figure 27. Static compaction and decompression curves for two starting densities of TiB$_2$ powder [49].](image-url)
Figure 28. Radial distribution of normalized axial stress and density in a Fe_{2}O_{3} compact obtained by uniaxial compaction [30].

Cooper and Eaton [51] have developed a model that describes the static compaction behavior of ceramic powders. They took into account two largely independent probabilistic compaction processes: the filling of large holes (about the same size as the powder particles) by rearrangement, and the filling of small pores by particle fracture or flow. Their expression for the fractional volume compaction, $v^{*}$, in terms of applied pressure, $P$ is:

$$v^{*} = (v_0 - v_p) / (v_0 - v_\infty) = a_1 \exp \left(-\left(k_1/P\right)\right) + a_2 \exp \left(-\left(k_2/P\right)\right).$$

(2.39)

Here, $v_0$ is the initial volume of the powder, $v_p$ is the powder volume at pressure $P$, and $v_\infty$ is the volume of the sample at theoretical maximal density.

Figure 29. Fractional volume compaction of alumina versus pressure [51].
The dimensionless coefficients, $a_1$ and $a_2$, indicate the fraction of theoretical compaction that would be achieved at infinite pressure by each process individually. The sum $(a_1 + a_2)$ equals unity when compaction can be completely described in terms of the two separate processes. When the sum is less than unity, it is an indication that other processes must become operative before complete compaction is achieved. The coefficients $k_1$ and $k_2$ indicate the magnitude of the pressure where the particular process has the greatest probability density. With the proper choice of coefficients, $a_i$ and $k_i$, the compaction behavior of powders of widely different hardness but with essentially the same particle size fraction could be described. Figure 29 shows an example of the static compaction behavior of alumina powder and a fit through the experimental results according to equation (2.40).

2.4.2 Static compaction compared to shock compaction

Comparing the shock compaction process with that of static compaction, four main differences are observed.

The first difference is found in the time scale of both processes. While the shock compaction of a powder sample occurs in the order of microseconds (and locally within the rise time of the shock front in the order of only tens of nanoseconds), the time scale of static compaction is in the order of seconds to minutes.

The second major difference is the volume in which the compaction process takes place. This is the total powder volume in the static compaction process, while compaction only occurs in the width of the shock front during shock compaction. Since the shock wave travels through the powder its compaction occurs progressively. This makes it possible to compact powders in bulk, while this is impossible in the static compaction due to friction losses and the size and costs of large high pressure machines.

The third large difference is found in the mass or particle velocity occurring in the powder during its compaction. This is a direct consequence of the two preceding differences. The particle velocity at which the static compaction process occurs is close to zero, while in shock compaction the particles are accelerated within the shock front to a value generally on the order of hundreds of meters per second. It is the occurrence of the so called micro-kinetic energy of the particles that is responsible for many of the unique phenomena (particle surface melting, jetting, amount of local deformation) observed during shock compaction and in the resulting compacts.

The fourth major difference between the two compaction methods is the thermodynamic path followed by the powder during the compaction process. In Fig. 27 the measured static compaction and release curves are shown for two TiB$_2$ powders with different starting densities. During static compaction the powder follows a compaction curve as shown in Figs. 27 and 29. Here, most compaction occurs at low pressure due to particle rearrangement. The compaction curve (indicated by the upward arrow) remains close to the isentropic release curve (indicated by the downward arrow) of the compacted powder. In the case of a stable shock wave during shock compaction, the powder follows the Rayleigh-line and release occurs along an isentrope (Fig. 23). Due to the large difference between those two thermodynamic routes, shock compaction is accompanied by a large increase in internal energy of the powder. This is the reason for the difference in temperature of the powders that
are compacted by the two compaction methods. Furthermore, due to the heterogeneous
distribution of the dissipated energy and again the high rate of the shock compaction process,
the temperature distribution in the powder directly after passage of the shock front is highly
heterogeneous. This makes it possible to melt only a fraction of the powder mass (at the
particle surfaces) followed by a extremely high cooling rate due to the enormous temperature
gradient that exists within the particles. The subsequent resolidification of the material, often
resulting in an amorphous phase since there is no time for crystallisation, provides a unique
dynamic consolidation mechanism.
Prümmer [52] compared the static and shock compaction behavior of several metallic
powders and found almost identical compaction curves for both processes, see Fig. 30.

Figure 30. Comparison of compact densities versus pressure obtained by static and explosive compaction [52].
Another interesting observation was done by Emeruwa et al. [53] during an investigation on the ultrasonic (US) assisted static compaction of a ceramic (SiYALON) powder. They observed that upon applying the ultrasound (duration 1 sec., frequency 20 kHz), a temperature rise in the powder (up to 70 °C) occurred that was roughly proportional to the magnitude of the applied pressure. The temperature rise resulted from the friction of the moving powder particles along the line of their rearrangement when applying ultrasound. Although in this work the pressure (in the order of tens of MPa) and amplitude of the movement of the particles are smaller than that occurring in a shock wave, it demonstrates the influence of local phenomena at the particle level.

Although the starting density and hardness of the powder material determine the macroscopic behavior of the shock compaction process, it is the local phenomena at the particle level at which the unique shock wave phenomena occur. The heterogeneity of the medium at the particle level and the, so far, impossibility to observe the process at this level real time, make it hard to get a clear picture of all phenomena that occur during the shock compaction process. Some attempts have, however, been made by some researchers, as can be seen in the schematic representations of the shock compaction process in Figs. 9 and 31.

The development of techniques that are capable of measuring process parameters at the particle level is a great challenge. In this respect, computer simulation of the process at a particle level are way ahead on our experimental capabilities [54, 55].

Figure 31. Schematic representation of the shock wave propagation through two grains in a loosely compacted brittle powder. A, B, C, D represent successive times in the shock process. At A, grain 1 on the left has been partially traversed by the shock S moving from left to right. It leaves in its wake a mass of material which has been fractured and deformed on a microscopic scale. It has also been accelerated outward and to the right, as indicated by the arrows. As time progresses, the shock passes through the first grain and into the second. Direct transmission occurs over a very small area. Most of the transmission results from the accelerated mass of grain 1 striking the surface of grain 2. It is this impact which also produces jets of material that travel outward at high speed.


45
REFERENCES


[33] ibid. p. 47.


Chapter 3

THE CYLINDRICAL CONFIGURATION

In the shock compaction of powders, shock waves are initiated either by high velocity impact of a solid object or by detonation of an explosive. In the latter case, the so called explosive compaction, a distinction is made between direct and indirect methods [1]. In the first method, the powder container is in direct contact with the explosive, and in the second, detonation of the explosive accelerates an object (tube or plate) that subsequently impacts the powder container. The methods for shock compaction of powders are further distinguished by the configuration used. Roughly, the configurations can be divided in three groups: plane, cylindrical and spherical. Most of the measurements of material response to shock wave loading (shock wave velocity, pressure, temperature) are performed using planar loading. Particularly, the development of the gas gun gave the ability to produce controlled, high pressure shock-wave loading with a controlled pulse duration to achieve a state of uniaxial strain over a sample volume large enough to perform measurements. Though ideal for scientific experiments, planar loading is not suitable for compacting bulk materials. The samples are typically only a few mm thick, because the large energy dissipation accompanying powder compaction reduces the strength of the shock wave very fast. Thus, scaling up this configuration requires an increase in surface area that the planar shock is acting upon, or the use of a grazing detonation (see Chapter 2). Some experiments have been performed to fabricate plates by shock compaction of AlN using grazing detonations [2].

The shock compaction of bulk materials requires the application of a uniform shock wave pressure over large distances in the sample. This means that use must be made of a phenomenon that can compensate for the energy loss inherent to shock compaction. A dimension analysis shows that pressure has the dimension of energy density (Joule per unit volume). Therefore, it is possible to maintain a constant energy density by compensating the inevitable loss of energy by a decrease in shock wave volume. This principle is used in converging shock waves. The spherical configuration is probably the best example. In this configuration the sample is contained in a hollow metal sphere, which is surrounded by a layer of explosive [3]. The explosive should be initiated on multiple places of the outer surface of the explosive simultaneously to generate a spherical converging detonation wave. Upon interaction of the detonation wave with the metal container, a spherical converging shock wave is generated in the sample. The surface area of the shock wave front diminishes rapidly during its propagation, reducing the shock wave volume which is necessary to be able to maintain (or even increase) the shock wave pressure. Although very high shock wave pressures can be obtained this way, compaction of bulk material is probably not economically possible. In the first place, this would require a large radius of the metal sphere, which increases the surface area of the explosive layer, making its uniform and synchronized initiation a formidable task. And in the second place, the influence of convergence of the shock wave on reducing its volume is relatively weak at larger radii.
Because of the drawbacks of the planar and spherical configuration, often the cylindrical configuration is used for the compaction of bulk materials. However, a pure radial shock wave suffers from the same drawbacks as the spherical configuration, since it just as well requires a synchronized multi-point initiation [4]. But in this configuration it is possible to use both a grazing detonation and the effect of convergence of the initiated shock wave, so that the main drawbacks of the other two configuration types are avoided.

In this chapter the cylindrical configuration is explained in more detail. In the first part the working principles are explained together with the influence of the most important parameters in the process. Subject of the second part is the prevention of cracking and other failure types that occur in the shock compaction process in general, and in the cylindrical configuration in particular. The problem of cracking is one of the main reasons that prevented the commercial application of this compaction process uptill now.

Figure 1. Standard cylindrical configuration for shock compaction of powders (cross-section).
3.1 THE EXPERIMENTAL PROCEDURE

The simplest shock recovery method to obtain a large sample volume is the cylindrical configuration. A schematic layout of the standard configuration used in this work is shown in Fig. 1. A cylindrical metal container (normally aluminum with an inner diameter of 30 mm, a wall thickness of 2.3 mm, and a length of 120 mm) is filled with the powder specimen. Normally, the filling of the container occurs batchwise by pouring a small amount of powder in the container followed by precompaction using tapping (Stampvolumeter, 50 times at 2 Hz) and uniaxial compression (10-300 MPa). The container is closed by metal plugs and placed at the center of a 50 mm longer polymer or cardboard tube with a diameter 2-4 times that of the metal container. Then, the tube is filled with a powder explosive and placed in a concrete bunker where the explosive compaction experiment is performed. Here, a detonator is placed on top of the configuration at the axis of symmetry. The electrically ignited detonator initiates the detonation of the explosive. After the explosive compaction, the container is removed and submitted to further analyses (for example: dimensional change of the container, density of the sample, porosimetry, microscopy and x-ray diffraction).

3.1.1 Propagation of shock and detonation waves

In this section, a more detailed description is given of the propagation of the detonation wave and the shock waves generated by it.

From its point of initiation, the detonation front moves radially away. When it reaches the upper plug of the container it continues to move as a grazing detonation along the metal container wall. Within the detonation front the explosive is transformed to a gas at very high pressure, $P_D$. The high pressure, of the order of GPa, generates a large force on the confining walls (see Table V in Chapter 2) and deforms them plastically, since the strength of the wall materials, in the order of MPa, is far below the generated stresses. Since the container is surrounded by the explosive, it will implode. From the instant that the inner wall of the container starts to move, it starts to work like a piston, pushing the powder forward. The powder near the container wall is accelerated to a particle velocity, $u_p$, which generates a shock wave in the powder traveling in the same direction. When $u_p$ is determined and the Hugoniot of the powder is known, then also the velocity of the generated shock wave velocity, $U_s$, can be determined.

As is shown in Chapter 2, from the ratio of particle to shock wave velocity ($u_p/U_s$), the relative compression of the powder can be calculated:

$$\Delta V/V_0 = (V_0-V)/V_0 = u_p/U_s. \quad (3.1)$$

Here, $V_0$ and $V$ denote the specific volume of the starting powder and the shocked powder, respectively.

When the detonation front travels at a constant speed, $D$, and when it is far enough from the plug regions of the container, a steady state between the shock waves and detonation wave will be attained. This means that the form of the initial shock front in the powder, its strength, velocity and all other parameters are not a function of time, but only depend on the radial position.

Due to their high compressibility, powders have a low shock impedance and obtain a relatively high particle to shock wave velocity ratio compared to solids. From equation (3.1), which also applies for detonation waves as will be shown in section 3.1.2, we can see that the
powder obtains a large relative compression. The large difference in density of the powder before and after the initial shock front can therefore be visualized by flash x-ray photography. In appendix A, a description of flash x-ray photography, also called radiography, is given. In Fig. 2 an x-ray photograph is shown, which is taken during the explosive compaction of B4C powder in an aluminum container. Through the aluminum container and the explosive, respectively detonation products, the powder is visible. Inside the powder the initial shock wave is visible due to the large difference in density of the powder before and behind it. The higher the powder density, the lower the intensity of the penetrating x-ray flash, resulting in a less illuminated, and hence darker spot on the photo. This is also clearly shown by the metal plugs. The upper plug is made of aluminum ($\rho_{\text{Al}} = 2.7 \text{ g/cm}^3$) and is much lighter then the two lower plugs made of iron ($\rho_{\text{Fe}} = 7.8 \text{ g/cm}^3$) and nickel ($\rho_{\text{Ni}} = 8.9 \text{ g/cm}^3$), respectively. The shock wave in the powder is generated by the grazing detonation wave, which is clearly visible, since it also is a shock wave in a low impedance material. As a rule of thumb for steady detonations, the particle velocity is about a quarter of the detonation velocity. This results, according to equation (2.9), in a relative compression of 25%. This, together with the rather low densities of normal explosives ($< 2 \text{ g/cm}^3$), makes it possible to photograph the detonation front in explosives using x-rays.

Finally, the acceleration of the confining walls can be seen. The expansion of the tube that contains the explosive is visible, while the aluminum container reduces in diameter (implosion). Both the inner and outer diameter of the aluminum container are visible. Due to the incompressibility of the solid metal, the inner wall has a slightly higher velocity than the outer wall, which results in an increase in wall thickness of the container during its implosion. When an empty container is imploded, a solid rod will be obtained with a diameter that has the same cross-section area as that of the starting container.

Figure 2. X-ray flash photograph during explosive compaction of B4C powder.
To examine if the steady state situation has been attained a second photograph can be taken some microseconds later. This second photograph generates also the possibility to measure the detonation velocity of the explosive; the progression of the detonation front divided by the time interval between the photo's equals the detonation velocity, D. The form of the shock front in the cylindrical configuration is determined by the shock wave angle with respect to the cylinder axis, \( \alpha \), as a function of radial position. In Fig. 2 the most simple case is shown, in which the shock front of the initial shock wave forms a cone. Here, the shock wave angle is constant over the radius of the container. Since the process is in a steady state and the shock wave is connected to the detonation wave sliding down the container wall with velocity \( D \), their intersection is traveling at the same axial velocity \( D \). From geometrical wave mechanics we find:

\[
\sin \alpha = \frac{U_s}{D}. \tag{3.2}
\]

When the steady state is reached, the detonation velocity is known, and the form of the shock front is determined, the shock wave velocity, \( U_s \), on any point of that shock front can be calculated. In Fig. 2 the shock wave angle is constant over the diameter, which means that the shock wave velocity is constant. A shock wave travels perpendicular to its front, as was pointed out in section 2.2, which means that when the form of the shock front is known, also the local direction of the shock wave and particle velocity are determined.

In the cylindrical configuration, four types of shock front forms have been observed [5], which are schematically represented in Fig. 3. There exist conical, hyperbolic, and parabolic shock front forms, and also the occurrence of a Mach stem has been observed. In the following, these four shock front forms will be described and explained.

![Shock front forms](image)

(a) pressure constant over cross-section  
(b) pressure decreasing towards center  
(c) pressure increasing over cross-section  
(d) Mach stem

Figure 3. Shock front forms: conical (a), hyperbolic (b), parabolic (c), Mach-stem (d) [from R. Prümmer, in Explosive welding, forming and compaction, T.Z. Blazynski (ed.),Applied Science Publishers, London, 1983].
A. The conical shock front

Figure 3(a) shows the cone shaped shock front, which was also observed in the flash x-ray photograph of Fig. 2. The constant shock wave velocity, and hence constant pressure, over the radius is possible due to the convergence of the shock wave in this configuration. Apparently, the energy dissipation occurring at the initial shock front is compensated by the constantly reducing volume of the shock wave. This results in a constant value for the pressure and shock wave velocity over the radius. It is unlikely that this balance is maintained at radii close to the cylinder axis, since here an finite amount of energy is situated in an infinitesimal volume. Unfortunately, the resolution of the flash x-ray photographs is too low to draw any conclusions about the form of the shock front in this particular region. A more indirect way of obtaining information about the characteristics of the shock front, is to inspect this region afterwards in cross-sections of recovered compacts.

B. Curved shock fronts

In many compaction experiments there is no balance between the two mechanisms that determine the energy density within the shock wave.

1. When energy dissipation dominates, the shock wave attenuates. It reduces in pressure and the shock wave velocity diminishes during its propagation towards the cylinder axis. From equation (3.2) we can see that this means that the shock front must be curved, i.e. $\alpha$ changes over the container radius, since the ratio $U_0/D$ is reduced. During propagation the shock wave angle $\alpha$ decreases, which gives a hyperbolic shock front as is shown in Fig. 3(b). Together with the shock wave velocity the pressure reduces, which is the reason that often uncompacted powder is found afterwards at the center of the compact (undercompaction).

2. When the convergence of the shock wave dominates, the shock wave intensifies. The pressure, and hence the shock wave velocity increase during propagation of the shock wave. Again, this means a curved shock front since the $U_0/D$ ratio increases. In this case, the shock wave angle increases with shock propagation, which results in a parabolic shock front, shown in Figure 3(c). The increase in shock wave pressure often leads to too high pressures at the center of the compact (overcompaction).

C. Reflection of shock front at axis

In all above described situations the initial shock wave will reach the cylinder axis, except in the case of the hyperbolic shock front where only a sonic wave has remained. At the axis a self-reflection of the shock wave will take place. The axis itself is responding like a material of infinite impedance, this singular line is incompressible. The initial shock wave reflects from this line and starts to diverge as a second or reflected shock wave. The pressure increases strongly in the reflected shock wave, but most of the compaction has already occurred in the initial shock wave [6]. The reflection at the cylinder axis is called a regular reflection. The cylindrical configuration is also known as a two shock method, since the pressure is applied by two shock waves, the initial and reflected one. However, under certain circumstances the reflection is changed to an irregular one, also known as the Mach stem.
D. **The Mach stem**

In the Mach-stem or irregular reflection a third shock wave is generated at the center of the cylinder. The initial shock wave now reflects from this third shock wave, as can be seen in Figure 3(d). This new shock wave is called the Mach stem. From the form of the shock front it can be learned that the shock wave velocity, and hence its direction, changes abruptly at the position where the initial shock front reaches the Mach stem. The shock wave angle of the Mach stem is 90°. This means that, at steady state, its shock wave velocity equals the detonation velocity of the explosive. In a low impedance material this high shock wave velocity is accompanied by a large particle or mass velocity. This very high particle velocity, obtained in only one shock wave, is accompanied by a very large increase in internal energy of the material, as can be found from the combination of equations (2.6) and (2.7), which yields:

\[ E - E_0 = \frac{1}{2} u_p^2. \]  

(3.3)

Here, \( E_0 \) and \( E \) are the initial internal energy and the energy behind the shock front, respectively, and \( u_p \) is the particle velocity of the material. Often the material melts or even vaporizes within the Mach stem [7]. Also behind the shock front energy is dissipated due to friction and turbulence of the hydrodynamically flowing material in the large velocity gradient at the interface between the Mach stem and two shock region. Usually, the material in the Mach stem is thrown out at the bottom of the container, thereby perforating the metal plugs. This type of reflection results in a compact with a axial hole at the center, surrounded by resolidified (or condensed) material.

E. **Further shock wave reflections**

When the reflected shock wave has reached the container-detonation products interface, the pressure will equalize. This means that release waves are entering the compact, which reduce the pressure and converge towards the center of the compact, where they will perform a self-reflection. The reflected release waves further reduce the pressure and their interaction can even generate a tensile stress in the compact. The reflected release wave travels through the compact, and also reaches the interface with the detonation products where again a local pressure equalization occurs. In this way many shock and release waves follow and catch-up with each other, until the pressure is back at ambient condition.
3.1.2 The parameters of the process

Since the goal of most compaction experiments is the fabrication of a homogeneous dense material, the ideal form of the shock front is that of the cone. How the parameters of the process should be chosen to obtain this ideal form of the shock front is usually determined experimentally. This is, of course, a large drawback since many parameters are involved. Basically there are three parts of the cylindrical configuration that can be changed independently;

- **The explosive system**: composition, thickness, confinement and density of explosive.
- **The metal container**: type of metal (alloy), wall thickness, and inner diameter.
- **The powder sample**: composition (mixture), starting density, particle size distribution, type and initial pressure of gas in the voids.

A. The explosive system

The explosive is the energy source of the explosive compaction process. The energy released by the detonation reaction is of the order of MJ/kg, which is not inordinately high compared with other exothermic types of reaction [8]. The unique aspects in detonation are the extremely high rate at which the energy is released and the fact that the gaseous reaction products are in a highly compressed state. A great amount of work is performed by the expansion of these gases, for which in calculations often the polytropic gas law (describing isentropic expansion of an ideal gas) is used:

\[ PV^\gamma = K. \]  \hspace{1cm} (3.4)

Here P and V are the pressure and specific volume of the gas, respectively, and \( \gamma \) is the polytropic gas constant (\( \gamma = - \frac{\partial \ln P}{\partial \ln V} |_S \)).

The activation energy for the detonation reaction is very high, of the order of 150 kJ/mol for high explosives [9]. This activation energy and the high pressure required for the fast explosive decomposition, requires initiation by a shock wave. The initial shock wave, that starts the detonation, is normally provided by an electrically activated detonator.

A detonation wave acts like any other shock wave, it only differs in the fact that it is supported by an energy source that is fast enough to provide energy to it. For a detonation wave also the jump-relations are used, although for the equation obtained from energy conservation (equation 3.3), an extra term Q for the reaction energy must be added.

It can be shown [9] that only one unique state is stable for a detonation wave. This state is called the Chapman-Jouget state, and it determines the pressure \( P_{CJ} \) and particle velocity \( u_{pCJ} \) of the detonation wave, which consequently travels with a constant detonation velocity D.

Using \( u_p = P/(\rho_0 D) \), and the polytropic gas law for the detonation products in the energy conservation equation, the following equation can be found,

\[ P = \rho_0 D^2/ (\gamma+1) \]  \hspace{1cm} (3.5)

The value of \( \gamma \) is found, for most explosives, to vary between 2 and 3. It is a function of gas composition and does not significantly depend on initial explosive density.
Table I: Parameters of some explosives.

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<th>Detonation velocity [m/s]</th>
<th>Heat of Explosion [J/g]</th>
<th>Polytropic gas constant (γ)</th>
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</table>

Data from [8]


Equation (3.5) makes clear that the detonation pressure increases linearly with explosive density and with the square of the detonation velocity. The detonation velocity depends on the composition of the explosive and its starting density (liquid, solid, porous solid or powder). In Table I some parameters of explosives are given. Some, so called non-ideal, explosives show a pronounced influence of the layer thickness on their detonation velocity. This is shown in Fig. 4 for Trimonite 1, a commercial explosive with a composition close to that of the TNO-melange AMPA: 81 % Ammonium nitrate, 10 % TNT, and 9 % aluminum powder. The term non-ideal explosive is used for explosives for which the reaction is not completed before rarefaction waves catch up on it. This results in rather low detonation velocities (low energy input), but longer pulse duration since the expansion of detonation gases is partly compensated by the forming of new reaction products. The latter aspect makes the non-ideal explosives popular for mining and powder compaction applications. The expansion of detonation gases, and hence the pressure drop, can be slowed down by using a confinement around the explosive. This also results in an increase in pulse duration of the detonation wave.

![Graph](image)

Figure 4. Influence of layer thickness on detonation velocity of Trimonite 1 (1 g/cc). [B. Crossland and J.A. Cave, 5th Int. Conf. on High Energy Rate Fabrication, Denver (Co), USA, 1975, pp. 498].
B. The starting density of the powder

The starting density of the powder sample is probably the most important parameter of the shock compaction process [6]. It is normally expressed relative to the theoretical maximal density of the material (TMD), or as the distention, which is the reciprocal value of the above-mentioned ratio. The relative starting density determines to a large degree the compressibility of a powder, and hence important shock wave parameters like the sound velocity, and the shock impedance. The latter determines the strength (pressure and shock wave velocity) of the initial shock wave in the powder during compaction. Figure 5 shows the relation between the sound velocity and relative density of two powder materials. Both powders show a large increase in sound velocity with increase in relative density. Since the shock impedance, at low shock wave pressures, can be approximated by the product of starting density and sound velocity, this means that also the impedance of the powder is a strong function of the starting density. The higher the impedance of the starting powder, the higher the pressure and shock wave velocity of the initially generated shock wave will be. This has been shown by flash x-ray photography during the shock compaction of TiB₂ powders in the cylindrical configuration (see Appendix A). This example demonstrates that using the same explosive system, the pressure and velocity of the initial shock wave can be varied by using different starting densities of the powder.

C. The role of the container

In most investigations the metal container is thin compared to its diameter. In this case it is thought to be just a pressure equalizer and transmitter without influencing the shock compaction process of the powder. However, when the wall thickness is larger or the diameter of the container is small, the energy required for its deformation may no longer be neglected. The resistance (F) for deformation of a tube during collapse is given by [10]:

\[ F = 2\sigma \frac{\pi}{d} \]  

(3.6)

![Graph showing sound velocities of copper and tungsten powders as a function of their relative density.](image)

Figure 5. Sound velocities of copper and tungsten powders as a function of their relative density [O.V. Roman, 6th Int. Conf. on High Energy Rate Fabrication, Essen, p. 6.6.11, 1977].
where \( \sigma_r \) is the stress at elastic limit, and \( t \) and \( d \) denote the thickness and diameter of the tube, respectively. Thus, the strength of the material determines at which \( t/d \)-ratio the energy for tube collapse is no longer neglectable.

**D. The E/M-parameter**

To find the right parameters for the compaction process, Prümmer [11] has developed a method in which only two explosive parameters are of importance:

- the ratio of mass of explosive (E) to mass of powder (M): \( E/M \)
- the detonation velocity of the explosive (D)

The mass of explosive (or actually its layer thickness) is a measure for the duration of shock pressure and the detonation velocity is a measure for the pressure during compaction. Both parameters have to be adapted to the properties of the powder to be compacted and have to be found experimentally. After many experiments using different explosives at various E/M-ratios, the obtained relative density and the used E/M-ratio can be plotted against the detonation pressure \( (P = 1/4 \rho D^2) \). In Fig. 6 the results of compaction experiments on two different \( \text{Al}_2\text{O}_3 \)-powders are shown. The lines in the top graph represent the E/M-ratio that give a homogeneous density distribution in a cross-section of the compacts. Above the line one finds overcompacted samples (hole or cracks in the center of the compact), below this line undercompacted samples are recovered which contain uncompacted powder at the center. Now the optimal parameters D and E/M can be found from the maximum in relative density.

![Diagram](image)

Figure 6. E/M method results for two alumina powders.

Considering the many parameters involved it is hard to rationalize why the process could be optimized by optimization of only two (E/M and D). However, some support is given by Yadav et al. [12] who derived an expression showing the influence of E/M by an energy balance. They assume the energy required for deformation of the container and compaction of the powder is proportional to the total energy of the explosive, or:

\[ nE_Q = ME_c + E_d. \]  \hspace{1cm} (3.7)

where \( n \) is a constant of proportionality, \( Q \) is the specific heat of the detonation reaction, and \( E_d \) and \( E_c \) denote energy of deformation and that of compaction per unit of mass of the powder under optimum condition. Equation (3.7) can easily be transformed to:

\[ nQ E/M = E_c + E_d/M. \]  \hspace{1cm} (3.8)

This equation shows that there is a relation between E/M and the energy required for powder compaction. Furthermore, it shows that the energy for tube collapse may play a role when \( E_d \) is large (strong material, or large t/d-ratio). However, the E/M-method only works for one powder sample (starting density, particle size distribution and morphology) in a fixed arrangement. It has little to no predictive value for the optimal parameters of the powder with an other particle size distribution or at a different starting density.

E. The initial gas pressure

The influence of the presence of gas in the voids between the particles, and its initial pressure is overlooked in many investigations. Most shock compaction experiments are performed with atmospheric gas pressures in the precompacted powder. Elliot and Staudhammer [13] demonstrated the effect of the initial \( N_2 \) gas pressure on the shock consolidation of a 67 %TMD stainless steel powder. They found a decrease in compact quality on increase of the initial gas pressure from \( 7 \times 10^{-4} \) Pa to 0.1 GPa. The lowest gas pressure was obtained by leaving the sample on the vacuum system for four days with periodic external vibration to increase pumping speed. Even after this time, the powder acted like a “virtual leak”, demonstrating that it is extremely difficult to remove the entrapped gas of a powder by pumping. During the very fast shock compaction process the entrapped gas cannot leave the system. Proportional to the initial gas pressure it hinders the complete pore collapse or even inter-particle contacts, preventing consolidation of the powder. The best consolidation results are obtained with the initial gas pressure as low as possible.
3.1.3 The role of computer simulations

Computer simulations of the process have been a valuable tool in the shock wave compaction of powders research. In Fig. 7 an example of a computer simulation of the shock compaction process is shown. Since the equations of state for most solid materials and for ideal explosives are well known, the success of the simulations is largely determined by the equation of state that is used for the powders. For the latter, mostly an improved P-α model fitted to experimental data is used [14]. Also the equation of state of the so called non-ideal explosives are difficult to obtain.

Wilkins [15] performed computer simulations of the shock compaction of powders in the direct and indirect cylindrical configuration. By this technique detailed information about the pressure, particle and shock wave velocities and their direction can be obtained for both the detonation wave as well as the shock and release waves in the powder. Also the effect of a central mandrel in the configuration is demonstrated by computer simulations [15]. It helps to avoid the Mach stem and reduces the strength of the release wave, since the reflected shock wave from the powder-mandrel interface reaches the container-detonation products closer to the detonation front where the pressure is still rather high [16]. The influence of parameters that play a role in the cylindrical configuration has also been analyzed by Trebinski et al. [17]. With their computer simulations of the process they are able to explain the influence of the confinement, and E/M ratio on the pressure and form of the initial shock wave in the sample, including the Mach stem [18]. Also the process of tube collapse by a grazing detonation is analyzed by them [19]. This process is important for understanding of the indirect explosive compaction configuration. The pressure produced by collision of solids driven by detonation products may exceed by one order of magnitude those produced in the case of direct contact between the tube and explosive. Furthermore, the efficiency of an external confinement around the explosive charge is demonstrated [20], together with the influence of material compressibility of the tube material on its launching by grazing detonation products [21].

![Velocity and Pressure Diagrams](image)

(a) Velocity Scale: 5 mm/us (b) Pressure Scale: [0.5, 7.5, 6.5, 5.5, 4.5, 3.5, 2.5, 1.5, 0.5, -0.5]

Figure 7. Result of a computer simulation of the shock compaction of B₄C powder in the cylindrical configuration, mass velocities (a) and pressure distribution (b) at a fixed time.
3.2 Crack prevention during shock compaction of powders

The occurrence of macro cracks in compacts fabricated by shock compaction of powders is a severe problem preventing this consolidation technique from commercial applications. Here, some macroscopic material failures are described that typically occur in the cylindrical configuration. They are: radial, transverse, and spiral cracks and a Mach stem. An explanation is given for each type of failure, as well as solutions for their prevention. The given solutions are supported by experiments.

3.2.1 Introduction

Shock compaction, i.e. the compaction of a powder by shock waves, is an alternative route to fabricate materials. Due to the very short duration of the process, normally performed at room temperature, unique mixtures of materials, such as polymer-ceramics [22,23], nano-crystalline [24] and meta-stable [25] materials have been compacted, without deterioration of their initial properties. The starting material is a powder. In the powder, a shock wave is introduced by the detonation of an explosive or the impact of a flyer plate. The compaction of the powder takes place in the shock front of the shock wave. Here, in a width of less then 5 to 50 times the particle diameter [26], the same void eliminating stages have been identified as in static compaction of powders [27]. The first compaction stage is particle rearrangement, decreasing the void volume up to about 40 percent. The second stage is particle deformation when the stress has exceeded the yield strength of the particles. If the fracture stress of the particle matrix is not exceeded, plastic deformation in stage 2 should lead to total void elimination. However, for ceramic materials this is rarely the case. Stage 3 of powder compaction is due to particle fracture and cold working. It must be emphasised that these three stages of compaction are not totally sequential but may overlap each other and, under certain circumstances, may be absent.

Rearrangement i.e. restacking of particles occurs in all powders with rather low starting density. The mechanical properties of the powder material (at the relevant stress situation, temperature and strain rate) determine what will be the main densification mechanism next. For ductile materials with low yield strength (metals like copper and aluminum) main densification occurs in stage 2. For hard and brittle materials i.e. covalent ceramics like SiC and B4C, stage 3 is where main densification takes place, since those types of material do not show much plastic deformation. The cracks occurring at the particle level, i.e. micro cracking, are necessary for the densification of brittle ceramics. In this way a more dense and rigid three dimensional particle matrix is formed. Breaking of the particle matrix, should be avoided since this forms macro cracks in the compact. One way to avoid this is to increase the ductility of the powder particles by increasing their initial temperature [28]. However, this complicates the experimental configuration since explosives and high temperatures are not compatible.

Elimination of macro cracks in final bodies is one of the most challenging problems to overcome. Most microstructures of dynamically compacted ceramic powders reported in the open literature show macro cracks [29,30,31]. The tendency for crack formation and intensity of cracking increases as the compact approaches theoretical density [1].

Strategy to circumvent compact failure during shock compaction is to reveal the mechanism responsible for the type of failure observed. When the mechanism is known, efficient counter

1 submitted to Metallurgical and Materials Transactions A.
measures can be made to prevent the type of failure. Here, this has been done for failure types found in bodies created in the cylindrical configuration.

The outline of this chapter section is as follows. First the cylindrical configuration is described in section 3.2.2. In section 3.2.3 some failure types are described and their mechanisms are explained. In section 3.2.4 experimental results are shown and suggestions to prevent the failure types are given, together with an example. The results will be discussed in section 3.2.5. Finally, some conclusions are drawn in section 3.2.6.

3.2.2 The cylindrical configuration

The cylindrical configuration consists of a metal cylinder, containing the powder to be compacted, surrounded by a layer of explosives contained in a second cylinder, see Figure 8. The explosive is initiated from the top creating a grazing detonation front around the powder container. Due to the high pressure generated in the detonation wave, the container implodes, thereby accelerating and compacting the powder in which a shock wave will be generated. From shock wave mechanics, assuming a stable shock front, it can be derived that the ratio between the local shock wave velocity in the powder, $U_s$, and the grazing detonation velocity, $D$, determines the angle, $\alpha$, between the shock front and the cylinder axis through:

\[
\sin \alpha = \frac{U_s}{D}.
\]

(3.2)

![Diagram](image)

Figure 8. Cylindrical configuration with fixation device.
During the further consolidation process there are two competing mechanisms operating: (1) the shock wave pressure tends to increase because of the cylindrically converging wave front; (2) the pressure tends to decrease because of energy dissipation caused by heat generation, plastic deformation, and comminution [32]. In order to produce a uniform and completely densified cylindrical compact, these two competing mechanisms must be properly balanced. If this balance is not achieved, shock pressure and velocity will be a function of radial position resulting in an inhomogeneous compact.

At the cylinder axis the initial shock wave is reflected creating a second shock wave which diverges towards the cylinder wall. The second shock travels through already compacted material, therefore, at a much higher speed, increasing the pressure severely. This is why this method is also called a two shock configuration. However, most of the compaction is done by the initial shock wave [6]. When the second shock wave arrives at the free surface of the cylinder, a converging rarefaction (release) wave reflects from this interface, hereby reducing the pressure.

A benefit of this configuration is its simplicity; no sophisticated machinery or heavy press is needed while very high pressures can be attained. This makes the process relatively cheap, while also the scale-up possibilities are attractive, since, because of symmetry, there is no physical limit for the length of the container to be compacted. Also the diameter of the cylinder can be scaled up, although this is less straightforward. For example, Coker et al. have compacted titanium alloy powders in cylinders ranging in diameter from 25 to 100 mm [33].

Drawbacks of the configuration are the macro cracks and radial inhomogeneity of the compacts that frequently result.

![Figure 9. Cracks occurring in the cylindrical configuration [34].](image-url)
3.2.3 Failure mechanisms

The main failures that can be found in bodies compacted in the cylindrical configuration are described below and are shown in Figure 9. Subsequently, they are: spiral, radial, transverse cracks, as well as a central hole as the result of a so called Mach stem. The mechanisms responsible for each failure type are described and some suggestions for their prevention are given.

A. Spiral cracks

The spiral or helicoidal crack, shown in Figure 10(a), is a macro crack typically observed in compacts fabricated in the cylindrical configuration. Apart from its form, it is unique in the sense that it is produced by the initial shock wave. The mechanism that leads to spiral cracks has been described by Meyers and Wang [34]. This type of fracture is a consequence of the convergence of the initial shock wave. In Figure 11 the sequence of compaction is shown for several cross sections of the cylinder with inner diameter $d$. The outer portion of the compact, which densifies first must continue to move inward to accommodate the densification of the inner portion of the compact until the inner diameter of the cylinder is reduced to $d_i$. From the initial and final densities $\rho_0$ and $\rho_f$, respectively, and the assumption that the length of the cylinder remains constant, for which there is ample experimental evidence, one finds:

$$\rho_f/\rho_0 = d^2/d_i^2. \quad (3.9)$$

The plastic strain imposed on the outer layer of the powder is according to Meyers et al. [34],

$$\varepsilon = (\pi d_f - \pi d)/\pi d = d_f/d - 1 = (\rho_0/\rho_f)^{1/2} - 1. \quad (3.10)$$

If the compacted material has sufficient ductility, this plastic deformation is accommodated uniformly. If ductility is not sufficient, cracking or shear localization along the surface of maximum shear stress will occur. This surface intersects the cross-section of a compact along a spiral with 45 degrees with respect to the radius, and makes an angle of 45 degrees with the cylinder axis as is shown in Figure 9. In Figure 11 only left turning spiral cracks are shown. Right turning spiral cracks occur just as well and normally both crack directions occur in one sample.

![Cross-section of B₄C compacts: with spiral cracks (a) and without due to a high starting density (b).](image)

Figure 10. Cross-section of $B_4C$ compacts: with spiral cracks (a) and without due to a high starting density (b).
Avoidance of spiral crack formation can be accomplished if the strain occurring during compaction is reduced, or if the ductility of the powder material is increased. The first can be done by increasing the starting density. The second, by preheating the powder [28] or by admixing it with a more ductile phase [23].

B. Transverse cracks

Transverse cracks occur in both the cylindrical and flat plate configurations, although they may have different origins. Linse [1] mentioned that it results if the compacted powder material does not have the strength or ductility to accommodate the tensile stress and lateral movement induced during the compaction process. Ferreira et al. [31] describe parallel lateral cracks in a compact of Al-Ti alloy powder, which they assign to be due to thermal stresses. We found that transverse cracks may also be caused by the way the starting density was obtained. This possibility was also mentioned by Batsanov [35]. The filling of cylinders with a high length to diameter ratio, normally occurs batchwise by uniaxial compression of the powder. The level of homogeneity in density attained within the powder, depends largely on the static densification behavior of the powder. Inhomogeneous compaction occurs mostly with powders that show a large densification during static (pre)compaction, like all powders with only small particles and very ductile materials like some metals with low hardness values (Cu, Al, Pb). Also the shape and surface roughness of the particles and the container wall, as well as lubrication, is important here, since this influences the inter-particle and particle-wall friction, and hence the pressure gradient within each powder batch. Discontinuity in starting density leads to local shock compaction and expansion differences within the powder. This leads to transverse cracks at the interface of areas with high and low starting density. This type of cracking can be prevented by the creation of a more homogeneous density distribution within the container before shock compaction. This can be accomplished by changing the particle size distribution of the powder to a less pressure dependent starting density (higher tap density) and by reducing the inter-particle and particle-wall friction using spherical particles or by applying a lubricant.
C. Radial cracks

Radial cracks, shown in Figure 12, are typically found in cylindrical compacts. Gourdin et al. [36] described them as a result of tensile hoop stresses which develop upon reflection of the initial shock wave at the cylinder axis. However, the compressive hoop stress occurring in the initial shock wave upon convergence and responsible for the spiral cracks, do not transfer to a tensile one upon reflection. This can be understood if the particle velocity before and after initial shock wave reflection at the cylinder axis is considered. Before reflection the initial shock wave converges, just as the accelerated mass behind it. After reflection at the cylinder axis, the radial component of the particle velocity will be dropped to zero. Although the shock wave diverges after its self-reflection, no tensile hoop stresses can develop, since there is no diverging mass velocity. This has been clearly shown by computer simulations of the process, as for example performed by Wilkins and Cline [15].

Radial cracks occur upon the reflection of the first rarefaction (or release) wave at the cylinder axis. There, due to the interaction of the self-reflecting rarefaction wave, locally high tensile stresses can be attained. The just created compact fails in tension, with cracks radiating from the cylinder axis of the compact. The intensity of the tensile stress is determined by the initial intensity of the first rarefaction wave and the amount of its convergence. In order to decrease this initial intensity, explosives with long pulse duration are used. At the moment the reflected (or second) shock arrives at the interface between the cylinder and detonation products, the pressure within the two media will be equalized. The higher the pressure in the detonation products still is, the lower will be the pressure reduction, and hence, the intensity of the first rarefaction wave. A problem is that the pulse duration of explosives decreases with increasing detonation pressure.

Figure 12. Radial cracks in a cross-section of a compact [36].
The shock pressure required for consolidation has been shown to be strongly dependent on the hardness of the powder material [37]. Explosives with higher detonation velocity, providing higher shock wave pressures, are required to consolidate harder powders. But they give only relatively short pulse duration. To circumvent this problem use can be made of a cylindrical configuration with two explosive layers [38]. The outer layer has a high detonation velocity and initiates an oblique detonation wave in the second slower detonating explosive surrounding the powder container. Due to the oblique detonation angle and the convergence of the detonation wave of the second explosive, high pressures with a longer pulse duration can be attained. In Figure 13 a schematic presentation of the detonation and shock waves with pulse duration are given for the normal one-layer (left) and the two-layer configuration (right).

D. Mach stem

The occurrence of a Mach stem at the center of the compact is another example of a failure typical for the cylindrical configuration. It is the result of an irregular reflection of the initial shock wave at the cylinder axis. The exact mechanism behind its formation is still a matter of research [39,40]. On exceeding a critical shock wave angle, $\alpha_{cr}$, the regular shock reflection at the cylinder axis (the two wave compaction) no longer occurs. Instead, an irregular reflection at the cylinder axis occurs, creating a third shock wave, which travels axially with the speed of the detonation wave, D, for stable shock fronts. This is shown in Figure 14.
Figure 14. Axial cross-section showing the creation of a Mach stem due to irregular shock reflection.

The formation of a Mach reflection is often observed in compacts with low starting density. The impedance of those powders is very low, resulting in a initial shock wave characterized by relatively low pressure and hence, low velocity. Using equation (3.2) for the shock wave angle learns that this will create a small angle. The shock wave travels almost purely radially toward the cylinder axis. Here, the increase in shock wave pressure due to its convergence is insufficiently counteracted by energy dissipation. The shock pressure and accompanying shock wave velocity may increase to such a level that the critical angle is exceeded and a Mach stem occurs. In this Mach stem the powder is compacted by only one shock wave with a velocity equal to the detonation velocity of the grazing explosive.

This requires a very high pressure and means that in this part of the powder much more energy will be dissipated than in the part where the powder compaction occurs by two shock waves. This often leads to melting or even vaporization of the material in the Mach stem. The material attains a high axial (particle) velocity parallel with the detonation wave velocity, and is thrown out at the bottom of the container, often perforating the metal closing plugs, resulting in a hole with a diameter of the Mach stem.

Thus, irregular reflection creates an undesired hole, melting and an inhomogeneous density distribution over the radius of the compact.

To avoid a Mach stem, one should prevent a large pressure increase within the compact. The standard solution for Mach stem prevention is the placement of a mandrel (or core) in the center of the cylinder [33]. The initial shock wave will reflect from the mandrel and no longer continue to converge in the powder, which prevents overcompaction at the center. Disadvantage is that in this way only tubes can be produced.

Another way to prevent a Mach stem is to increase the total amount of dissipated energy within the initial shock wave. This is possible by increasing the distance the initial shock wave must travel before its self-reflection. For an ideal cone shaped shock front, this distance \( L \) is determined by the cylinder radius \( R \) and the shock wave angle \( \alpha_0 \):

\[
L = \frac{R}{\cos \alpha_0}.
\]  

(3.11)

Increasing \( \alpha_0 \) requires a higher shock wave velocity, which can be obtained by increasing the impedance of the starting powder. Increasing the impedance of a powder can be realised by increasing its starting density (see 3.1.2 B).
3.2.4 Experimental results

In all experiments use has been made of so called non-ideal powder explosives. They are based on ammonium nitrate (AN) and are characterized by rather low detonation velocities of 2 to 4.5 km/s and a relatively long pulse duration. The explosives used are AMPA, a TNO-melange consisting of 81 % AN, 10 % TNT, and 9 % aluminum powder, and Wetter-Permit-B, also called WPB (Dynamite Nobel, Leverkusen, Germany), a commercially available explosive made of gelatinized ammonium nitrate mixed with alkali chlorides. Due to the rather low detonation velocities the shock wave pressures generated in the powder are estimated to be only a few GPa. This is insufficient to obtain full compaction and/or particle bonding in hard ceramic powders. Yet it illustrates very well the different failure mechanisms and ways to prevent them. Eventually, the compacts can be further processed to full density by subsequent sintering [41] or by infiltration with a liquid binder [42]. In the experiments use was made of aluminum cylinders (AA 6063) with an inner diameter of 30 mm, a wall thickness of 2.45 mm and a length of 120 mm, unless otherwise stated.

A. Spiral cracks

This problem is most severe in the compaction of brittle materials like ceramics.
In Figure 10(a) a cross-section of a B₄C compact is shown, in which numerous spiral cracks are visible. The starting powder had a normal size distribution with an average diameter around 45 microns. After a batchwise precompaction by tapping and uniaxial pressing at 20 MPa, a starting density of 51 % of theoretical maximum (TMD) was obtained. After the shock compaction with AMPA (D=4.3 km/s), the density was increased to 80 %TMD. This value was obtained from the reduction of the cylinder inner diameter using equation (3.9).
From equation (3.10) we can see that the plastic strain will be reduced if the ratio of the cylinder diameter before and after compaction is close to unity. This can be accomplished by a reduction of the final density or, preferably, by increasing the starting density of the compact. In Figure 10(b) a cross-section of a B₄C compact (82 %TMD dense) is shown to be free of spiral cracks. The starting density of the powder has been increased to 68 %TMD by using a mixture of three powders with normal size distributions around 10, 50 and 106 microns, respectively, in a mass ratio of 12:23:65. The explosive used for the compaction experiment was WPB with a detonation velocity of 2.4 km/s.

Another way to prevent spiral cracks is to increase the ductility of the powder. This will allow a larger amount of strain due to plastic deformation. Ductility can be increased by mixing brittle particles with a more ductile component like a metal or a polymer, which creates a composite material. In this way the spiral cracking of hydroxyapatite (HA, a bio-ceramic) was prevented by the introduction of only 10 volume percent of more ductile polymer (PMMA) particles [23]. Figure 15 shows the fracture surfaces created after the shock compaction of HA with and without PMMA particles. No spiral cracks were found in the composite material, while they are numerous in the HA monolith. The fact that spherical PMMA particles (< 50 microns) fractured upon creation of the fracture surface indicates bonding with the HA-matrix.
Finally, it is possible to make use of the special high-strain-rate phenomena which occur within the spiral crack region, to obtain a spiral crack free compact.
Figure 15. Fracture surface of a Hydroxyapatite-PMMA composite (a) and the lapped surface of a monolithic Hydroxyapatite compact (b).

Figure 16 shows an electronmicrograph of the cross-section of a $\text{B}_4\text{C}$ compact, in which a spiral crack is seen. It has produced a surprisingly flat transgranular crack surface inside the powder. On the crack surfaces evidence of a very superficial melting and solidification process is found, indicating that high temperatures have locally been reached. This high temperature is the result of friction between the two crack surfaces sliding over each other under very high shear rate and compressive stresses. The melting temperature of $\text{B}_4\text{C}$ at ambient conditions is 2350°C.

Figure 16. Electron microscope image of a spiral crack in a $\text{B}_4\text{C}$ compact.

Lately, Nesterenko et al. have used controlled shear bands in shock compaction of powders to investigate the role of shear and high shear rates (in the order of $10^6$ s$^{-1}$) in reaction initiation of reactive mixtures of powders [43]. Figure 17 shows a micrograph of a shear-zone in a cross-section after the shock compaction of the same $\text{B}_4\text{C}$ powder mixed with 17 mass% Ti powder. Only inside the shear-zone a porous third phase was formed, identified by X-ray diffraction to be $\text{TiB}_2$. The porosity visible in the reaction product indicates that the $\text{TiB}_2$ was a liquid upon forming, both due to the shear cracking and the exothermic reaction. A good bonding exists between $\text{TiB}_2$ and the unreacted Ti and $\text{B}_4\text{C}$ phases. As a consequence of the large differences in temperature between the phases, periodic cracks are created in the reaction product due to the difference in thermal expansion coefficients.

Here, in a way spiral cracks in the compact have been circumvented by a reaction product linking the two phases.
B. Transverse cracks

In Figure 18 an AlN compact with transverse cracks is shown. The particle size of the starting powder was between 3 and 8 microns. Those rather small sizes prevent a high density to be obtained by pressing or tapping the powder. The main increase in density occurs during the uniaxial compression of this powder. Apparently, there exists a pressure gradient in the powder during its static compression, creating within each batch a drop in density from the top (near the die) to the bottom (earlier precompacted powder).

Although after shock compaction a high final density may be obtained and a cross-section of the material is crack free, the compact consists of a number of pills. Their height and number correspond to the height and number of the batches created during filling of the container.

Prevention of transverse cracking caused by an inhomogeneous precompaction may be reached by reducing the pressure gradient within each powder batch. This can be done for instance by lubrication of the container wall and by adjusting the particle size distribution in order to obtain a higher tap density of the powder.
C. Radial cracks

In Figure 12 a cross-section of a compact with radial cracks was shown. Tensile stresses, as a consequence of the interaction of release waves, are responsible for this type of cracking. The problem of the pressure versus pulse duration of detonations is circumvented by using a cylindrical configuration with two explosives. Here only a short explanation will be presented, since a full description of this two-layer configuration is given in Chapter 4 or [38]. In this cylindrical configuration, shown in Fig. 13, a layer of explosive with low detonation velocity is surrounded by a sheet explosive with high detonation velocity. Upon initiation of the sheet explosive, an oblique detonation wave is formed in the explosive with low detonation velocity. The latter detonation wave creates a high shock wave pressure in the powder due to its oblique detonation angle, and due to its convergence. Since this detonation wave is produced by an explosive with low detonation velocity, it still has its rather long pulse duration. On top of this, the expansion of the explosion products is delayed, since they are confined by the expanding detonation products of the sheet explosive. This is demonstrated in Chapter 4 by numerical simulation of the process. Some pressure versus position results of this simulation are presented in Fig. 13. This shows that in the two layer configuration the shock wave pressure reaches 18 GPa and after 4 µs a pressure of 4 GPa is still present.

For comparison, with the standard one-layer configuration using only the explosive with a low detonation velocity, the detonation pressure reaches 3.5 GPa of which after 4 µs a pressure of 2.5 GPa remains.

If high pressure is needed at a position further away from the detonation front, use could be made of another effect. Computer simulations of an alternative configuration showed that a reflection of an oblique diverging detonation wave increases the pressure within the detonation products again behind the detonation front. In this configuration the layer of faster detonating explosive is situated directly against the metal cylinder, and is surrounded by an explosive layer with lower detonation velocity. This configuration is shown in Figure 19. A pressure increase in the detonation products is obtained at the position the reflected shock wave in the detonation products reaches the metal cylinder.

![Pressure distribution diagram](image)

Figure 19. Two-layer configuration with shock wave reflection on confining wall.
Figure 20. Optimized two-layer configuration to reduce the intensity of rarefaction waves in the powder.

By careful adjustment of the detonation angle and the dimensions of both the metal cylinder and the explosives arrangement, the position at which this pressure increase occurs can be made to coincide with the position at which the reflected shock wave in the powder reaches the same interface. This is shown in Figure 20 for two high explosives; PETN with $D=8.3$ km/s and TNT with $D=6.93$ km/s. Here, both the reflected shock wave in the powder and the reflection of the detonation wave meet at the same position at the cylinder wall, thereby reducing the intensity of the rarefaction wave in the powder.

D. Mach-stem

Figure 21(a) shows the result of a Mach stem in a cross-section of a copper compact which was shock-compact with AMPA from a density of 51 \% TMD to a density of 95 \% TMD. The powder consisted of particles with a dendritic structure with a length of about 40 microns and a width of about 10 microns. Such a particle morphology suffers from a rather high interparticle friction, as well as friction with the cylinder wall, preventing a high starting density.

Figure 21. Cross-section of a copper compact shocked with a starting density of 55 \% TMD shows the result of a Mach-stem (a), while the one shocked with a density of 75 \% TMD no Mach reflection occurred (b).
The Mach stem has been prevented by increasing the starting density up to 75 %TMD by using a bimodal powder mixture. Here, the powder used in Figure 21(a) forms the fraction (20%) smaller copper particles. They have been mixed with a copper powder with particles of about 150 micron. The result after shock compaction is shown in Figure 21(b). The cross-section of the compact shows a homogeneous density distribution of the material (99 %TMD). There is no indication that an irregular reflection has occurred.

3.2.5 Discussion

A. Crack-free shock compaction of powders

The examples given in the preceding section, show that in principal material failure during shock compaction can be reduced or even prevented. When the failure mechanism is understood, effective counter-measures can be taken. Some of the counter-measures can be applied externally to the powder, like an adjusted explosives configuration. However, the main counter measures require an adjustment of the powder itself. The success of the dynamic compaction process depends largely on the particle assembly which is a product of the particle size distribution and its precompaction.

The counter-measures which were used in the preceding examples are not in conflict with each other. This is promising for the potential of this configuration in fabricating dense compacts that are free of failures.

However, in the examples given here, full crystal density (100 %TMD) has not been obtained. For a hard and brittle ceramic, like boroncarbide, the final density of a compact does not exceed 90 %TMD, even though a high starting density of 68% TMD was used. For higher final densities in these materials much higher pressures should be used. And as was already earlier mentioned, the tendency for crack formation and intensity of cracking increases as the compact approaches theoretical density [1]. This means that obtaining a full dense crack free compact remains a difficult task. That is why in some investigations the shock compaction process is used as an precompaction method for a further processing of the compact towards a fully dense material by sintering [41], HIP or infiltration [42].

The task to obtain dense shocked compacts is further complicated when also particle bonding (consolidation) is required. This introduces further restrictions for the parameters of the process. Some models for particle bonding require a minimum fraction of melt to be attained during shock compaction [6]. For this a minimum amount of energy must be dissipated within the compaction process. The dissipated energy can be roughly estimated by:

\[ E = \frac{1}{2} P\Delta V. \]  
(3.12)

The pressure necessary for the compaction of the powder is determined by the hardness of the material and the starting density of the powder [31]. This means that the volume reduction within the initial shock wave (\(\Delta V\)) must have a minimum level. To obtain this volume reduction the starting density of the powder can not be at its maximal level, as is required for the prevention of most failures.

In order to circumvent these conflicting conditions, more parameters should be involved. This could be the starting temperature of the powder or the use of chemical reactions (synthesis) during shock consolidation. Furthermore, on approaching crystal density the gas pressure within
the pores is getting more important. This gas prevents full pore closure and enhances the expansion of the compact during pressure release. The best results have been obtained with as low as possible gas pressures during compaction [13].

B. Additional cracking of compacts

Sometimes cracking of the cylindrical compacts occurs after the compaction process due to impact of the compact with the ground or bunker walls. The compact obtains a high axial velocity either in the direction of detonation propagation or, when this is prevented by placing the experiment directly on a firm support, in opposite direction upon expansion of the detonation products. This problem can rather simply be circumvented by using a specially designed fixation bar, like one shown in Figure 8, that keeps the container in a fixed position prior, during and after its compaction.

Additional cracks can also be introduced in the compacts inadvertently, in the process of making cross-sections. This occurs especially in compacts with low strength due to retained porosity. Compacts fabricated in a cylindrical configuration normally are confined by a compressive internal residual stress due to the mismatch in expansion upon unloading between the powder and the solid container wall. These stresses will be suddenly released when the container wall is sawed in the axial direction, often resulting in the formation of macro-cracks in the compact. Of course this type of cracking has no direct relation with the compaction process. They can be reduced by a stress releasing heat treatment of the cylinder wall prior to the axial sawing process.

3.2.6 Conclusions

It has been shown that when the failure mechanism is known, in principle it is possible to prevent macro failures during shock compaction. Like in all processing with powders, the properties of the powder assembly used as the starting material determine the success of further processing to great extent. Inhomogeneity created during precompaction will cause problems during further compaction of the powder. In shock compaction of powders the starting density of the assembly is a major parameter, since it determines most of the relevant shock phenomena and the compaction behavior of the powder. Generally, high starting densities reduce the amount and number of cracks in the compact, since its compaction involves a lower amount of strain. This makes manipulation of the particle size distribution and precompaction of the starting powder important. The examples given were obtained with explosives with low detonation velocities which are unsuccessful for the full compaction of hard and brittle materials like ceramics. The avoidance of cracking still is very difficult when full density is to be approached. But the principle of avoiding these failures remains the same; knowing the cracking mechanism gives directions for its prevention.

Acknowledgment

Prof. J. Schoonman and Prof. Katgerman are kindly acknowledged for useful discussions and carefully reading the manuscript.
REFERENCES


Appendix A.

Flash X-ray photography

Introduction

The relative compression ($\Delta V/V_0$) of powders and explosives is large during shock (or detonation) propagation, as is shown in Section 3.1.1. The changes in density can be registered by x-ray photography (also called radiography), since high density material absorbs more energy of the x-ray beam than low density material. The absorption of a homogeneous x-ray beam is given by the following well-known expression [1]:

$$I = I_0 \exp (-\rho d \mu).$$  \hspace{1cm} (A.1)

where $I_0$ and $I$ denote the incident and emergent intensities, respectively, of the emitted radiation. $\mu$ is the mass absorption coefficient and $d$ is the thickness of the absorber. As the coefficient $\mu$ is independent of the physical state of the absorber, the above formula shows thickness variation to be equivalent to density variation. On a photographic film, placed behind the object to be photographed, the variations in radiation intensities are registered. Since the process of shock and detonation wave propagation is very fast (on the order of km/s or mm/μs), the photograph must be taken within a extremely short duration (an x-ray flash on the order of 10 - 100 ns). In order to emit enough energy for the film to respond, this flash should be of very high energy (the electronic system generating the x-ray radiation is typically on the order of MV with a peak current of 10 kA). Also the total absorption should not be too high, limiting this technique to either low density materials or very thin material thicknesses. Fortunately, explosives and some powders meet the first requirement.

In order to take photographs during the explosive compaction process, the moment of flashing must be accurately synchronized. This is accomplished by use of a computer which can activate the different x-ray flashes at predetermined delay times (of the order of microseconds). The computer itself is triggered by an ionization pin (charged by an voltage of 100 V) placed in or against the explosive layer above the place where the photographs should be taken. At the moment the detonation front reaches this charged pin, its short-circuiting signal is sent to the computer which then will initiate the flashers at the right moments.
Experimental procedure

Both TiB₂ and B₄C powders were shock compacted with an explosive layer of Triamite (a commercially available explosive) having a detonation velocity of 4.3 km/s. From the flash x-ray photographs taken during the shock compaction process, the shock wave angles were measured.

In Fig. A1 the experimental set up is shown in which two x-ray photographs can be taken during the explosive compaction of a powder. Here, the cylindrical configuration is situated between the x-ray flashers and the films. The x-ray flashers (Scandiflash Model 1200 Pulse Generator System [2], flash time 20 ns) are situated just outside of the bunker and are protected by an aluminum sheet covering a hole in the bunker wall. The x-ray beam is penetrating through this rather low density material, while the aluminum sheet forms an efficient barrier to the impact of fragments and the blast caused by the detonation. The films are situated inside the bunker and are protected from impact of blast and fragments by film cassettes and again by aluminum sheets. The films are positioned at a distance of about 1.5 m from the experiment.

The starting density of the powders was influenced by the particle size distribution of the powders, and by the precompaction process. A low relative density of 45.5 %TMD was obtained by tapping a powder with a particle size of about 45 μm, while the powder with a high relative density of 65.2 %TMD was obtained by tapping and pressing a mixture of powders with particle sizes of about 10, 50 and 150 μm, respectively.

Table A1: Results of shock wave velocity measurements using x-ray photography.

<table>
<thead>
<tr>
<th>exp. nr.</th>
<th>sample</th>
<th>( \rho_0 ) [%TMD]</th>
<th>( \alpha ) [deg.]</th>
<th>D [km/s]</th>
<th>( U_s ) [km/s]</th>
</tr>
</thead>
<tbody>
<tr>
<td>167</td>
<td>B₄C</td>
<td>51.4</td>
<td>-</td>
<td>4.3</td>
<td>-</td>
</tr>
<tr>
<td>161</td>
<td>B₄C</td>
<td>65.5</td>
<td>34-38</td>
<td>4.3</td>
<td>2.5</td>
</tr>
<tr>
<td>168</td>
<td>TiB₂</td>
<td>45.5</td>
<td>18-21</td>
<td>4.2</td>
<td>1.4</td>
</tr>
<tr>
<td>162</td>
<td>TiB₂</td>
<td>65.2</td>
<td>28-31</td>
<td>4.3</td>
<td>2.1</td>
</tr>
</tbody>
</table>
Results and Discussion

An example of an x-ray photograph during the shock compaction of TiB₂ is shown in Figure A2. The photograph shows the initial shock wave in the powders, although the contrast between the shocked and unshocked regions is low. The shock wave in the powder appears to be rather straight, approaching the perfect conical shock front form. Unfortunately, the resolution and lack of contrast in the pictures do not show the form of the initial shock front at the cylinder axis.

By using equation (3.1), the velocities of the initial shock waves in the powders could be calculated, see Table A1. From the results obtained with the two TiB₂ powders, we observe an increase in shock wave velocity with an increase in starting density of the powder. Since the powders were compacted with the same explosive and in the same configuration, the increase in shock wave velocity with density demonstrates the effect of the shock impedance of the powders, which is determined by the starting density.

Figure A2. X-ray flash photograph during shock compaction of TiB₂ powder.

References


Chapter 4

DYNAMIC COMPACTION OF POWDERS BY AN OBLIQUE DETONATION WAVE IN THE CYLINDRICAL CONFIGURATION¹

A new method has been applied to dynamically compact ceramic powders in the cylindrical configuration. In this method a converging oblique detonation is used instead of the sliding detonation used in the standard method. The oblique detonation is generated by a configuration using two explosive layers. X-ray flash photographs have been made that show the detonation and shock fronts in both the standard and new configuration. In this chapter the shock wave and particle velocities in the B₄C powder have been calculated using the shock and detonation angles obtained from the photographs in combination with the measured detonation velocity. In the two-layer configuration the pressure applied to the powder was increased by a factor of 3.5 compared to the one-layer configuration, in agreement with calculations. The working principle of the two-layer configuration is discussed and compared with a computer simulation of the process.

4.1 INTRODUCTION

4.1.1 Dynamic compaction of powders

Dynamic compaction, i.e. compaction by a shock wave [1], is an alternative way to consolidate plastic, ceramic and metallic powders and combinations thereof. For some materials it is the only way to obtain products without deterioration of the special properties of the starting materials. For example products of rapidly solidified powders (RSP [2]) can be formed with this technique since cooling rates that occur in dynamic compaction are at least as high as they were during their production process. Since no sintering aids are needed the process is also interesting for the compaction of strongly covalent bonded ceramics [3,4], because their intrinsic high temperature strength remains unaffected.

Also powders have been modified by shock wave propagation in order to increase their reactivity (catalysts [5]) or sinterability [6]. The principle behind the shock-modification of powders is the generation of a high concentration of defects in the lattice (especially vacancies and dislocations), by the propagating shock wave. The high pressures and strain-rates that occur in dynamic compaction of powders can result in phase transformation of the material. This phenomenon is used in the synthesis of non-equilibrium phases as w-BN [7] and diamond [8], the latter even on a commercial basis.

Research activities in the dynamic compaction of powders started in the 1940's [9]. To avoid the complexity of multi-axial stress and mass flows in shock waves, scientists have made use of special devices to generate plane shock waves in the material to be investigated [10]. A plane shock wave can be generated by a plane-wave lens initiating a plane detonation wave in an explosive or by the perpendicular impact of a flat projectile accelerated by a gas gun [11]. Especially with a gas gun a great variety of shock pulses can be introduced in the target with high accuracy due to the high accuracy with which the velocity of the projectile can be measured. For large surfaces a mouse-trap configuration is an economical alternative method [10].

![Figure 1. Detonation front and shock front during compaction.](image-url)
Drawbacks of using plane wave techniques are the high cost of the equipment and the lack of possibilities to scale up the process. This is because in a plane shock wave there is no possibility to compensate for the energy dissipation which occurs in any shock wave. Especially in powders, shock wave propagation is accompanied by a large dissipation of energy due to the large irreversible change in specific volume occurring in the dynamic compaction process. For bulk fabrication of compacted materials the cylindrical configuration is more convenient. In this configuration the energy absorption is compensated by the geometrical effect of convergence of the shock wave. Prümmer has pioneered this method in the seventies [12]. This configuration can be scaled up by changing the length of the container and, although this is less straightforward, by changing its diameter.

### 4.1.2 Standard cylindrical configuration

In the standard cylindrical configuration powders are compacted by an axi-symmetrical shock wave initiated by the axially moving (sliding) detonation front in the surrounding explosive. The angle between the shock front in the powder and the cylinder axis is a function of the ratio between the shock wave velocity, \( U_s \), and the detonation velocity of the explosive, \( D \), as shown in Fig. 1:

\[
\sin \alpha = \frac{U_s}{D}
\]  

(4.1)

Due to its radial component and to the cylindrical geometry the shock wave converges as it propagates through the powder. The area on which the shock wave energy is acting decreases and hence the energy density increases. As a consequence the pressure, \( P \), and shock wave velocity, \( U_s \), also increase. On the other hand energy is dissipated during compaction by processes taking place in the shock front such as particle rearrangement, cracking, plastic deformation, friction, and melting. This energy dissipation results in a decreasing pressure and shock wave velocity. Whether the pressure and shock wave velocity in the powder increase or decrease depends on the relative strength of the convergence and absorption processes. If both processes just balance, the pressure and shock wave velocity are constant. From Eq. (4.1) it follows that, for a constant detonation velocity \( D \), this leads to a conical shock front with an angle \( \alpha \), equal to \( \arcsin (U_s/D) \). If one of the processes predominates the other, \( P \) and \( U_s \) will be a function of the radial position in the powder and the form of the shock wave will change (see Fig. 2).

**Figure 2. Shock wave front forms in the cylindrical configuration.**
Dynamic compaction of powders with this method is a rather inefficient process. The energy generated by the explosive is sliding by rather than directly acting upon the container (see Fig. 1). This reduces the pressure acting on the container with approximately a factor of two compared to the pressure generated with the same explosive when the detonation front strikes perpendicularly (see Table V in Chapter 2).

In general, non-ideal explosives with low detonation velocities (2-4 km/s) are used to avoid cracks in the compact due to rarefaction waves. The rarefaction waves originate from reflections of the shock wave at the free surface of the container. The longer pulse length of the non-ideal explosive reduces the intensity of these waves.

Since the detonation pressure is quadratically proportional to the detonation velocity, pressures, obtained with low detonation velocity explosives, are limited. In order to increase the pressure acting on the container, indirect methods such as flyer-tubes can be used [13]. In this case shock waves are generated in the powder by the impact of an explosively accelerated flyer-tube. During impact higher pressures can be generated compared to the case where the detonation is acting directly on the container.

A higher pressure and a better energy efficiency can also be obtained by directing the detonation wave towards the container by using two explosive layers, as will be explained below.

4.1.3 Refraction of shock waves

Since shock waves and detonations are wave-phenomena they can be compared to other wave-phenomena like sound, light and surface waves. All these wave-phenomena have to obey to general laws of wave physics like Huygens principle and Snell's law [14, 15]. We can direct a shock wave in the same way we can focus light using refraction and reflection. The direction in which a detonation is propagating through an explosive will change according to Snell's law when it passes the interface with an explosive having another detonation velocity, just like light changes its direction when travelling from one medium to another. In Ref. 15 Weinheimer gives examples in which the principles of shock wave mechanics can be derived from the science of geometrical optics. For example Eq. (4.1) can be obtained directly from Snell's law (with θi=90°):

\[
\sin \theta_i / \sin \theta_r = c_i / c_r, \tag{4.2}
\]

in which subscripts i and r represent the incident and refracted wave, respectively and c is the velocity of propagation of the wave phenomenon through the medium.

If an explosive with a detonation velocity (D1) is initiated by a faster detonating explosive (D2), an oblique detonation front will form in the latter (see Fig. 3).

![Figure 3. Oblique detonation wave (D2) in a plane explosive layer initiated by a faster detonation wave (D1).](image-url)
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![Diagram showing Detonation front and shock front during compaction.](image)

Figure 1. Detonation front and shock front during compaction.

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Chapter 4

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in which subscripts i and r represent the incident and refracted wave, respectively and c is the velocity of propagation of the wave phenomenon through the medium.

If an explosive with a detonation velocity \( (D_1) \) is initiated by a faster detonating explosive \( (D_2) \), an oblique detonation front will form in the latter (see Fig. 3).

Figure 3. Oblique detonation wave \( (D_2) \) in a plane explosive layer initiated by a faster detonation wave \( (D_1) \).
Drawbacks of using plane wave techniques are the high cost of the equipment and the lack of possibilities to scale up the process. This is because in a plane shock wave there is no possibility to compensate for the energy dissipation which occurs in any shock wave. Especially in powders, shock wave propagation is accompanied by a large dissipation of energy due to the large irreversible change in specific volume occurring in the dynamic compaction process. For bulk fabrication of compacted materials the cylindrical configuration is more convenient. In this configuration the energy absorption is compensated by the geometrical effect of convergence of the shock wave. Prümmer has pioneered this method in the seventies [12]. This configuration can be scaled up by changing the length of the container and, although this is less straightforward, by changing its diameter.

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Due to its radial component and to the cylindrical geometry the shock wave converges as it propagates through the powder. The area on which the shock wave energy is acting decreases and hence the energy density increases. As a consequence the pressure, $P$, and shock wave velocity, $U_s$, also increase. On the other hand energy is dissipated during compaction by processes taking place in the shock front such as particle rearrangement, cracking, plastic deformation, friction, and melting. This energy dissipation results in a decreasing pressure and shock wave velocity. Whether the pressure and shock wave velocity in the powder increase or decrease depends on the relative strength of the convergence and absorption processes. If both processes just balance, the pressure and shock wave velocity are constant. From Eq. (4.1) it follows that, for a constant detonation velocity $D$, this leads to a conical shock front with an angle $\alpha$, equal to $\arcsin \left(\frac{U_s}{D}\right)$. If one of the processes predominates the other, $P$ and $U_s$ will be a function of the radial position in the powder and the form of the shock wave will change (see Fig. 2).

![Figure 2. Shock wave front forms in the cylindrical configuration.](image)
The angle $\theta$ between the oblique detonation front and the interface between the two explosives is given by Eq. (4.1) after substitution of $D_1$ for $U_1$ and $D_2$ for $D$:

$$\sin \theta = \frac{D_1}{D_2}. \quad (4.3)$$

This planar arrangement is used to investigate regular and irregular reflections of detonation and shock waves on flat surfaces [16].

### 4.1.4 Two-layer configuration

Also in the cylindrical configuration an oblique detonation with angle $\theta$ will form when a layer of a fast detonating explosive ($D_2$) is surrounding an inner layer of explosive with a lower detonation velocity ($D_1$) (see Fig. 4b). The detonation in the second, slower, explosive has a radial component and is converging while propagating towards the axis. This arrangement increases the efficiency of the dynamic compaction process since both the convergence of the detonation wave and the angle $\theta$ at which it strikes the container lead to an increased pressure in the powder. The pulse length of the detonation in the two-layer configuration is longer than in the case that an ideal explosive in the one-layer configuration is used, not only because a non-ideal explosive with a long pulse length is used as the inner explosive but also because the detonation products of the inner explosive layer are confined by the expanding detonation products of the outer explosive layer. This is important in order to avoid (the interaction of) strong rarefaction waves that generally lead to cracking of the compact.

In this chapter experiments are described during which x-ray photographs were taken that show the differences that occur using the two-layer configuration compared with the standard one-layer configuration. The organization of this chapter is as follows. The experimental arrangement is explained in Sec. 4.2. Then, in Sec. 4.3, the results of the experiments are presented. In Sec. 4.4 the pressures and shock wave velocities are calculated from the x-ray photographs. Computer simulations of both configurations are presented in Sec. 4.5, followed by a discussion of the results in Sec. 4.6.

![Figure 4. Shock front in the standard one-layer configuration (a) and in the new two-layer configuration (b).](image)
4.2 THE EXPERIMENTAL ARRANGEMENT

Experiments were performed in order to compare the standard (one-layer) arrangement with the new (two-layer) arrangement (see Fig. 4(a) and 4(b)). During the experiments x-ray photographs were taken using x-ray flashers with a flash time of 20 ns. From the photographs both the detonation waves and the shock waves could be observed and their angles with respect to the tube axis were measured.

From experiments in which two photographs with a known time difference were taken, the detonation velocity could be determined. Triamite, a mining explosive manufactured by PRB, Belgium, was used in both the standard and the new arrangement. Its detonation velocity is measured to be 4.3 km/s. Demex 200, a sheet explosive manufactured by Royal Ordnance Inc., UK, was used in the new arrangement because of its high detonation velocity of 7.8 km/s. In both experiments the explosives were placed in a 220 mm long PVC cylinder with an inner diameter of 68 mm. A detonator was placed on top of the explosives at the cylinder axis. In the new arrangement the upper part of the Demex sheet explosive was folded towards the detonator to ensure that initiation took place in the Demex sheet first. In Table I the experimental details are given.

The powder to be compacted was boron carbide (B₄C), a hard to sinter, strongly covalent bonded ceramic with a theoretical maximum density (TMD) of 2.52 mg/mm³ (manufactured by ESK, Germany). In order to avoid spiral cracks a trimodal powder mixture with a high starting density ($\rho_0$) was used. Three particle sizes (4, 16-49 and 100-150 mm) with a mass ratio of 10:28:62 were mixed in a turbulator for 20 minutes. A 120 mm long aluminum cylinder (outer diameter 34.8 mm and wall thickness 2.3 mm) was filled with the powder mixture by mechanical tapping and uniaxial pressing at 20 MPa. In this way, a starting density of 65.5 %TMD was obtained.

After the experiments the aluminum cylinder was cut perpendicularly to the tube axis in order that the compacted powder could be analysed microscopically.

Table I: Experimental details

<table>
<thead>
<tr>
<th>Arrangement</th>
<th>One-layer</th>
<th>Two-layer</th>
</tr>
</thead>
<tbody>
<tr>
<td>Explosive</td>
<td>Triamite</td>
<td>Triamite</td>
</tr>
<tr>
<td>Layer thickness (mm)</td>
<td>16.6</td>
<td>13.6</td>
</tr>
<tr>
<td>D (km/s)</td>
<td>4.3 ± 0.1</td>
<td>4.3 ± 0.2</td>
</tr>
<tr>
<td>$\theta$</td>
<td>90° ± 1°</td>
<td>33.5° ± 1°</td>
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<tr>
<td>$\rho_0$ (%TMD of B₄C)</td>
<td>65.5</td>
<td>65.5</td>
</tr>
</tbody>
</table>

*a calculated using Eq. (4.3).

4.3 EXPERIMENTAL RESULTS

4.3.1 Measured angles

In Fig. 5 an x-ray photograph of the experiment with the standard arrangement is given. The grazing detonation front ($\theta = 90^\circ$) in Triamite is clearly visible and also the (conical) shock front in the powder can be seen.

Figure 6 shows the new arrangement during the explosive compaction process. The sheet detonation initiates the detonation in Triamite and an oblique detonation front is formed in the latter.
Figure 5. Flash x-ray photograph of powder compaction in standard configuration (a), and a schematic picture of angles visible in x-ray photograph (b).

Figure 6. Flash x-ray photograph of powder compaction in two-layer configuration (a), and a schematic picture of angles visible in x-ray photograph (b).

The detonation angle \( \theta \) is 34 ± 2 degrees as could be expected from the ratio of the detonation velocities (see Table I). Due to the non-ideal initiation of the bent Demex, its detonation front is not at the same axial position left and right from the aluminum cylinder. Also the shock wave front in the powder is visible in Fig. 6.

The experiments were performed to show the working principle of the configurations and are not intended to be a measuring technique.
Table II: Experimental results.

<table>
<thead>
<tr>
<th></th>
<th>$\alpha$ ($^\circ$)</th>
<th>$\beta$ ($^\circ$)</th>
<th>$\theta$ ($^\circ$)</th>
<th>$U_s$ [km/s]</th>
<th>$u_p$ [km/s]</th>
<th>$P$ [GPa]</th>
</tr>
</thead>
<tbody>
<tr>
<td>One-layer</td>
<td>36 ± 1</td>
<td>7 ± 2</td>
<td>90 ± 1</td>
<td>2.5 ± 0.1</td>
<td>0.6 ± 0.1</td>
<td>2.5 ± 0.6</td>
</tr>
<tr>
<td>Two-layer</td>
<td>42 ± 4</td>
<td>6 ± 2</td>
<td>34 ± 2</td>
<td>5.2 ± 0.5</td>
<td>1.0 ± 0.2</td>
<td>9 ± 2</td>
</tr>
</tbody>
</table>

Figure 7. Cross-section of a $\text{B}_4\text{C}$ compact obtained with the one-layer configuration (a), and idem with the two-layer configuration.

Nevertheless, using the angles ($\alpha, \beta, \theta$) and the jump-relations for shock waves (conservation of mass, momentum and energy), it is possible to calculate the shock wave and particle velocity of the initial shock wave. Using these the pressure and density of the powder can be calculated. For higher accuracies measurements using specific sensors should be used. In Table II the measured angles ($\alpha, \beta, \theta$) are given for both arrangements (see Figs. 5(b) and 6(b)).

4.3.2 $\text{B}_4\text{C}$ compacts

In Figs. 7(a) and 7(b) the cross-sections of the cylinders after dynamic compaction are shown. The boroncarbide powder, compacted with the standard arrangement (Fig. 7(a)) shows a homogeneous material. Apparently the pressure and shock wave velocity were approximately constant over the radius, like in Fig. 2(a). The compaction process has not been able to densify the powder to full density. The density of the material, calculated from the reduction in diameter of the cylinder, is 86% TMD and no bonding, apart from mechanical interlocking, has occurred. The material compacted in the two-layer arrangement is inhomogeneous (Fig. 7(b)). In the center an area with a diameter of 6 mm shows bonding and has a high density. The cracks shown in Fig. 7(b) are probably the result of differences in expansion of the material in the center and the periphery during pressure release.
4.4 CALCULATIONS

4.4.1 Calculations from the experimental results

In the standard configuration the shock wave velocity in the powder can be calculated from the angle $\alpha$ using Eq. (4.1), (see Table II).

In the two-layer configuration the shock wave velocity in the powder can be found from the combination of Eqs. (4.1) and (4.3), resulting in:

$$U_s = D_2 \sin \alpha,$$

(4.4)

in which $D_2$ is the measured detonation velocity of the Demex sheet explosive. The particle velocity ($u_p$) can be obtained from the angles $\alpha$ and $\beta$, where $\beta$ is the angle between the cylinder axis and the interface between the powder and the container wall (see Figs. 5 and 6). For a stationary condition, in which the form of the shock front (see Fig. 2) moves down with the axial velocity $D$, the powder/container interface moves with velocity $u_i$:

$$u_i = D \sin \beta.$$

(4.5)

The direction of the particle velocity of the powder is parallel to the direction of the shock wave velocity ($U_s$). This means that we have to take into account the difference in direction of propagation between the interface and the particle velocity of the powder ($u_p$). The difference in direction of propagation between the two is $(\alpha - \beta)$, and the particle velocity of the powder is:

$$u_p = u_i / \cos (\alpha - \beta) = D \sin \beta / \cos (\alpha - \beta).$$

(4.6)

From the jump relations (conservation of mass, energy and momentum) we can derive an equation relating the pressure in the shock wave to the shock wave velocity ($U_s$), particle velocity and the starting density ($\rho_0$):

$$P = \rho_0 U_s u_p.$$

(4.7)

The calculated shock wave pressures for both arrangements are shown in Table II. The pressure in the two-layer arrangement appears to have increased with a factor of approximately 3.5 with respect to the one-layer arrangement.

4.4.2 Calculations from theory

The increase in shock wave pressure obtained with the two-layer configuration compared to the standard one-layer configuration can be explained by both the obliqueness and the convergence of the detonation wave.

The oblique detonation wave is partly directed towards the cylinder, in contrast to the grazing detonation in the case of the one-layer configuration. The pressures, resulting from the impact of an oblique shock wave on the interface between two materials, can be calculated in the same way as for the perpendicular impact of a shock wave by using the perpendicular component of the particle velocities. The resulting pressure $P_2$ in the impacted material is then given by the relation:
\[ P_2 = P_{Cl} \frac{(1 + \cos \theta)}{(I_1 \cos \alpha + I_2)}, \]  

(4.8)

where \( P_{Cl} \) is the Chapman-Jouguet pressure of the impacting detonation wave, \( \theta \) is the angle between the impacting shock front and the interface and \( \alpha \) is the angle of the shock front in the impacted material. \( I_1 \) and \( I_2 \) are the shock impedances of the two materials (\( \rho_u U_u \)), which are assumed to be independent of pressure here.

When we apply Eq. (4.8) to the cases of an oblique detonation wave and a grazing detonation wave, it follows that the pressures are 1.30\( P_{Cl} \) and 0.52\( P_{Cl} \) respectively. The pressure in the two-layer configuration is increased with a factor of 2.50 by this mechanism.

When a shock wave propagates in a cylindrical geometry at an oblique angle to the axis, its energy density will increase when it approaches the axis due to the decreasing surface area. An estimate of the size of this effect has been given by Booger [17]. In his calculations it is assumed that the pulse length is a constant and the energy density change is given by:

\[ \frac{dE}{dr} = -\frac{E}{S} \cdot \frac{dS}{dr}, \]  

(4.9)

where \( E \) is the energy of the shock wave per unit mass, \( S \) is the surface of the shock wave and \( r \) is the average distance to the cylinder axis. Using \( S = 2 \pi r h \), where \( h \) is an infinitesimal height of the shock front, it follows that \( E \sim 1/r \). From the jump relations we find:

\[ E = P (V_0 - V) \sim 1/r, \]  

(4.10)

where \( P \) is the pressure of the shock wave and \( V_0 \) and \( V \) are the specific volumes, respectively before and behind the front of the shock wave.

In order to be able to apply this equation to a converging detonation in Triamite we need a relation for the Hugoniot of the explosive. Such an expression has been estimated with use of the computer code Tiger [18], yielding the result:

\[ P = 15.91 - 24.68 \frac{1}{V} + 11.82 \frac{1}{V^2}. \]  

(4.11)

From Eqs. (4.9) and (4.10), using the assumption that the pressure at the interface with the sheet explosive is equal to the Chapman-Jouguet (CJ) pressure of Triamite (5.14 GPa as obtained from Tiger), we can now calculate the pressure at the interface with the aluminum cylinder. It then follows that since the diameter of the shock front decreases from 62.0 mm to 34.8 mm, the pressure increases to a value of 7.14 GPa, an increase of 38% over the CJ value. Therefore, the total increase in pressure from both mechanisms is calculated to be a factor of 3.45.

### 4.5 SIMULATIONS

Computer simulations have also been carried out for both the one-layer and the two-layer configuration. With these calculations it is possible to test our ideas about the propagation and reflection of the shock waves, occurring in these configurations, and to examine the resulting values of the shock wave velocity, the shock wave pressure and the compression. The calculations have been performed with use of the hydrocode Autodyn [19]. To describe the shock behaviour of the ceramic powder use has been made of the porous model, intrinsic to Autodyn. Unfortunately the current porous model in Autodyn is a very simple one and is not very reliable especially for high pressures such as that occur near the axis of the tube.
Another problem with carrying out the calculations is that the material properties of porous B₄C, which are necessary as input data for the code, are not very well known. An estimate of the material properties has been made, using as a starting point the model for the Hugoniot of porous materials, developed by Booger et al. [20] and adjusted to comply with the intrinsic porous model. In this way a material description was obtained to give a good description of the shock behavior of the material, except near the center of the tube.

As an example of the results of the simulations in Fig. 8 a pressure contour plot is shown of the compaction process, taking place in the two-layer configuration. Although the absolute values of the pressure in the figure are not very reliable, the appearance of the figure is in good agreement with the x-ray radiograph of this configuration (shown in Fig. 6) and it also shows how the pressure increases when the shock wave travels in the direction of the axis, both in the explosive and in the powder. In the center of the porous material around the axis a region with a very high pressure develops, with a value well above the Hugoniot elastic limit for solid B₄C (19.4 GPa [21]). This high pressure region has the appearance of a Mach stem, but this is probably due to the deficiencies of the porous model at these pressures, since experimentally no evidence is seen of the occurrence of a Mach stem. The angle of the shock front in the powder agrees with the experimentally observed one within a few degrees (see Tables II and III). The same applies to the simulation of the one-layer configuration (not shown here, see Table III). Although the absolute values of the pressures are not very reliable, it appears that the values, reached in the two-layer configuration, are several times as high as in the one-layer configuration, in agreement with the experimental results.

Figure 8. Pressure contours in the two-layer configuration, obtained from the computer simulation.
4.6 DISCUSSION

4.6.1 The pressure increase

From Table II we see that the shock wave pressure in the powder using the two-layer arrangement is increased by a factor of 3.5 with respect to the pressure in the one-layer arrangement. Both the obliqueness and the convergence of the detonation wave contribute to this effect:

(i) The oblique detonation wave in the new arrangement is partly directed towards the container, in contrast to the grazing detonation in the case of the standard arrangement. Using the detonation angle (θ = 34°) the pressure was calculated to increase by a factor of 2.50. Shtertser [22] calculated that it is not necessary to lower θ to 0 degrees for the optimum result. Angles smaller than 30 degrees give already an almost maximum increase in pressure. The detonation angle can easily be controlled by changing the ratio of detonation velocities of the two explosives.

(ii) Since the oblique detonation wave is converging towards the axis of symmetry, its energy density and hence its pressure and detonation velocity will increase as it travels through the explosive, a similar process as occurring for the shock wave in the powder. The dimensions of the configuration (the inner and outer diameter of the inner explosive layer) determine the amount of convergence of the detonation. Calculations (see section 4.4.2) showed that the convergence in the presently used two-layer arrangement has led to a pressure increase by a factor of 1.38.

The above explanations together account for a pressure increase with a factor of 3.45 which is in good agreement with the experimental results.

Another benefit of the two-layer configuration is that although high pressures are generated in the powder, the pulse length of the shock wave is longer than in the case of the one layer configuration using a high explosive. This is because in the two-layer configuration a non-ideal explosive with a long pulse length is used as the inner explosive layer, and furthermore the expansion of detonation products of the inner explosive is hindered by the expansion of the detonation products of the outer high explosive. The latter can be seen in Fig. 8 in which a line is drawn that separates the expanding detonation products of both explosives. The longer pulse length reduces the intensity of the rarefaction waves and therefore reduces the danger of cracking that could occur when the rarefaction waves interact.

4.6.2 Regular/irregular reflection

From Fig. 6 it is clear that the reflection of the oblique detonation wave at the container wall is a regular reflection because the shock front in the Triamite and the front of the reflected wave meet at the container wall. In the case of an irregular reflection the intersection of both waves would occur in the explosive and at their intersection they would join a third shock wave, a so called Mach stem [23].

Although in the experiments, described here, a Mach stem apparently does not occur, it is quite possible that it will occur under only slightly different circumstances e.g. when the detonation angle becomes larger than some, pressure dependent, critical angle [23]. For instance, in experiments of Adamec et al. [16] for aluminum and steel layers, irregular reflection was found to occur when θ became 39° (carbon steel) and 41° (Al) respectively. In our experiments the detonation angle in the two-layer experiment was 34 ± 2°, while θe will probably be larger than
in the above-mentioned situations, since the large compressibility of the powder leads to an increase in $\theta$, [24]. Furthermore, in the case that an irregular reflection would occur, pressure would still be expected to be increased while also the benefit of the long pulse length would still be present.

4.6.3 Mass-ejection

Another feature to be seen in the x-ray photograph of Fig. 6 is a straight line at the outer surface of the PVC cylinder that contained the explosives. This line is not visible in the one-layer configuration (Fig. 5). The angle $\gamma$ (14°) of the line with respect to the axis of the container suggests a velocity of 1.9 km/s. The fact that it is visible on the x-ray photograph can only be explained by a high density material escaping from the surface of the PVC container wall. This process of mass-ejection from a free surface has been observed before [25, 26, 27] and occurs when a strong shock wave is reflected in vacuum or in air.

4.7 CONCLUSIONS

A two-layer configuration has been applied for the dynamic compaction of powders in the cylindrical configuration. In this configuration an oblique converging detonation front occurs, the angle of which is controlled by the ratio of the detonation velocities of the two explosives used. The amount of convergence of the detonation wave can be controlled by the inner and outer diameter of the inner explosive. The pressures achieved with this two-layer configuration are considerably higher than those achieved with the standard one using the same explosive. The pressure increase was determined from measurements of the shock and detonation angles which were visualized by flash x-ray photography. Both the obliqueness and the convergence of the detonation contribute to the increased pressure of the shock wave generated in the powder. The detonation angle and the convergence of the detonation can be controlled separately. The computer simulations confirm this and show a good resemblance with the experimental results. There is a regular reflection of the oblique detonation wave at the aluminum cylinder. The absence of a Mach reflection has been explained although its presence, in the case of a different detonation angle, would still mean that high pressures are generated in the powder.

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REFERENCES


Chapter 5

TEMPERATURE MEASUREMENTS¹

The measurement of the temperature history of a powder during the shock compaction process requires a very fast measuring principle. Since the response time of normal thermocouples is too slow for the extremely fast temperature changes occurring in the shock compression of powders, here thermocouples formed by the powder to be compacted are used. The temperature measurements are performed in the cylindrical configuration. Copper and constantan powders are used in the development of the measuring technique. This resulted in measurements of the temperature history in these metallic materials. By changing the powders to electronical conducting ceramics, it is expected that in future work this measuring technique could also be used to measure the temperature history of ceramic powders during the shock compaction process.

5.1 INTRODUCTION

The heterogeneous temperature distribution occurring in the shock compaction of powders is believed to play an important role in the consolidation process. Temperature measurements can be a tool to determine the rise time of the shock front and the energy dissipation which are important to understand the bonding mechanisms between the particles. Within the shock front (having a rise time less than one microsecond in powders) most compaction, mass acceleration and energy dissipation occurs. The increase in internal energy ($\Delta E$) of the powder material in the shock wave can be approximated by $\Delta E = \frac{1}{2} P \Delta V$, in which $P$ is the shock wave pressure, and $\Delta V$ the accompanying change in specific volume of the powder. In shock waves propagating in powders, the increase in internal energy is rather large compared to solids, due to the large irreversible volume change ($\Delta V$) during its compaction. Most of this energy is dissipated at the surface of the powder particles and results in local heating of these areas. This creates a very heterogeneous temperature distribution in the powder compact, which homogenizes fast due to heat conduction toward the interior of the particles. This is schematically shown in Fig.1, together with the corresponding pressure profile. Measurement of the very fast temperature variations in materials under shock compression have been performed optically by pyrometry [1] and Raman scattering [2]. For metallic powders in a plane wave geometry, the temperature history has been measured using the thermoelectric (or Seebeck) effect, for example by Schwarz et al. [3] and Mutz et al. [4]. In this chapter the development of a measuring technique capable of similar measurements in the cylindrical configuration is described.

![Diagram of temperature distribution and pressure profile during shock compaction of a powder.](image)

Figure 1: Temperature distribution and pressure profile during shock compaction of a powder.
5.2 THERMOCOUPLE PRINCIPLE

The measurement of a temperature difference by a thermocouple is based on the Seebeck-effect [5]. If a finite conductor with a uniform distribution of charge carriers is perturbed by a temperature gradient, the charge particles diffuse from the hot to the cold side of the conductor. This gives rise to a back emf, which opposes further flow of charge. This counter-emf-per unit-temperature gradient is the Seebeck coefficient [6].

In Fig. 2 the Seebeck voltage \( U_{\text{EMF}} \) between two points with a difference in temperature \( (T_1 - T_0) \) is shown, within an electric conducting material A. Within a wide temperature range, the Seebeck-coefficient \( S_A \) can be considered a constant: \( U_{\text{EMF}} = S_A (T_1 - T_0) \).

A second material with a different Seebeck-coefficient \( (S_B) \) connected at the hot side (hot junction) is needed in order to measure a potential difference between the two materials at the cold side with temperature \( T_0 \) (the cold junction):

\[
\Delta U_{\text{EMF}} = (S_A - S_B) (T_1 - T_0)
\]  \hspace{1cm} (5.1)

Combinations of any of the electrical conducting materials will generate Seebeck voltages [5]. The difference in relative Seebeck-coefficients \( (S_A - S_B) \) determines the thermoelectric power of the thermocouple.

In order to measure the temperature of a medium, usually a thermocouple (basically two wires of material A and B which are on one side electrically connected) is inserted in it. This couple then is heated by the medium via heat conduction. Even the small response time of very thin thermocouples is not enough to measure the extremely fast heating of the particle surface occurring in the shock compaction of a powder [4]. However, when the shock compacted powder itself forms the thermocouple (powders of material A and B) it is possible to measure the extremely fast temperature changes, since they do not depend on the process of heat conduction from the particles to the temperature sensor.

\[
V = (S_A - S_B)(T_1 - T_0)
\]

Figure 2: Schematic representation of a thermocouple.
 Ideally, the powders which form the thermocouple should have the same shock impedance. Then the shock wave will not be disturbed when it passes the powder interface. Also the temperatures generated in the powders behind the shock front should have the same value. Both the impedance and the temperature depend strongly on the initial density of the powder. Although this makes it possible to compensate for differences in solid material properties, preferably materials are chosen which have the same shock impedance in the solid phase, like copper and constantan.

Also the pressure dependence of the thermoelectric powder should be considered. The pressure dependence should ideally be zero or at least very weak. Assuming the pressure dependence to be the same in shock compression as is observed in hydrodynamic compression, the pressure dependence for Alumel-Chromel and copper-constantan couples is weak indeed. Bundy [7] measured their pressure dependences to be $-0.12 \, \mu V \, GPa^{-1} \, K^{-1}$ and $-0.28 \, \mu V \, GPa^{-1} \, K^{-1}$, respectively. The pressure correction corresponds to about 1.5% decrease in expected emf at 5 GPa for copper-constantan [8].

5.3 EXPERIMENTAL ARRANGEMENT

The first experiments during the development of the measuring technique, were performed with copper and constantan powders with a normal particle size distribution around 50 and 150 $\mu m$, respectively. The starting density of both powders was 55% of theoretical maximum density (TMD). The experimental set-up for the temperature measurement in the cylindrical configuration is shown in Fig. 3. In order to obtain the full temperature history of the powder, a fixation system for the powder container was developed. It prevents the signal wires from breaking due to movement of the container. Without a fixation system, the container is accelerated by the forces generated on it by the detonation or its rapidly expanding products. Just above the fixation system, the container is not surrounded by the explosive layer. In this region the shock wave will attenuate, reducing the forces acting on the fixation device and the simple pin-hole bonding between the device and the powder container. After the experiment the container can easily be removed and the fixation device can be used many times. During the development of the dynamic temperature measurement, several sources of noise have been avoided or reduced to an acceptable level. The main source of electromagnetic noise appeared to be the PVC-tube that was used as the explosive container.

After replacing this material with card-board only the electromagnetic noise due to the electric detonator and the ionization pin, which triggers the oscilloscope, was still present. By using a wire explosive on which the detonator and the ionization pin were applied, their signals could be separated in time from the thermocouple signal. Between the explosive and the explosive wire a booster charge had to be used, since the wire explosive could not directly initiate the explosive layer.

In the experiments described here, the interface of the two powders making up the thermocouple is flat and normal to the detonation direction. This means that the oblique shock wave generated in the powder can not cross the entire interface instantaneously. However, when the angle of the shock wave towards the cylinder axis is known, for example by measuring it from a flash x-ray photograph [9], the interface can easily be shaped as a cone with the right cone angle. This can be accomplished by using a die with the cone shaped hole in the bottom during the static precompaction of the powder. This shaped interface will be crossed instantaneously by the shock front, which is required to be able to measure the rise time of the shock front and the accompanying temperatures.
5.4 RESULTS AND DISCUSSION

After shock compaction with AMPA (an AN based explosive with a detonation velocity of 3.6 km/s), the density had increased to 97 %TMD and a hole in the center of the compact had been formed. Apparently a Mach reflection (Mach stem) had occurred here. In the Mach stem the material melts and attains a high axial velocity (see Chapter 3). In Fig. 4 the measured temperature profile is shown. Here the thermovoltage has been converted to temperature using the results of a calibration with copper and constantan wires in an oven. At t=0 the ionization pin triggers the oscilloscope. Around 10 microseconds after arrival of the shock wave at the copper-constantan interface the melting point of constantan
Figure 5. Experimental result of a temperature measurement with bimodal copper-constantan powders with higher starting density.

(1388 °C) is measured. Thereafter the temperature reduces gradually to the melting point of copper at normal pressure (1083 °C). Although this experiment is not a good example of the heterogeneous temperature distribution at the particle level within the powder, it shows that the measured thermovoltage corresponds well with temperatures occurring during the shock compaction process.

The Mach stem can be prevented by using a higher starting density of the powder materials [10]. This can be obtained by using a bi- or trimodal particle size distribution. Here, bimodal particle size distributions of both the copper (50 and 150 μm) and constantan (150 μm, mixed with 20 vol% alumina particle of 50 μm) were used.

This increased the starting densities to 73 %TMD and 63 %TMD, respectively. The temperature measurement is shown in Fig. 5. The signal has been recorded from the moment of triggering (t=0) for a period of 100 μs. From the distance between the ionization pin and the copper-constantan interface and the detonation velocities of the explosives used, a lower bound for the expected starting time of the temperature increase has been calculated to be 40 μs. This is in reasonable agreement with the measured starting time of the temperature increase at 47 μs. At this moment the signal jumps in about 1 μs to 37 mV, representing a temperature of about 650 °C. The second temperature increase could be due to the reflected shock wave at the cylinder axis, increasing the pressure for the second time. Although the pressure increase in the second shock wave can be considerable, main compaction (ΔV) and hence temperature increase is obtained in the initial shock wave [11]. The temperature stayed well below the melting point of the materials. A cross-section of the compact after the experiment showed a homogeneous density distribution, without indications that a Mach stem had occurred.
5.5 REQUIREMENTS FOR CERAMIC POWDER-TERMOCOUPLES

Since the compaction behavior of (brittle) ceramic powders is different from metallic powders, future research should be concentrated on applying ceramic powders to form the thermocouple. It proved to be hard to get data concerning the thermoelectric properties of ceramic materials [12], let alone its pressure dependences. A first selection should be made on the basis of Seebeck-coefficient and electric conductivity.

The thermoelectric power of the couple should be high in order to get measurable signals, so the materials that make up the couple must have a large difference in values of their Seebeck-coefficients. Here, the (extrinsic) semi-conducting ceramics are an interesting group of materials, since semi-conductors have much higher Seebeck coefficients than metallic materials [6].

The electric conductivity of most ceramics is rather poor compared to metals, and for a powder the conductivity is reduced at least one order of magnitude with respect to the value for the dense solid material. Therefore, the borides, carbides and some nitrides with electrical conductivities close to that of metals are interesting materials. For example the couple TiB₂ and WC have electric conductivities of the same order of magnitude as metals, and a thermoelectric powder of 20 μV/K [12].

5.6 CONCLUSIONS

A fixation device has been developed enabling electrical measurements to be performed during and right after shock compaction of powders in the cylindrical configuration.

A temperature measuring technique has been developed using a powder-thermocouple. This enables the measurement of the temperature history of metallic powders during their shock compaction. A good relation between the measured temperatures and the physically occurring processes during the shock compaction was obtained. The latter were concluded from macro- and microscopic observations of the preserved samples.

The requirements for a first selection to construct a ceramic thermocouple has been discussed. This selection should be made on the basis of their Seebeck-coefficients and electrical conductivity values.
References


Chapter 6

SHOCK COMPACTION OF CERAMIC COMPOSITES

In this chapter two examples are presented that demonstrate some unique possibilities of the shock wave compaction process. First example is a ceramic-polymer composite, which shows that material combinations, which are not compatible in conventional processes, can be fabricated in this process. Due to the very short duration and the low temperature of the process, decomposition of the polymer component can be prevented. The material combination used is Hydroxyapatite (HA) and Polymethylmethacrylate (PMMA or Perspex). This composite is an interesting type of material for medical applications as bone-substitute material, since synthetic HA is a bio-active bone binding material. In a later stage, the bio-inert PMMA should be replaced by a bio-resoluble polymer, which would make the whole composite bio-active. The second example concerns the shock initiation of a reaction between components of a metal-ceramic mixture. Due to the high hardness of many non-oxide ceramics, they are hard to consolidate by shock compaction. To still obtain high density compacts, use can be made of combustion synthesis from the elements, like Ti and C or B, to obtain TiC and TiB₂, respectively. Shock compaction is performed either before, or directly after the reaction, or the shock is used to initiate and enhance the reaction. Nowadays, much research on shock induced reactions is performed, especially in the USA [1]. In the example presented here, a B₄C powder was mixed with titanium particles and was shock compacted in the cylindrical configuration. In this way compacts consisting of B₄C, Ti and TiB₂ have been created. During shock compaction the flow of the ductile Ti particles increases the relative density of the compacts, while the reaction product (TiB₂) provides a bonding mechanism between the particles.
6.1 Shock-Wave Fabricated Hydroxyapatite-Polymer Composites

Using shock compaction i.e. the technique of densification of powders by shock-waves, composites of hydroxyapatite (HA) and polymethylmethacrylate (PMMA) have been fabricated. Here the fraction of hydroxyapatite ranged from 50 to 90% by volume. From SEM-images of fracture surfaces it is shown that high density compacts with bonding between the HA and PMMA can be obtained. Also, the PMMA is shown to be homogeneously distributed. Due to the short duration of the compaction process, no reaction or decomposition of the polymer has been determined using infra-red spectroscopy and gel-permeation chromatography. Composites with a high fraction of hydroxyapatite are promising as bone substitute materials.

6.1.1 INTRODUCTION

A. Shock compaction

Shock compaction is a technique in which the energy released by the detonation of an explosive, or the kinetic energy of a high speed projectile, is used to generate a shock wave in a powder. The compaction of the powder takes place within the very short rise time of the shock wave. The typical rate of propagation and the rise time of a shock wave in a powder are 2 km/s and 50 ns, respectively [2]. The technique can be performed at room temperature. Both the low temperature and the short duration of this process prevents the components of a powder mixture to react or decompose. In this way composites of polymers and ceramics, with a high fraction of the ceramic component can be obtained [3].

B. Biocompatible materials

Bone is a natural biocomposite that is mainly composed of inorganic bone material (hydroxyapatite-like material) and an organic matrix [4]. Bone substitute materials should ideally have the same composition with a high fraction of hydroxyapatite (HA) for strength and stiffness. It is very difficult to make such a composite using conventional techniques. Although for medical applications a biodegradable bone-bonding polymer will be more appropriate, also a bio-inert polymer, like polymethylmethacrylate (PMMA), can be used. Here, preliminary results are presented of the fabrication of such a composite using the shock compaction of a HA-PMMA powder mixture.

6.1.2 EXPERIMENTS

The starting powders consisted of mixtures of hydroxyapatite and polymethylmethacrylate particles. Both components had a particle size distribution between 1 and 60 μm. The HA powder (Merck, Germany) was prepared by sintering followed by crushing and sieving of the fragments. The particles were jagged and showed porosity since the sintering was not complete (Figure 1a). The PMMA powder was fabricated by suspension-polymerization and consisted of almost perfectly spherical particles (Figure 1b).

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Firstly, some initial experiments were done on the shock compaction of the individual materials, in order to gain experience with shock compaction of polymers and this large particle size of HA.

Secondly, composites of HA and PMMA were fabricated by shock compaction. Volume fractions of HA ranging from 0.5 to 0.9 were mixed with the PMMA powder in a turblulator for at least 20 minutes. The powders were put into an aluminum container (14.0 mm outer diameter, and 9.5 mm inner diameter, with a length of 100 mm) in small batches (~ 0.5 g). Each batch was mechanically tapped (JEL Stampfiometer Stav 2003) and uni-axially pressed at 270 MPa. The container was closed at the ends with metal plugs (Al or Fe). Shock compaction was performed in the so-called cylindrical configuration. Here AMPA, a TNO-melange having a detonation velocity of 3.6 km/s, was used as the explosive. It was applied in a 18 mm thick layer surrounding the aluminum tube.

Figure 1. SEM images of the starting powders of HA (a) and PMMA (b).

Figure 2. Optical photograph of the shocked HA powder (a) and SEM image of a fracture surface of the PMMA powder after shock compaction (b).
6.1.3 RESULTS AND DISCUSSION

A. Shock compaction of pure HA and pure PMMA

A lapped cross-section of the pure hydroxyapatite sample after shock compaction (217) is shown in Figure 2(a). The final density of the compact is high, 97% of the theoretical maximal density (TMD). However, the cross-section shows many macro cracks. These so called spiral cracks are frequently observed when brittle materials are shock compacted in the cylindrical configuration. They can be reduced or even be avoided by increasing the starting density of the powder, which reduces the amount of strain necessary for the compaction to the theoretical maximal density of the material (Chapter 3). In the case presented here, the starting density (77.6 %TMD) was already relatively high for a ceramic powder. In Fig. 2(b) a scanning electron micrograph is shown from a fracture surface of the pure PMMA compact. This fracture surface was made after the shock compaction experiment, by sawing the aluminum container, and subsequently breaking the compact by bending. Comparing Fig. 1(b) with Fig. 2(b) clearly demonstrates the deformation of the PMMA particles. The points of contact between the particles of the starting powder have been transformed to areas of contact due to the deformation of the particles to a polyhedral form. Some of the plastic deformation has occurred already during the static precompaction of the polymer performed at 300 MPa, as could be determined from electron microscopy. The fracture surface shows interparticle cracking of the compact, which indicates that no strong bonding between the particles exists.

B. Density of the compacts

In Table I the different compositions of the compacts are shown together with the starting and final relative density of the samples given as a percentage of the theoretical maximal density (%TMD). The starting densities are measured from the weight and the initial volume of the sample. The starting density of the powder mixture is higher at larger volume fractions of the PMMA. Apparently the relatively ductile PMMA improves the precompaction. The final density is determined by the water immersion method. The compacts are not fully dense and the remaining fraction of pores makes it difficult to perform accurate density measurements. To prevent the water to enter the sample by capillary action of the pores, the samples were coated with a thin layer of grease before immersion in the water. Using this method, the relative measuring error is about 3 %. All compacts show a high relative density of about 90 %TMD. For the application as bone substitute material some remaining microporosity can be advantageous, since it allows internal biological fluid circulation, thus promoting bioactivity [5].

Table I: Experimental results of HA, PMMA, and their composites.

<table>
<thead>
<tr>
<th>Experiment number</th>
<th>HA volume fraction (%)</th>
<th>Starting density (%TMD)</th>
<th>Final density (%TMD)</th>
<th>Fracture type</th>
</tr>
</thead>
<tbody>
<tr>
<td>228</td>
<td>0</td>
<td>99</td>
<td>100</td>
<td>Interparticle</td>
</tr>
<tr>
<td>233</td>
<td>50</td>
<td>87</td>
<td>95</td>
<td>I en II</td>
</tr>
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<td>226</td>
<td>60</td>
<td>85</td>
<td>91</td>
<td>I</td>
</tr>
<tr>
<td>237</td>
<td>70</td>
<td>82</td>
<td>88</td>
<td>-</td>
</tr>
<tr>
<td>229</td>
<td>80</td>
<td>81</td>
<td>86</td>
<td>II</td>
</tr>
<tr>
<td>249</td>
<td>90</td>
<td>78</td>
<td>94</td>
<td>I</td>
</tr>
<tr>
<td>217</td>
<td>100</td>
<td>77</td>
<td>97</td>
<td>Spiral cracks</td>
</tr>
</tbody>
</table>
C. Microstructure and analysis of the compacts

All compacts of the composite materials are shown to be free of macro-cracks. An optical micrograph of a lapped cross-section of a compact with 70 vol% of HA (Figure 3) shows that the PMMA and HA particles are homogeneously distributed. From fracture surfaces of the compact obtained by bending, one can see the weakest links of the composites. There appear to be two types of fracture surface, type I and II. In type I, the fracture surface follows the HA-matrix, leaving the PMMA particles intact. An example of this type of fracture is shown in Figure 4. In type II, the fracture surface runs through the PMMA particles as is shown in Figure 5. In Table I, the type of fracture occurring in the fracture surface of the different composites is indicated. The fact that the PMMA particles break, means that there exists bonding with the HA-matrix. The bonding occurs during the shock compaction process and it is probably due to a mechanical locking of particles caused by deformation (or flow) of the polymer around the particles of the HA-matrix. This is supported by the micrograph in Figure 6, where a deformed (and later broken) PMMA particle in a fracture surface is shown. The occurrence of fracture type II is important as is makes toughening of the composite by a ductile phase possible. Infrared spectroscopy and gel-permeation chromatography (GPC) analysis of the PMMA has been performed.

Figure 3. Optical micrograph of a lapped surface of the 70 vol% HA compact.

Figure 4. Type I fracture surface.  
Figure 5. Type II fracture surface.
Figure 6. Deformed PMMA particle in a fracture surface.

Figure 7. Infrared spectra of PMMA before (a) and after (b) shock compaction. (vertical axis: normalized absorbance; horizontal axis: wave numbers).

Figure 7 shows the result of the infrared spectroscopy before and after shock compaction of PMMA in the 50 vol%-mixture. No differences between both measurements were found, indicating that no decomposition of the polymer phase has occurred. This is further supported by the results of the measurement of the molar weight of PMMA, using gel-permeation chromatography (not shown). The GPC-spectra of PMMA before and after shock compaction are identical, and the molar weight of shocked PMMA was only 5% lower than that of the starting material. This small weight difference however is within the inaccuracy of the measuring method.

6.1.4 CONCLUSIONS

Composites with a high HA to polymer ratio are believed to be suitable as bone substitute materials. Here it is shown that by shock compaction crack free composites of hydroxyapatite (HA) and PMMA can be fabricated without decomposition of the PMMA as was determined from IR spectroscopy and gel-permeation chromatography (GPC). In the compacts, the PMMA and HA particles are homogeneously distributed while the fraction of HA ranges from 50 to 90% by volume. The compacts have a final density typically of about 90 %TMD. Fracture surface analysis shows that bonding between the PMMA and HA particles is possible through plastic deformation of the PMMA-particles.
6.2 Shock compaction of a B₄C-Ti mixture

Shock compaction of the B₄C monolith is difficult due to the very high hardness of this material (> 30 GPa). Here it was tried to use a shock-induced reaction with 17 wt% Ti to improve the relative density and consolidation of the compacts. Titanium has a much lower hardness value, deforms plastically and can react with the B₄C matrix to form TiB₂. X-ray diffraction analysis showed that B₄C, Ti and TiB₂ were present in the compacts. It was found that the reaction between B₄C and Ti was initiated only in the, so called, spiral cracks generated during the shock compaction process. The reaction to TiB₂ occurred in these cracks due to the local high temperature and large shear strain. Due to the fact that the reaction is highly exothermic [6], TiB₂ was formed in the liquid phase, but no self-propagating high-temperature synthesis (SHS) occurred [7], probably as a result of the heat loss to the excess B₄C mass. The unreacted metallic Ti was shown to stop microcracks within the compact.

6.2.1. EXPERIMENTAL PROCEDURE

B₄C powder (F280, ESK, Germany) with a particle size distribution between 22 and 59 μm was mixed with 17 wt% Ti powder with a particle size distribution between 1 and 50 μm using a turbulator. An aluminum tube of 30 mm inner diameter and 120 mm length was filled batchwise with 95 gram of the powder mixture and was closed by metal plugs. The starting density of the powder was 53 percent of the theoretical maximal density (%TMD) of the mixture. This starting density was obtained by first tapping (for 30 seconds at a frequency of 2 Hz) and subsequently uni-axial compression of each batch at 20 MPa. Shock compaction of the mixture was performed by detonation of a 19 mm thick layer of Triamite explosive surrounding the aluminum tube in a bunker. The detonation velocity of the explosive was about 3.8 km/s, generating a pressure of about 4 GPa in the detonation front. After shock compaction the samples were analyzed using electron microscopy and X-ray diffraction (XRD).

Figure 8. Backscattered electron image of a shock compacted B₄C-Ti mixture, showing Ti white.

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2 This section is based on a poster presentation "Reactive shock compaction of B₄C", by E.P. Carton, J. Schoonman, and M. Stuiwing at the of Scheikundig Onderzoek Nederland-meeting, Lunteren, The Netherlands, 7 & 8 Januari 1996.
6.2.2. RESULTS AND DISCUSSION

From the change in inner diameter of the aluminum tube (it was found that it changed less than 5 percent in length), the final density of the compacts was calculated to be 97 %TMD of the mixture. This rather high density is probably the result of the plastic flow of the Ti particles into voids between the B₄C-particles and -fragments during shock loading. This is confirmed by electron microscopy of a lapped surface of a cross-section of the compact. In Fig. 8, a backscattered electron image shows the two phases in the compact, due to the large difference in atomic weight between Ti on the one hand, and B or C on the other hand. The Ti phase is white and follows the contours of the surrounding hard B₄C particles. At some places Ti was pushed into the canals and pores between the B₄C particles and their fragments. In Fig. 9 results of the XRD analyses are shown. In Fig. 9(a) the diffractogram of the mixture before shock compaction shows only peaks that correspond to either B₄C or Ti. In Fig. 9(b) the diffractogram of the mixture after shock compaction shows some extra peaks that were identified to be due to TiB₂ and TiC, although the latter are hard to discriminate from the noise level.

![Diffractograms](image)

(a)

(b)

Figure 9. Diffractograms of unshocked (a) and shocked (b) B₄C-Ti mixtures.
Electron microscopy showed that the new phases did not occur homogeneously throughout the compacts. They were just found in some narrow bands with a width of 10 to 20 micrometer. In the cross-section of the samples, the bands were curved and spiraled from the powder/container interface towards the center of the compact. This location and form of the bands indicates that the reaction only occurred inside the helicoidal or spiral cracks that are frequently observed in cylindrical compacts of brittle materials [8,9]. Due to sliding under high pressure of both crack sides, here locally high temperatures and high shear rates occur which can initiate reactions.

A detail of such a band is shown in Fig. 10. The secondary electron image (SEI) shows the TiB$_2$ band surrounded by the unreacted B$_4$C and Ti. The surface of the samples has been prepared by grinding and lapping, which was accompanied by some break-out of particles and fragments when there is insufficiently particle bonding, like in the regions without reaction products. The backscattered electron image (BEI) shows the TiB$_2$ phase (grey), between B$_4$C (black) and Ti (white) phases. In both images (BEI and SEI) the TiB$_2$ reaction product is shown to be inhomogeneous and porous. There seems to be a good bonding of TiB$_2$ with the surrounding B$_4$C particles and a very sharp transition between the two phases. Some (equidistant) transverse cracks in the TiB$_2$ band are thought to be the result of shrinkage. The Ti-B$_4$C reaction is highly exothermic [6] and the TiB$_2$ product is probably created in the liquid state (melting temperature of TiB$_2$ at ambient condition is 2980 K).

![Image](a)

![Image](b)

Figure 10. Electron microscopic images of reactive bands containing TiB$_2$, (a) SEI, (b) BEI.
The surrounding unreacted material (mainly B₄C) has a much lower temperature, quickly cooling the rather thin layer of TiB₂. By heating of the surrounding B₄C matrix, a lot of energy is leaking away and this prevents the occurrence of a self-propagating high temperature synthesis (SHS) and therefore the reaction stops. Upon cooling, the TiB₂ phase solidifies and shrinks. Since it is well bonded to the B₄C matrix, high thermal stresses occur within the material. These stresses are relieved by the occurrence of (equidistant) transverse cracks in the TiB₂-layer. Sometimes the transverse cracks continue in the surrounding B₄C particle (as in Fig. 10), but the crack is stopped when it arrives at the more ductile metallic Ti, as is shown in Fig. 11. In this figure, also the porosity of the reaction product and the partial flow of Ti in the canals between the B₄C fragments, are visible.

![Image](image.png)

Figure 11. Ductile metallic Ti phase (white) stopping a transverse crack.

It is interesting that the occurrence of spiral cracks, which normally reduce the integrity of the compacts, is used here for the initiation of a reaction of which the reaction product binds the two crack surfaces. This leaves a compact that is free of macro-cracks. The Ti phase left in the B₄C bulk of the compact can further be used in a subsequent heat treatment for a diffusion controlled reaction in the solid state [11].

6.2.3. CONCLUSIONS

A reaction between Ti (17 wt%) and B₄C was initiated within the spiral cracks that occurred during the shock wave compaction of the powder mixture in the cylindrical configuration. The initiation here is probably the result of the locally obtained high temperature and shear strain and -rate due to friction during the spiral cracking. The reaction products, TiB₂ and some TiC, could be detected by XRD and SEM analyses. They filled up the spiral cracks and bonded the two crack surfaces. Upon cooling large thermal stresses occurred, resulting in equidistant transverse cracking of the porous solidified reaction products. Although high temperatures were obtained, both due to friction and the large heat of reaction, and the reaction product initially was in the liquid state, no self-propagating high-temperature synthesis occurred. This is probably caused by the large heat flow (energy loss) towards the excess B₄C mass.
REFERENCES


Chapter 7

MELT-INFILTRATION OF SHOCK COMPACTED CERAMICS

Shock compaction (also called dynamic compaction) of ceramics to fully dense crack-free materials has proven to be very difficult. In this chapter it is shown that fully dense ceramic-metal composites can be fabricated when shock compaction of a brittle ceramic powder is followed by capillary-driven melt infiltration.

Shock compacted TiB₂ and B₄C powders were infiltrated with aluminum. During the infiltration of B₄C compacts reactions with aluminum occur, while the infiltration of TiB₂ appears to be non-reactive. For comparison, also conventionally pressed powders of B₄C and TiB₂ were subjected to aluminum infiltration. In this case the TiB₂ powder could not be infiltrated. The microstructure and some physical properties of the cermets are presented.

1 Submitted to Journal of the American Ceramic Society, E.P. Carton, M. Stuivinga, and J. Schoonman (authors).
7.1 INTRODUCTION

7.1.1 Dynamic compaction

For several decades the dynamic compaction of powders, i.e. the compaction of powders by shock waves has been the subject of many investigations [1]. Here, the main goal has been the optimization of the process in order to obtain a fully dense and bonded solid material. Many of the research efforts have been performed in an empirical way in order to obtain the relations between the process parameters influencing the dynamic compaction, i.e. densification and consolidation. To date, many different models are used for the description of the bonding criteria [1,2,3]. An "engineering" correlation was shown to exist between the hardness of the material and the required compaction pressure [1]. This correlation is influenced by the thickness of the oxide-layer on the particle surface, as is also the case in the explosive welding of metals [2].

A heterogeneous temperature distribution occurs during the dynamic compaction of powders, which can result in melting of the particle surfaces. Schwarz et al. [3] introduced a critical fraction of molten material required for bonding. In their model bonding is obtained by a fast solidification of the particle surfaces through heat conduction to the bulk of the particles. In fact solidified particle surfaces have been found in compacts with good bonding. The cooling rate occurring in the dynamic compaction process (up to $10^{10}$ K/s) is even higher than that occurring in the production process of rapidly solidified powders ($10^5$ K/s). This means that rapidly solidified powders can be consolidated without deterioration of their amorphous or nanocrystalline structure, which is the base of their unique properties [4].

Experiments have shown that densities above 99 percent of theoretical maximum density (%TMD) can be obtained with good interparticle bonding for relatively soft and ductile metals like Al, Cu, and Fe. Hard, refractory, and brittle materials like many ceramics have proven to be much more difficult to consolidate for the following reasons. Firstly, the brittle nature of these materials prevents the material from filling the voids by plastic deformation (void collapse). Instead, the particles break by micro-cracking and the voids are filled by the rearrangement of the particle fragments. Secondly, due to the high hardness of ceramics the required pressure for bonding is very high. As a consequence the release waves that follow the shock wave also are very intense. Macro-cracks will develop due to the high tensile stresses that occur at the interaction of release waves. Ceramics, generally being about ten times weaker in tension than in compression, will easily crack under those extreme circumstances.

By using lower shock wave pressures than required for bonding, the formation of macro cracks can be avoided. Yet the stress occurring in the particles, and certainly on the small contact areas of particle-particle contacts, is high enough to break the particles. Especially the weaker particles (with closed porosity or other stress raisers) are likely to crack during passage of the shock wave. Fragments of the particles, due to multiple cracking, rearrange reducing the void content, thus leading to a densified powder with a reduced, but open porosity.

Lee et al. [5] have studied the change in specific surface area of ceramic powder compacts fabricated with different shock pressures. With increasing shock pressure several brittle ceramics showed an increase in specific surface area due to particle comminution. Other more soft ceramics like ZnO showed a decrease in specific surface area characteristic of a shock-induced
particle bonding. Though in many publications the fracturing of brittle powder particles has been observed and described, relatively little attention has been paid to the pore structure of the compacts. To our knowledge no use has been made of the pore structure obtained by the dynamic compaction of ceramic powders.

In our experiments we observed that just after cutting the dynamically compacted samples using a water cooled high speed diamond saw, the sample surface appeared to dry within seconds. The water is absorbed by the sample through the capillary action of its pores. If instead of water a binder material is used, fully dense composites with good mechanical properties can be obtained by melt infiltration.

7.1.2 Melt-infiltration process

Melt-infiltration is a well known process in which molten metal infiltrates a porous green form e.g. a porous ceramic body [6]. In the infiltration process the most important parameters are the wetting angle between the liquid metal and the ceramic, the surface tension and viscosity of the liquid and the effective radius of the open pore structure. Washburn [7] derived an expression for predicting the distance to which a liquid spontaneously infiltrates into a porous, packed powder as a function of infiltration time. The porosity of the porous body was considered to be modeled by a parallel array of capillaries with a constant radius, in which the liquid flows according to a viscous Poiseuille flow. Others have modified the Washburn equation to compensate for the deviation from the cylindrical form of real pores and the tortuosity of the pore canals [8].

At high temperatures reactions between the ceramic body and the liquid metal may occur. This affects the wetting of the ceramic body and the bonding strength at the interface [9]. It also will lead to another time dependence of the infiltration process compared to Washburn's expression, because now the rate of the infiltration process will be determined by the reaction kinetics [10].

In this work the fabrication process of two cerments called BORCAL (B₄C-Al) and TIBAL (TiB₂-Al) is studied [11]. The particle and pore size distributions of both the starting and shock compacted powders are measured. Then, the pore structure is used for aluminum infiltration of the compacts. The influence of the shock compaction process is illustrated by comparing the cerments with cerments fabricated by melt infiltration of unshocked (only precompacted) powders. The microstructure of the resulting cerments is studied and discussed. Finally, some measurements of their physical properties are presented.
7.2 EXPERIMENTAL PROCEDURES

Powders of B₄C and TiB₂ were uni-axially pressed in aluminum tubes and dynamically compacted. The particle and pore size distributions of the starting powders and shock compacted powders have been determined. The particle size distribution of the trimodal powder mixtures was obtained by laser scattering (Malvern Particle Size Analyser 2600C, Malvern Instruments, England), and the pore size distribution of the powders was measured using mercury-porosimetry (Porosimeter 2000, Carlo Erba Instruments, Italy).

Cermets were fabricated by melt infiltration of the (shocked and unshocked) compacts with aluminum. The cermets were machined using a high speed resin-bonded diamond cutoff wheel and also by spark erosion. Samples were prepared by grinding and lapping for examination of the microstructure using x-ray diffraction (XRD) and scanning electron microscopy (SEM).

7.2.1 Precompaction

The starting materials were powders of B₄C and TiB₂ (ESK, Germany). To obtain a high starting density a trimodal mixture of different particle sizes was used. The mixtures were made with normally distributed powders with particle sizes of <5 µm, between 16-49 µm, and 106-150 µm for B₄C (ESK, Germany) and 10 µm, 10-45 µm, and 45-100 µm for TiB₂ (id.) in an optimal mass ratio of 12:25:63. This ratio was obtained from earlier work [12]. The mixture was homogenized with a turbulator for at least 15 minutes.

Aluminum AA6063 containers (length: 120 mm, 30 mm inner diameter, and a wall thickness of 2.45 mm) were filled with the powder mixtures batch by batch, by mechanical tapping and pressing at 20 MPa. In this way a starting density of 68 percent of the theoretical maximum density (%TMD) of both B₄C (TMD = 2.52 g/cm³) and TiB₂ (TMD = 4.52 g/cm³) could be obtained. Finally, the container was closed with metal plugs.

![Diagram](image)

Figure 1. Cylindrical configuration for the dynamic compaction of powders.
7.2.2 Dynamic compaction

After precompaction, both the B₄C and TiB₂ powders were shock compacted in the direct cylindrical configuration as follows. The aluminum container was placed in the center of a PVC-tube having an inner diameter of 72 mm. The remaining space between the container and the PVC-tube (18.5 mm) was filled with a mining explosive (Triamite, PRB, Belgium) with a detonation velocity of 3.6 km/s. In Figure 1 the configuration is shown. During detonation of the explosive a shock wave, with a pressure of 2-4 GPa, is generated in which the compaction of the powder takes place [13].

7.2.3 Melt infiltration

Precompacted (68 %TMD), as well as shocked powders of B₄C and TiB₂ were used for infiltration with the aluminum of the container (AA 6063). The containers were put in BN-coated alumina cups, placed in an oven and heated at a rate of 200 °C/hour to 1055 °C. A nitrogen or argon flow (H₂O and O₂ concentration both <5 vpm) through the oven protected the aluminum from oxidation. It is important that the oxygen partial pressure of the protecting atmosphere is kept as low as possible, in order to make wetting of the ceramic particles with liquid aluminum possible [14]. The BN coating is not wetted by liquid aluminum and it protects the underlying alumina from diffusion bonding and infiltration with aluminum. At a temperature of 1055 °C, the molten aluminum fills the pore structure of the compacts by capillary-driven infiltration. A time of five hours is sufficient for complete aluminum infiltration of the compact. During cooling to room temperature the aluminum solidifies and the cermets TIBAL (TiB₂-Al) and BORCAL (B₄C-Al) are formed.

7.3 RESULTS

After shock compaction of the powders, the initial inner diameter, d₀, of the aluminum container was reduced from 30.0 mm to a final inner diameter, d, of 26.8 mm. Neglecting the small change in length of the container (3%), which is believed to be the result of the constriction of the container near the metal plugs, the final density of the powder can be derived from multiplying the starting density of the powder (68 %TMD) with (d₀/d)². In this way, the final density of the compacts can be determined to be about 85 %TMD. Cross-sections of the compacts appeared to be free of macro-cracks.

7.3.1 Particle size distribution

A typical example of the particle size distribution of a starting powder mixture (here B₄C) is shown in Figure 2. The trimodal particle size distribution is clearly visible. In Figure 3 the particle size distribution of the shocked B₄C shows that the distribution has shifted towards the smaller particle sizes and that a relative large fraction of fines has formed. For the TiB₂ powder similar results were obtained.
Figure 2. Trimodal particle size distribution of $\text{B}_4\text{C}$ starting powder.

Figure 3. Particle size distribution of shocked $\text{B}_4\text{C}$ powder.

### 7.3.2 Pore size distribution

By mercury-porosimetry both the sample volume and the open pore volume can be obtained as follows. First the sample is dried (16 hours at 117 °C in vacuum), then at room temperature and under vacuum the mercury is added. The volume of the sample is measured at atmospheric pressure. Here, the non-wetting behavior of mercury towards most materials is used. This prevents the pores smaller than 100 microns from infiltration with mercury. In this way a true sample volume is measured. This value is used together with the mass of the sample in order to obtain its density. Then from the theoretical maximal density of the material, the total pore volume can be calculated. By increasing the external pressure on the mercury up to 2 kbar, the pore size distribution and the accumulated open pore volume is obtained. The pore size distribution of the precompacted $\text{B}_4\text{C}$ powder (67.5 %TMD) is given in Figure 4. A large fraction of pores have a diameter around 6 µm. Using the total cumulative (open) pore volume of 0.179 cm$^3$/g and the TMD of the material, here 2.52 g/cm$^3$ for $\text{B}_4\text{C}$, a density of 68.9 %TMD is obtained. Considering the 2% inaccuracy of the measuring methods, both density values are in conformity with each other.
In Figure 5 the pore size distribution of the shock compacted B₄C powder is shown. The density was found to be 84.9 %TMD, in good agreement with the calculated density of 85%TMD using the reduction of the container diameter.

Figure 4. Mercury-porosimetry of the starting TiB₂ powder.

Figure 5. Mercury-porosimetry of the shocked TiB₂ powder.

The pore size has a large distribution ranging from 20 nm to 4 µm, with an average at about 800 nm. The total cumulative pore volume of this compact amounts 0.0744 cm³/g, which indicates a compact density of 84.2 %TMD.

This change in pore size distribution occurs in the TiB₂ compacts to the same extent, although the average pore sizes of the unshocked and shocked powders are somewhat lower, 2 µm and 300 nm, respectively. The relative density of the TiB₂ compacts is 86.6 %TMD (using the true sample volume) and 88.3 %TMD as determined by using the total cumulative (open) pore volume of 0.0294 cm³/g.
7.3.3 Al-infiltration of shocked powders

After an infiltration time of 5 hours at 1055 °C both shock compacted powders were completely infiltrated with aluminum. The density of a fully infiltrated B₄C-sample was 2.55 ± 0.02 [g/cm³] as measured by Archimedes' method. The density of TIBAL, determined in the same way, was 4.22 ± 0.05 [g/cm³].

Figure 6 shows the penetration depth of aluminum in a B₄C compact after an infiltration time of 3 hours at only 925 °C. Because this sample was shock compacted with an aluminum mandrel (6 mm in diameter) placed in the center of the container, two infiltration fronts are visible. One infiltration front was converging from the container wall to the center and one was diverging from the mandrel to the periphery. Apparently, this infiltration time and temperature combination was not enough for a total infiltration of the sample. It does, however, show the homogeneity of the infiltration process. A further illustration of the homogeneity of both the shock compaction and infiltration processes is shown in Figure 7. Here a cross-section of BORCAL is shown to be dense and crack-free.

![Figure 6. Partial infiltration of a shocked B₄C compact.](image1)

![Figure 7. Cross-section of a crack free Al infiltrated B₄C compact (BORCAL).](image2)

7.3.4 Al-infiltration of unshocked powders

Of the unshocked powders only the B₄C powder could be infiltrated with aluminum. Figure 8 shows a scanning electron micrograph of a lapped surface of the unshocked BORCAL. All attempts to infiltrate the unshocked TiB₂ powder were unsuccessful. Table I shows the conditions which were used in the infiltration experiments. Despite a longer infiltration time, a higher infiltration temperature and different inert atmospheres, no infiltration of the unshocked TiB₂ occurred.

The difference in infiltration behavior with the shocked TiB₂ powder was further investigated. X-ray Photoelectron Spectroscopy (XPS) of unshocked, and shocked TiB₂ particles was performed. Figures 9(a) and 9(b) show the XPS curve fit of the starting (unshocked) and shocked TiB₂ powders, respectively, at the binding energy of Boron-1s electrons.
Figure 8. Scanning electron micrograph of unshocked aluminum infiltrated B,C.

Figure 9. XPS of unshocked TiB$_2$ particles (a), and shocked TiB$_2$ particles (b).
Table 1: Experimental conditions for aluminum infiltration of unshocked TiB₂ powder.

<table>
<thead>
<tr>
<th>Atmosphere</th>
<th>N₂ ¹, Ar ², air, vacuum (0.1-1 Pa)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Temperature</td>
<td>925 - 1080 °C</td>
</tr>
<tr>
<td>Infiltration time</td>
<td>0.5 - 8 hours</td>
</tr>
</tbody>
</table>

¹O₂ and H₂O concentration both <5 vpm

7.3.5 Microstructure of the cermets

The microstructure of the cermets was studied by SEM. Figure 10 shows a back-scattered electron image (BEI) of a lapped surface of the aluminum infiltrated B₄C (BORCAL). The broken B₄C particles are clearly visible. The heavier aluminum atoms light up more compared to the lightweight atoms in B₄C. The enclosed space between the fragments is completely filled with aluminum, no porosity is left. Figure 10 shows that even the smallest cracks in the B₄C particles are filled with aluminum.

![Figure 10. Scanning electron micrograph of BORCAL (BEI, lapped surface).](image)

In Figure 11 an XRD-plot of BORCAL is shown in which, besides those of B₄C and aluminum, additional peaks are found. The additional peaks correspond to reaction products between aluminum and B₄C, like Al₂B₄C and AlB₂. The phases produced by the reaction between aluminum and B₄C have been investigated by Pyzik et al. [15,16].

Figure 12 shows a micrograph (BEI) of a lapped TIBAL surface. Also in this image it is clear that the TiB₂ particle fragments are completely surrounded by aluminum. The cermet did not show any porosity within the investigated cross-sections.

From the XRD-plot in Figure 13, no reaction products were detected in the aluminum infiltrated TiB₂ compacts (TIBAL). All XRD-peaks could be identified as coming from aluminum or TiB₂. Apparently the infiltration of TiB₂ with aluminum is non-reactive.
7.3.6 Physical properties of the cermets

In Table II several physical properties of the cermets are presented. Due to the high hardness of the materials, samples were machined with a high-speed, resin-bonded diamond blade. The low specific electrical resistivity makes it very well possible to machine the cermets using spark erosion (electrical discharge machining). The elastic moduli and Poisson's ratio were calculated from the densities as measured by the Archimedes method and the measured longitudinal and transversal sound velocity, respectively. The very high speed of sound and hardness (Vickers macro-indentations with a load of 200 N) of the cermets can be explained by the high stiffness of the materials due to the high ceramic fraction. The TIBAL was used as a nozzle for the testing of solid fuel rocket propellants [17]. Probably as a result of the high thermal conductivity of the material, it functioned well in this application.
7.4 DISCUSSION

7.4.1 Powder compacts

Using the correlation with the hardness of the materials a pressure of about 40 GPa would be required for bonding of the ceramic particles to occur [1]. The shock wave pressure, used here, typically 2-4 GPa [13], is well below this value. From the SEM images it is shown that instead of bonding, the brittle particles fracture and rearrange during passage of the shock wave, leaving a densified powder compact behind. No chemical or physical bonding has occurred. However, the compacts do not fall apart when the container is removed, due to some mechanical interlocking of the particles.

Comparison of the particle size distribution of the starting and the shocked powders (Figs. 2 and 3, respectively) also demonstrates that particle fracture occurs during the shock compaction process. The fragments have rearranged in such a way that a compact with a lower void fraction is obtained. The reduction in void fraction due to the shock compaction process is clearly revealed by a comparison of the pore size distributions of the starting and shocked powders (Figs. 4 and 5, respectively). The void fraction is indicated by a line in the pore size distribution. The intersection of this line with the vertical axis shows the cumulative pore volume per gram of powder. The pore size distribution also shows a remarkable change from a preferential pore size of about 6 micron to a wide pore size distribution, with an average at about 800 nm for B$_4$C. From the agreement between the density values obtained in different ways using mercury-porosimetry, it can be concluded that within the measuring error no closed porosity can be detected within the starting powders or the shocked compacts. The inaccuracy of the measuring methods (2%) does not rule out a small amount of closed pores. Furthermore, the powders have been compacted uniformly as could be established from flash x-ray photographs, see Ref. 13.

7.4.2 Cermets

The influence of the shock wave compaction on the morphology of the powder compact can be seen by comparing the microstructure of cermets fabricated with shocked (Figs. 7 and 10) and unshocked BORCAL (Fig. 8).

Two differences are obvious, i.e. the particles of the unshocked BORCAL show no fracture and a few particles show some closed (or internal) porosity, while the micrographs of the shocked BORCAL and TIBAL do not show particles with internal porosity. The measured reduction in particle size (Figs. 2 and 3) and the observed disappearance of closed porosity can be explained by preferential fracturing of the particles with internal pores. The pores will act as stress-raisers which promote the fracturing of those particles which have internal porosity. Even in the starting powders, the number of particles with closed porosity, and the amount of porosity in them is not large enough to be observed by mercury porosimetry.

7.4.3 Aluminum volume fraction

The XRD spectrum of TIBAL (Figure 13) shows that no (crystalline) reaction products have formed during the infiltration process. The only phases present are aluminum and TiB$_2$. The fraction of aluminum in TIBAL can be calculated from the density of the cermet (4.22 ± 0.05 g/cm$^3$) using the rule of mixtures. Assuming no porosity and taking the densities of aluminum
Table II: Material properties

<table>
<thead>
<tr>
<th>Property</th>
<th>TIBAL</th>
<th>BORCAL</th>
<th>BORCAL unshocked</th>
</tr>
</thead>
<tbody>
<tr>
<td>Density$^{(a)}$</td>
<td>$\rho$ [g/cm$^3$]</td>
<td>$4.1 \pm 0.2$</td>
<td>$2.55 \pm 0.05$</td>
</tr>
<tr>
<td>Longitudinal sound velocity$^{(b)}$</td>
<td>$C_l$ [km/s]</td>
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<td>12.5</td>
</tr>
<tr>
<td>Transversal sound velocity$^{(b)}$</td>
<td>$C_t$ [km/s]</td>
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<td>7.5</td>
</tr>
<tr>
<td>Young's modulus</td>
<td>$E$ [GPa]</td>
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<td>350</td>
</tr>
<tr>
<td>Shear-modulus</td>
<td>$G$ [GPa]</td>
<td>161</td>
<td>144</td>
</tr>
<tr>
<td>Bulk-modulus</td>
<td>$K$ [GPa]</td>
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<td>208</td>
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<td>Poisson's ratio</td>
<td>$\nu$ [-]</td>
<td>0.17</td>
<td>0.22</td>
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<td>Vickers hardness (macro)</td>
<td>$H_v$ [GPa]</td>
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<td>9.1</td>
</tr>
<tr>
<td>Ball-on-ring strength</td>
<td>$\sigma_{br}$ [MPa]</td>
<td>$526 \pm 51$</td>
<td>$453 \pm 14$</td>
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<tr>
<td>Fracture toughness</td>
<td>$K_{IC}$ [MPa m$^{1/2}$]</td>
<td>$6.1 \pm 0.9$</td>
<td>-</td>
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<td>Linear thermal expansion</td>
<td>$\alpha$ [K$^{-1}$]</td>
<td>7.75</td>
<td>5.5</td>
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<tr>
<td>Electrical resistivity</td>
<td>$\rho_d$ [$10^6$ W m]</td>
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<td>4.7</td>
</tr>
<tr>
<td>Thermal conductivity</td>
<td>$\sigma_{th}$ [W/mK]</td>
<td>105</td>
<td>20</td>
</tr>
</tbody>
</table>

$^{(a)}$ Archimedes method in water (TNO-PML).
$^{(b)}$ Ultra sound measurement (TNO-TPD, Delft, The Netherlands).
$^{(c)}$ Ball-on-Ring tests [23] (TNO-CTK, Eindhoven, The Netherlands).
$^{(d)}$ Notched specimens, three-point bending (TNO-CTK, Eindhoven, The Netherlands).
$^{(e)}$ Thermo-Mechanical Analysis TMA (TNO-PML).
$^{(f)}$ Four-point measurement on a 25 mm long bar (TNO-PML).
$^{(g)}$ Laser flush method (ECN, Petten, The Netherlands).

(AA 6063) and TiB$_2$ as 2.69 g/cm$^3$ and 4.52 g/cm$^3$, respectively, the volume fraction aluminum in TIBAL is calculated to be 16%.

In the case of aluminum infiltrated B$_4$C, the reaction products can be responsible for some dilatation of the compact. It is certainly responsible for reducing the fraction of free aluminum in the cermet. The microstructure consists of much more phases than aluminum and B$_4$C, as can be seen from the XRD spectrum of this material (Fig. 11). Pyzik et al. [16] pointed out that using the reaction between Al and B$_4$C, it is possible to optimize the properties of the cermet by a heat treatment after its infiltration. The fraction of free aluminum can be reduced in this way to less than 4 vol% [15].
7.4.4 Powder modification

In contrast to B\textsubscript{4}C, the unshocked TiB\textsubscript{2}-powder could not be infiltrated with aluminum. Since the pore size distributions for unshocked TiB\textsubscript{2} and B\textsubscript{4}C are very similar, and unshocked B\textsubscript{4}C could be infiltrated, it is unlikely that the pore structure is the reason for the unsuccessful aluminum infiltration of the unshocked TiB\textsubscript{2} powder. Also insufficient wetting of the particles by liquid aluminum is unlikely, since the same aluminum was used for the infiltration of both the shocked and unshocked TiB\textsubscript{2}-powders.

It is, therefore, more likely that the surfaces of the TiB\textsubscript{2} particles have changed due to the shock treatment.

In Figure 8(a) the XPS-results at the energy level corresponding to B-1s show that the surface of the unshocked TiB\textsubscript{2} powder particles exists mainly of B\textsubscript{2}O\textsubscript{3} and BN. The existence of BN was also detected at the N-1s energy level (not shown in the figure). Only a small concentration of TiB\textsubscript{2} is present at the surface of the starting powder. TiB\textsubscript{2} is known to react to TiN and BN at high temperatures in a nitrogen environment [18]. Probably the BN detected here was formed during the production process of the TiB\textsubscript{2} powder [19]. During the infiltration experiments, a BN-coating on the alumina cup was used because of the non-wetting behavior of this material towards liquid aluminum.

The surface of the shocked TiB\textsubscript{2} particles (Figure 9(b)) shows a much lower concentration of BN and mainly consists of TiB\textsubscript{2} and B\textsubscript{2}O\textsubscript{3}. Due to the much lower concentration of BN on the shocked particle surfaces, TiB\textsubscript{2} is wetted by aluminum and this facilitates the capillary-driven infiltration. The presence of B\textsubscript{2}O\textsubscript{3} on the particle surface is not problematic, since it is highly volatile above 900 °C and will readily be reduced by the high reactivity of liquid aluminum towards oxygen. Also, dissolved oxygen is believed to improve the interaction between the metal and a ceramic by the formation of oxygen-metal clusters which will develop Coulomb interactions with the ceramic surface [20].

Hence, the lack of success in infiltration of the unshocked TiB\textsubscript{2} powder with aluminum can well be explained by the presence of BN on the unshocked TiB\textsubscript{2} particle surface. The observed change in chemical composition of particle surfaces after shock compaction is an example of the shock-modification of a powder. The change is either a consequence of the fracturing of the particles during shock compression, creating fresh particle surfaces, or a direct influence of the
shock wave on the surface of the particles. At the free surface of a solid the pressure is zero and the shock wave adjusts to this by reflecting from this surface as a rarefaction (or release) wave. The interaction of the shock wave and rarefaction wave accelerates the surface to a value up to twice the particle velocity of the solid behind the shock wave. Here, a mechanism known as mass-ejection [21] could create clean particle surfaces. Another surface cleaning mechanism is described by Shtertser and involves the hydrodynamic flow of a material under high pressures [22]. Upon collision of two powder particles, a shock wave is introduced from their plane of interaction; the particle surfaces. Due to the high pressure the material at this surface (oxides, hydroxide or other layers) will flow under the action of surface tension forces. By deformation of the surface layers their surface is reduced. This creates room for the clean bulk material to appear at the surface.

7.5 CONCLUSIONS

The infiltration of aluminum in shock compacted TiB$_2$ and B$_4$C powders leads to two new cerments; TiB$_2$-Al and B$_4$C-Al, designated TIBAL and BORCAL, respectively. The shock compaction of the ceramic starting powders results in a high ceramic fraction of these cerments (~85 vol%). It also fractures the particles, especially those which contain stress-raisers like internal pores. The surface of shock compacted TiB$_2$ particles exhibited a different chemical composition compared to their unshocked state. This shock-modification of the particle surface increased the wetting behavior towards aluminum and facilitated the melt infiltration of the TiB$_2$ compact.

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References


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[19] Private communication with Elektroschmelzwerk Kempten GmbH, Germany.


Chapter 8

FORMING DURING SHOCK COMPACtion\textsuperscript{1}

Methods are presented for the forming of articles during shock compaction of powders in the cylindrical configuration. The forming methods make use of mandrels of either a polymer or a metal, since those materials can easily be machined in the required shape. The polymer mandrel decomposes during the shock compression process, forming a hole in the compact with the dimensions of the mandrel. Aluminum mandrels do not decompose, but may change their shape during the compaction process. The aluminum of the mandrel can further be used for a subsequent melt infiltration of the remaining pores in the compacts. It is shown that near-net shaping of articles is possible using this combination of techniques. In this way fully dense venturi shaped nozzles of TiB\(_2\)-Al (TIBAL) have been fabricated. The nozzles have been exposed to the harsh environment encountered in a rocket motor using solid propellants: a combination of an extremely strong thermoshock, very high temperatures, erosion and attack by particles and aggressive gases flowing at a supersonic speed. During the tests with a duration of 3-7 seconds the TIBAL nozzles functioned well, even when used repeatedly. This can be explained mainly by the high thermal conductivity of the TiB\(_2\)-Al cermets and the short test durations, although also the in situ forming of a protective Al\(_2\)O\(_3\)-based layer could have played a role.

\textsuperscript{1} Based on the articles "Forming during shock compaction", presented at the APS conference Shock Compression of Condensed Matter 1997, Amherst (MA), USA, 27 July - 1 August 1997, and "Shock-wave fabricated ceramic-metal nozzles", submitted to Applied Composite Materials.

8.1 INTRODUCTION

In shock compaction of powders in the cylindrical configuration, usually mandrels are used to avoid an irregular reflection of the initial shock wave at the cylindrical axis [1]. Without a mandrel, the irregular reflection or Mach stem can result in an axial hole at the center of the compact (see Chapter 3). With the cylindrical method tubes, and in the case that without a mandrel no Mach stem occurs, rods can be produced. Although in this configuration the articles to be formed are limited to have a cylindrical symmetry, the length and the number of articles can easily be increased. This possibility to scale up the process is a great advantage compared to other configurations.

Coils of oxide superconductors have been fabricated by Takashima et al. [2], by putting a hollow metal coil, which contained the powder to be compacted, inside a tube with SiC powder. During the shock compaction of the tube, the SiC powder merely acted as a transmission medium for the shock waves.

In this work, cylindrical and venturi shaped articles were fabricated in two ways:

Firstly, by using the decomposition of a polymer during the shock compaction process. This formed a hole in the compact at the position that was earlier occupied by the polymer.

Secondly, aluminum mandrels were used that after the shock compaction process can be removed by melting. The ceramic powder is formed around the mandrel during the shock compaction process. When melted, the aluminum can be used for the infiltration of the remaining pores in the compact [3]. This may result in near-net shaped metal ceramic composites. As an example, the fabrication of venturi shaped nozzles is shown, and their functioning is tested in a test rocket motor for solid rocket propellants.

8.2 EXPERIMENTAL PROCEDURES

8.2.1 Polymeric mandrel

A cylindrical PVC mandrel with a diameter of 6 mm, was centered in an aluminum container filled with B₄C powder (ESK, Germany) of 68 %TMD. The container was closed by metal plugs and surrounded with a 18 mm thick layer of AMPA, a TNO explosive melange, having a detonation velocity of 3.6 km/s.

The accumulation of shock waves in the polymeric mandrel can increase the internal energy to such a high level that decomposition of the polymer may occur. The decomposition products are gaseous and they can leave the system by a venting hole in the top plug, which was earlier used to center the mandrel in the powder. The result is a hole in the compacted powder with the size and position of the former polymer mandrel.

8.2.2 Aluminum mandrel

For the case of an aluminum mandrel, at first cylindrically formed tubes surrounded by a stainless steel container were fabricated. In this case, the Al-mandrels (rods with a diameter of 5.9 mm) remained intact during the compaction process. After shock compaction of the ceramic powder (B₄C or TiB₂ with a starting density of about 68 %TMD) in a stainless steel container (wall thickness 3.5 mm), a macro crack-free material was manufactured by infiltrating the compact with the aluminum of the mandrel [3,4]. The production process of the hereby formed B₄C-Al and TiB₂-Al cermets, designated by BORCAL and TIBAL,
respectively, is described in Chapter 7. The samples were further processed to cylindrical inserts for a metallic modular nozzle (consisting of TZM, a Molybdenum alloy, and a stainless steel part for the intake and exhaust sections, respectively). The steel wall was machined to fit in the nozzle throat, and a hole at the center of the compact, with a diameter of 6.45 mm was formed by spark erosion (electrical discharge machining). With specially formed mandrels, this fabrication process was further used to manufacture venturi shaped nozzles of TIBAL with a distinct throat diameter and cone angles for the intake (α), and exhaust (β) sections, respectively. In Fig. 1, a typical example of the axial cross-section of the venturi shaped aluminum mandrel is shown. In the cylindrical parts of the mandrel a hole (with a diameter of 3 or 5 mm) was drilled in order to compensate for the reduction in tube diameter caused by the TiB₂-powder compaction.

![Figure 1. Axial cross-section of the venturi shaped Al-mandrel.](image)

The mandrel was placed inside a 120 mm long stainless steel tube having a wall thickness of 8 mm and an inner diameter of 30 mm. The remaining space between the tube and mandrel was filled with TiB₂ powder, and the tube was closed by metal plugs, as is shown in Fig. 2. The detonation direction was from left to right in Fig. 2. The starting density of the TiB₂ powder was about 65 %TMD and was obtained only by tapping (at 2 Hz). After the shock compaction experiments, the compacts were radiographed in order to determine the change in shape of the mandrel. From the radiographs the resulting cone angles can be determined. Since the mandrel contains more aluminum than can be infiltrated in the powder compact, the radiographs were also used to guide the workshop where to machine the aluminum surplus without touching the ceramic compact. Before the melt-infiltration process the metal plugs are removed by sawing to avoid contamination of the aluminum. The compact was infiltrated by the mandrel material in an oven (5 hours at 1050 °C in a Ar or N₂ atmosphere). Hereafter, only the external surface of the stainless steel container, and some remaining Al in the nozzle throat needed to be machined to complete the nozzle fabrication process.

![Figure 2. Axial cross-section of the experimental arrangement to produce a complete nozzle.](image)
8.2.3 The test equipment

The test rocket motor used in the experiments is schematically shown in Figure 3. In a solid propellant rocket motor, the combustion chamber pressure is a function of the nozzle throat diameter and the burning surface of the propellant. Cylindrical disks of propellant with a constant burning surface were fired in a 10 cm small scale test-burner. The duration of the test is controlled by the height of the propellant disk burning at a velocity of about 1 to 2 cm/s, depending on the pressure in the chamber. The inner surface of the modular nozzle and test rocket motor wall was protected by a layer of silicon grease.

The modular nozzle has been used for testing the materials as inserts. The throat diameter of 6.45 mm results in a combustion chamber pressure of approximately 6 MPa. Although this configuration is not optimal from a propulsive point of view, representative conditions are achieved with respect to thermoshock, temperature field and combustion gas properties. For an actual nozzle design, the maximum thermal load occurs just in front of the throat section [5]. Compared to the cylindrical inserts a realistically contoured nozzle will encounter slightly higher thermal loads. In the case of testing the TIBAL nozzles, the modular nozzle was replaced by this complete nozzle.

For a solid propellant rocket motor, degradation of the nozzle throat will result in a decrease of the combustion chamber pressure and rocket motor thrust. The rocket motor operating pressure is determined by two pressure transducers inside the combustion chamber. The thrust delivered by the rocket motor is measured by installing the test motor on a static test bench with thrust measurement equipment.

After the tests, the materials have been investigated by SEM, EDX and XRD.

Figure 3. Burner test to simulate solid rocketed fuel nozzle conditions (a), and the modular nozzle (b) in which: 1 TZM intake cone, 2 insert, 3 copper ring, and 4 stainless steel exhaust cone.
8.3 RESULTS AND DISCUSSION

8.3.1 The PVC-mandrel

After shock compaction the recovered B₄C compact had a hole at the position and with the dimensions of the former polymer mandrel, see Fig. 4(a). It is assumed that the polymer decomposes into gaseous products during the pressure build-up occurring inside the impedance trap formed by the polymer and the compacted powder, see Fig. 4(b). The starting powder has a very low impedance \( Z = \rho U_a \) being of the same order of magnitude as the impedance of the polymer. After the initial shock wave the increase in impedance of the powder is much greater than that of the shocked polymer. In Fig. 5 the impedance of solid copper and a powder of copper (72 \% TMD) is shown as a function of pressure of the initial shock wave. The impedance of a solid is not a strong function of the initial shock wave pressure, as can be seen in Fig. 5 for solid copper. The impedance of a powder, however, strongly increases with shock wave pressure [6]. Using the P-\( \alpha \) model the impedance of the powder after its partial compaction by a preceding shock wave can be calculated. The result of this calculation is also shown in Fig. 5. A large difference in shock impedance between the powder and the polymer will be created after the compaction of the powder by the initial shock wave. As a consequence, the shock wave is trapped inside the polymer, since it is surrounded by a material with higher impedance. The pressure and temperature of the polymer increase due to the dissipation of energy caused by the multiple reflections of the shock waves. Wylie et al. [7] made use of this principle to create small axial holes during shock compaction of tubes.

![Cross-section of compact](a)
![Schematic representation](b)

Figure 4. Cross-section of compact (a) and schematic representation of the forming of the hole during shock compaction of powder with a PVC mandrel (b).
Figure 5. Shock impedance versus initial shock wave pressure in solid copper and copper powder for the second shock wave propagated into the partially compacted material [6].

8.3.2 The Al mandrels

A. The nozzle inserts

As an example, in Fig. 6 some pieces are shown of a shocked and Al-infiltrated TiB2 compact. The pieces are shown in different stages of their electric discharge machining toward samples that can be used as inserts in the modular nozzle. Both the BORCAL and TIBAL materials have been used as an insert in the hot region (throat) of the modular rocket nozzle.

Figure 6. Electric discharge machining of TiB2-Al infiltrated nozzle inserts.
B. The TIBAL nozzles

An example of an x-ray photograph of the nozzle after shock compaction is shown in Fig. 7. From the x-ray photographs, taken with an exposure time of about one minute, the cone angles of the mandrel after shock compaction have been measured. In Table I the cone angles before and after compaction are shown, together with the nozzle throat diameters (φ). The throat diameter φ₂ was measured after removal of the aluminum. The final density of the powder (about 80 %TMD) has been determined from the initial density and the reduction in container size after compaction.

During the forming process the dimensions of the mandrel change. The throat diameter increases, because the pressure is high enough to cause some flow of the Al towards that region during compaction. With the detonation direction as indicated before, the small angle β almost does not change. The angle α increases about 10°, while the ratio φ₂/φ₁ is ranging from 1.2 to 1.3, for an initial throat diameter between 5 and 6.4 mm.

The reproducibility of the results (experiments 196 and 219) and the relation found between the dimensions after and before forming indicate that for samples which are shock compacted under the same circumstances near-net-shape forming during shock compaction is possible. A completed TIBAL nozzle, ready for testing, is shown in Fig. 8.

Table I: Experimental results of throat diameter (φ), and intake and exhaust cone angles (α and β, respectively) of the aluminum mandrel, before (1) and after (2) shock compaction.

<table>
<thead>
<tr>
<th>Experiment</th>
<th>α₁ [°]</th>
<th>β₁ [°]</th>
<th>φ₁ [mm]</th>
<th>α₂ [°]</th>
<th>β₂ [°]</th>
<th>φ₂ [mm]</th>
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<tr>
<td>186</td>
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<td>9</td>
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<td>5.30</td>
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<td>5.00</td>
<td>48</td>
<td>15</td>
<td>6.00</td>
</tr>
</tbody>
</table>
8.3.3 The burner tests

The materials were tested by using them as nozzles or nozzle inserts during the burning of solid rocket propellants (CK50, and the aluminum containing CK52, respectively) in a test rocket motor.

A. The nozzle inserts

BORCAL

In two test, each taking 2 seconds but with different types of propellants CK50 and CK52 respectively, BORCAL was shown to wear out strongly into a diverging nozzle throat (clock form). In the test with CK50 a glassy layer with some little spheres (= 10μm), consisting of Al, Si and O was detected with EDX at the nozzle surface (probably an aluminosilicate), while in the case of CK52 (containing Al-particles for higher gas temperature), a layer of crystalline Al₂O₃ could be detected, probably originating from the propellant. For the bulk of this insert material, the oxygen peak in the EDX diagram for both propellant types indicated that a part of the Al-infiltrant was oxidized. From the microanalysis it is not clear if the BORCAL material has eroded by wear and/or oxidation. Tests with BORCAL were discontinued thereafter.

TIBAL

The inserts functioned properly in tests with both type of propellants, as can be seen from the pressure-time trace and the thrust-time trace (Figure 9(a) and (b)) shown for the nozzle with a TIBAL insert in the 3 s CK50 test. Two short duration tests were performed with TIBAL, one using CK50 and the other using the CK52 propellant. They were followed by longer duration tests (6 s). In Table II the results of the mass and diameter measurements before and after the tests are shown.

The decrease in diameter is due to the creation of a deposition layer. From XRD measurements Al₂O₃ has been found as a crystalline phase in this layer, while the occurrence of O, Al and Si peaks in the EDX diagram indicates that also (alumino)silicates have been formed. In the 6 s test with CK52 however, no Si was found in the deposition layer.
The bulk of the TIBAL material still consists of Al and TiB$_2$ as crystalline phases, as was seen from XRD measurements. Also by EDX no other element apart from Al, Ti and B has been detected.

From the diameter values after removal of the deposition in the short duration test (see Table II), one can conclude that with CK50, the diameter was constant, indicating no erosion. The diameter increase in CK52 could mean that first some erosion has taken place (e.g. oxidation of the boride) followed by a deposition of alumina (from the propellant), which protected the nozzle from further erosion.

For CK50 in the 3 s test, an increase in combustion chamber pressure is found, which seems to level off. Under the assumption of a perfectly steady burning propellant, this pressure increase can be related to the decrease in nozzle throat diameter. Given the diameter decrease from 6.43 mm to 6.16 mm and the pressure at the beginning, 5.35 MPa, the end pressure is calculated to be 6.27 MPa. This agrees well with the actual pressure measured: 6.24 MPa. Also for CK52, pressure and thrust seem to level off. This was further confirmed in the longer duration tests, which showed that for both CK50 and CK52 pressure and thrust approach a constant value after about 2 s.

Table II: Mass and diameter measurements of TIBAL inserts. The values inside brackets indicate the diameter after removal of the deposition layer.

<table>
<thead>
<tr>
<th>propellant &amp; test-duration</th>
<th>mass before test [g]</th>
<th>mass after test [g]</th>
<th>diameter before test [mm]</th>
<th>diameter after test [mm]</th>
<th>diameter without deposition [mm]</th>
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</thead>
<tbody>
<tr>
<td>CK50 3 s</td>
<td>10.7</td>
<td>11.3</td>
<td>6.43</td>
<td>6.16</td>
<td>6.40</td>
</tr>
<tr>
<td>CK52 1.8 s</td>
<td>11.2</td>
<td>11.2</td>
<td>6.43</td>
<td>6.06</td>
<td>6.58</td>
</tr>
<tr>
<td>CK50 6 s</td>
<td>10.9</td>
<td>10.9</td>
<td>6.44</td>
<td>6.37</td>
<td>-</td>
</tr>
<tr>
<td>CK52 6 s</td>
<td>11.0</td>
<td>11.1</td>
<td>6.44</td>
<td>6.04</td>
<td>-</td>
</tr>
</tbody>
</table>
B. Complete TIBAL nozzles

The complete TIBAL nozzles were tested in the test burner, in which they functioned well [8]. In Table III the results of the burner tests are presented. Nozzle 188 (I), was tested with CK52 for 2.5 s. After the test a deposition layer consisting of Al₂O₃ and some amorphous (alumino)silicates, as in the insert tests was observed. The nozzle showed to be intact, and erosion was found to be small (0.07 wt%). Here the increase in throat diameter (0.2 mm) was compensated by the formation of a small oxygen layer. Pressure and thrust were of the right order of magnitude (see Fig. 10, only chamber pressure is shown here) and seemed to approach a constant value. In order to confirm this behavior, longer duration tests were planned. Since the nozzle was still intact, it was decided to put it to test for a second time (sample 188(II) from Table III). Here the deposition layer was removed mechanically. This second test confirmed the good functioning of the nozzle: after about 2 s, pressure and thrust reached a constant value of about 6 MPa (see Fig. 10 for the chamber pressure).

![Figure 10. Measured chamber pressure against test duration for TIBAL nozzle (188) with the CK52 propellant.](image)

The other nozzles were tested with the CK50 propellant for a relatively long test duration of 7 seconds. Test nozzle 189 had a relatively large throat diameter as a consequence of the dimensions of the mandrel used in its manufacturing. This large diameter reduces the pressure in the test chamber and hence the burning rate of the propellant. This creates relative mild test conditions (however also a longer test duration) as was anticipated. Test nozzle 196, on the other hand, had a too small throat diameter (for the same reason), and it was tried to increase it by drilling, but during this process the nozzle was probably damaged. During the burner test a part of the nozzle broke off, creating a larger throat diameter with the same test results as with nozzle 189.

<table>
<thead>
<tr>
<th>sample nr.</th>
<th>propellant type</th>
<th>test duration (s)</th>
<th>mass before test (g)</th>
<th>mass after test (g)</th>
<th>diameter before test (mm)</th>
<th>diameter after test (mm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>188 (I)</td>
<td>CK52</td>
<td>2.5</td>
<td>235.08</td>
<td>235.39 (234.9)</td>
<td>6.77</td>
<td>(6.98)</td>
</tr>
<tr>
<td>188 (II)</td>
<td>CK52</td>
<td>6</td>
<td>234.80</td>
<td>236.15</td>
<td>6.98</td>
<td></td>
</tr>
<tr>
<td>189</td>
<td>CK50</td>
<td>7</td>
<td>236.15</td>
<td>234.80</td>
<td>7.29</td>
<td>7.32</td>
</tr>
<tr>
<td>196</td>
<td>CK50</td>
<td>7</td>
<td>214.22</td>
<td>211.82</td>
<td>6.22</td>
<td></td>
</tr>
</tbody>
</table>
From the tests on TIBAL nozzles it can be concluded that this material has functioned properly using the CK52 propellant, showing no decrease in combustion pressure or thrust. This is probably due to the combination of the short test durations and the relatively high thermal conductivity of the TIBAL material, preventing too high temperatures to develop in the nozzles. Also the in situ forming of a protective layer, mainly consisting of Al₂O₃, has played a role in protecting the integrity of the nozzles.

It has still to be confirmed that TIBAL can also be used for the more corrosive (but less erosive) CK50 propellant, though the TIBAL insert tests are a good indication that this will in fact be the case.

8.4 CONCLUSIONS

The near-net-shape forming possibilities of shock compaction in the cylindrical configuration have been demonstrated. During shock compaction a hole can be formed in the compact by using a polymer mandrel inside the powder. Due to the powder compaction an impedance trap is formed in which the polymer decomposes due to pressure build-up and excessive energy dissipation.

Using an aluminum mandrel, the powder (B₄C or TiB₂) was formed around the shape of the mandrel. The remaining porosity of the formed compact could be eliminated in a subsequent infiltration process in which the cermets B₄C-Al and TiB₂-Al were formed, designated by BORCAL and TIBAL, respectively. In this way, crack-free fully dense nozzles and nozzle inserts have been manufactured.

Furthermore, the nozzles and nozzle inserts have been subjected to burner tests using solid rooked propellants. In these tests the materials had to resist extreme conditions formed by the combination of an extremely large thermoshock, very high temperatures, and erosion and attack by particles and aggressive gases flowing at a supersonic speed. Both cermets were tested first as nozzle inserts in a modular metallic nozzle. Here, the BORCAL nozzle insert showed severe erosion and was excluded from further testing. The TIBAL nozzle inserts functioned well in the tests using two type of propellants. Several complete nozzles of this material have been manufactured and subsequently tested in the test burner. In these tests the TIBAL nozzles functioned well using the CK52 propellant; a test with the right throat diameter will still have to be performed to demonstrate the functioning of the TIBAL nozzles using the CK50 propellant.

Acknowledgments

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References

Chapter 9

CONCLUSIONS

More understanding of the processes occurring during the shock compaction process has been obtained both from information collected from literature, as described in Chapter 2, and by experimental work supported by computer simulations of the process. Especially, the flash X-ray photographs that were taken during the explosive events proved to be a valuable research tool. The photographs can be easily compared with the computer simulations, since they show the position and form of both the detonation and shock waves that occur in an experiment. Here, the experimental work has been restricted to the direct cylindrical configuration. The following results have been obtained:

Using the standard (one-layer) configuration, where a single type of explosive generates a shock wave in the powder through a grazing detonation, it has been shown that it is possible to compact powder mixtures to often unique composite materials. Due to the fact that the shock compaction can be performed at room temperature and that the bulk temperature remains low, generally no reactions, crystallization or grain growth take place. The experiments performed with Hydroxyapatite and PMMA powder mixtures demonstrated the possibility to fabricate ceramic-polymer composites (ceramers) with a high fraction of ceramics. This could be an interesting bio-medical (bone-substitute) material, especially if the bio-inert PMMA would be replaced by a more bio-degradable polymer in order to fabricate a fully bio-active material.

Cracking and other compact failures have prevented the commercial application of the shock compaction process. Due to the increased knowledge of the reflection and refraction of shock waves, the failure mechanisms of some types of cracking typically occurring in the cylindrical configuration could be explained. With this knowledge, the failures (spiral, transverse, radial cracks, and the irregular reflection or Mach-stem) could be avoided effectively, though a full density of the compacts has not been achieved. The shock compaction of the Ti-B₄C mixture demonstrated that within spiral cracks locally high temperatures and strain rates occur, which can initiate a chemical reaction.

A fixation device has been developed that keeps the powder container at a fixed position during and after the shock compaction process. This enables one to perform electrical measurements during and right after the explosive event and helps to recover the compact intact, since it does no longer fly freely causing compact damage upon impact with the ground or surrounding walls.

The fixation device was used in the development of a time-resolved measuring technique for the temperatures occurring during the shock compaction of powders in the cylindrical configuration. In order to obtain the extremely short response time required to perform time resolved measurements, the powders to be compacted were used to comprise the active thermocouple components. Copper and constantan powders were used in the development of this measuring technique. In a later stage it was thought that ceramic powders could comprise the active components of the powder thermocouple.
A patent application has been filed for the fabrication process of cermet and ceramers that use a (capillarity-driven) liquid infiltration of the remaining pores after shock compaction of a ceramic powder. As far as known by the author, no use has been made of these pores before. Here, the cerments BORCAL and TIBAL are just examples of a whole class of composite materials. The infiltration with liquid aluminum proved to be reactive in the case of a B₄C compact and non-reactive with TiB₂. Both materials are dense and strong and show high electrical and heat conductivities. The BORCAL material has a rather low density (2.55 g/cm³) and is currently investigated as a lightweight armor material, while the TIBAL material has a high heat conductivity and has shown to withstand large thermoshocks. Both cerments can be machined by spark erosion (electric discharge machining) due to their high electrical conductivity.

The shock compaction of TiB₂ powders changed the chemical composition of the particle surfaces, as was apparent from the difference in aluminum infiltration behavior of shocked and unshocked TiB₂ powder. X-ray photoelectron spectroscopy (XPS) of the particle surface of unshocked TiB₂ powder showed BN to be present, known to be non-wetting towards liquid aluminum. The XPS results on shocked TiB₂ showed almost no BN to be present at the particle surfaces enabling a good wetting of the TiB₂ particles with aluminum. This change in average particle surface composition can be explained by the creation of fresh particle surface due to micro-cracking (fragmentation) of the particles. However, also the occurrence of some unique shock wave phenomenon cannot be excluded.

The possibility of forming objects by shock compaction of powders has been investigated. Different shaped mandrels of two materials have been used. When centered in the powder container, the polymer (PVC) mandrels decomposed during the shock compaction process leaving a hole in the center of the compact. Preshaped aluminum mandrels were centered in a thick-walled stainless steel tube filled with TiB₂ powder, in order to fabricate inserts and complete nozzles of TIBAL. Here, surface modification, forming, and compaction of TiB₂ powder took place in one process. The TIBAL nozzles and nozzle-inserts functioned well during burner tests with two solid rocket propellants. In these tests the BORCAL material suffered from severe erosion.

High shock wave pressures are required for the compaction of materials with high hardness, like ceramic monoliths. The explosives with a high detonation pressure (and velocity) have a small pulse duration, generating intense rarefaction waves which increase the chance on macro-cracks. The standard (one-layer) configuration, in which detonation pressure and energy travel by in a grazing detonation front, has been improved to a more efficient two-layer configuration, in which an explosive is surrounded by an explosive layer with a higher detonation velocity. This new configuration generates higher pressures, through an oblique and converging detonation wave in the explosive with lower detonation velocity with the benefit of a long pulse duration. The configuration reduces the chance of radial cracks, since it helps to reduce the intensity of rarefaction waves. Here, also the reflection of an oblique detonation wave at the confinement of the explosive can be used. In this alternative two-layer configuration the faster detonating explosive layer is situated directly in contact with the powder container. The new configurations can also be used in indirect cylindrical configurations, in which the detonation accelerates a flyer-tube that strikes the powder container.

The starting relative density of the powder is the main parameter in the shock compaction process. A high starting density will result in a compact with a higher final density, reduces the strain necessary to reach the final density and increases the shock impedance of the powder, enabling a higher pressure of the initial shock wave. The starting powder should have
a homogeneous density distribution in order to prevent inhomogeneous compaction and transverse cracks. The importance of the starting density implies a large role for the static (pre)compaction technique which is used and the particle size distribution of the powder. Furthermore, it is shown that knowledge of the static compaction mechanisms is important since the same mechanisms are shown to occur within the shock front during shock compaction of a powder.

The consolidation mechanisms occurring during the shock compaction process, which are required in order to obtain strong and dense compacts, are still not very clear. It is expected that future time-resolved temperature measurements of the particle surfaces during shock wave propagation will lead to answers about whether surface melting occurs in ceramic powders or not. This is particularly interesting for the hard and brittle ceramic materials, since their covalent type of bonding does not allow a large amount of strain, contrary to materials with a metallic bonding type. Without melting of particle surfaces and plastic deformation it is unlikely that a ceramic monolith can be consolidated. They probably require a hot compaction technique that keeps the material above the ductile-brittle transition point during its shock compaction. This can, for example, be accomplished by making use of the combination of self-sustained high temperature synthesis (SHS) and dynamic compaction of the reaction products, while they are still hot.

As was shown in this work compaction of powder mixtures with a ductile component is possible at room temperature. Using powders as starting material and using room temperature (low bulk temperature) processing enables one to fabricate very different composites due to a very large freedom of mixture. Unique composites and materials with unique properties due to a metastable structure or composition as well as functionally graded materials can be compacted by the shock compaction technique.

The cylindrical configuration is a rather simple and economical one, capable of compacting bulk materials since it is possible to scale up the process. However, any commercial application of the process requires that either a unique shock wave bonding mechanism is used, or that a unique material that can not be processed to the same product in a more conventional way.

Examples of unique shock wave phenomena are the occurrence of micro-kinetic energy within the shock front in a powder (chapter 2) and the extremely heterogeneous temperature distribution followed by a very high cooling rate to a rather low bulk temperature (chapter 5).

Examples of unique materials, in this respect, are the consolidation of amorphous and other meta-stable materials, as obtained for example by rapid solidification or mechanical alloying, and composite materials of ceramics and metals with polymers.

This work demonstrated that even within the limitation of room temperature operation, using only the direct cylindrical configuration, ceramics, polymers as well as metals can be compacted and macro-cracking of the compacts can be effectively prevented.

There are indications that industrial interest has been attracted for this promising compaction technique. From the increase in use of high technology materials today, it is expected that this compaction technique will play its role in materials processing.
Dynamic, explosive and shock compaction are all terms for the process in which a shock wave is used to compact a powder to a compact with a high relative density and strength. Here, the shock waves have been generated by the detonation of an explosive in direct contact with a metal tube. The tube contains the ceramic powder to be compacted, or a mixture of powder materials, and is surrounded by an explosive layer. This configuration is the standard cylindrical direct shock compaction method.

After a theoretical investigation to the field, several failure mechanisms are described that result in various compact failures in the cylindrical configuration. Countermeasures that can be taken are presented and demonstrated by experimental results and computer simulations of the process.

Flash x-ray photographs taken during explosive compaction experiments, show the form and velocity of the shock- and detonation fronts.

A reusable fixation device has been developed that prevents the compact from flying freely, which prevents additional cracking to occur and makes electrical measurements during and right after the compaction process possible. It has been used in the development of a thermocouple method for the measurement of the temperature of the powder particles. In order to obtain a fast response, necessary to follow the extremely fast temperature fluctuations of the process, here the powders to be compacted are used as the active components of the thermocouple.

The main starting materials used were TiB₂ and B₄C powders, in an optimized particle size distribution, that belong to the very hard ceramics due to their strong covalent type of bonding. This makes their compaction difficult and using the standard cylindrical configuration, a relative density of 85 % of the theoretical maximum was obtained. By infiltration of their remaining pores in an oven after the compaction process, the fully dense and strong cermets TiBAL and BORCAL have been fabricated. Both have a high ceramic fraction (>80 vol%) and therefore a high hardness, however they proved to be machined easily by spark erosion (electric discharge machining) due to their low specific electrical resistance. Also some other physical properties of the cermets have been measured.

Furthermore, composites have been fabricated by the compaction of B₄C-Ti powder mixtures, in which a reaction to TiB₂ occurred locally in spiral cracks. Hydroxyapatite-PMMA composites have been compacted and they are expected to be further developed for future biomedical application. No reactions or decomposition of the polymer occurred in the compaction process.

Also the possibility of near-net shaping by shock compaction of powders has been investigated. Here, mandrels of PVC and aluminum have been used. The latter can be used also in the infiltration process as the Al source. In this way inserts and complete nozzles of TIBAL have been fabricated and tested in a testburner for solid rocket propellants. This proved the possibility to fabricate near-net shaped axis-symmetrical objects, while the TIBAL materials withstood the extreme material conditions during the burner tests.

The shock compaction of especially pure ceramics requires a very high shock wave pressure. Explosives that can generate these pressures have a very short pulse duration. Therefore they
introduce release waves with high intensity, which upon their interaction lead to tensile stress and hence radial cracks. In order to be able to generate shock waves with both high pressure and long pulse duration, a new cylindrical configuration has been designed and tested. The configuration uses two explosives layers that both surround each other and the powder container. When the explosive with a high detonation velocity is surrounding the second layer, an oblique detonation wave is generated in the later. Due to this change in detonation angle and the convergence of the detonation wave, a shock wave with high pressure and long pulse duration is generated in the powder. When the faster detonating explosive is surrounded by the other, a diverging detonation wave is generated in the second, and its reflection on the confinement of the explosives can be used to reduce the intensity of the release waves in the compact and hence the chance of radial cracks.
SAMENVATTING

Dynamisch, explosief en schok verdichten zijn termen voor het proces waarbij door middel van een schokgolf een poeder tot een compact wordt verdicht welke een hoge relatieve dichtheid en sterkte heeft. In dit werk werden de schokgolven door de explosie van een springstof opgewekt. Hierbij zat het te verdichten keramische poeder (of composiet materiaal) in een metalen buis, die omringd werd door de laag springstof. Dit is de standaard cilindrische verdichtingsmethode. Na een theoretische inwijding in het vakgebied, worden de breukmechanismen behandeld die verantwoordelijk zijn voor verschillende macro scheuren in het compact. Vervolgens worden mogelijke tegennatregelen aangegeven en gedemonstreerd middels experimentele voorbeelden en computer simulaties van het proces, ter voorkoming van scheuren en andere problemen.

Door het nemen van röntgenflits foto's tijdens het verdichtingsproces, werden de vorm en snelheid van de schok- en detonatiefronten worden vastgesteld.

Door de ontwikkelde fixeerstaaf wordt het vrij rondvliegen van de explosief verdichte buis voorkomen, hetgeen additionele scheuren voorkomt en elektrische metingen tijdens en direct na het proces mogelijk maakt. Dit laatste is aangewend bij de ontwikkeling van een thermokoppel methode voor het meten van de temperatuur van de poederdeeltjes. Voor een voldoende snelle respons voor de zeer snel variërende temperatuur in het proces, worden hierbij de te verdichten poeders (koper en constantaan) zelf als aktief element van het thermokoppel ingezet.

De voornaamste uitgangs materialen waren TiB₂ en B₄C poeders (met een geoptimaliseerde deeltjesgrootte verdeling) die tot de zeer harde keramieken behoren door hun sterk covalente binding. Hierdoor is hun verdichting erg moeilijk en werd met de standaard methode een dichtheid van ongeveer 85% van de theoretisch maximale behaald. Door de overgebleven poriën na het verdichtingsproces voor een capillaire aluminium infiltratie te benutten, werden de volledig dichte en sterke cermets TIBAL en BORCAL verkregen. Beide hebben een hoge fractie (>80 vol%) keramiek en daardoor een grote hardheid, maar zijn door hun lage specifieke elektrische weerstand goed met vonkverspanen te bewerken geblekken.

Tevens zijn composieten gefabriceerd door het B₄C te mengen met Ti-poeder, hierbij traden spiraalscheuren in het compact op die plaatselijk een reactie tot TiB₂ initieerden. Hydroxylapatiet-PMMA composieten werden verdicht en kunnen wellicht ten behoeve van biomedisch toepassingen verder worden ontwikkeld. Tijdens het schokverdichten traden geen degradatie, reacties of onteden van het polymeer op.

Ook zijn de vormgevingsmogelijkheden onderzocht, teneinde de poeders niet alleen te verdichten, maar ook van een productvorm te voorzien. Hierbij zijn kernen van het polymeer PVC en van aluminium gebruikt. Deze laatste kunnen nadien tevens als infiltratie materiaal worden gebruikt. Hiermee zijn inserts en volledige nozzels van TIBAL gefabriceerd en vervolgens in een testopstelling voor raket stuwstof verbranding getest. Hierbij bleek het vormgeven van as-symmetrische produkten mogelijk, en het TIBAL materiaal bleek de extreme materiaal omstandigheden van de tests te doorstaan.
Het verdichten van vooral puur keramiek vereist een zeer hoge schokgolf druk. De springstoffen die deze druk kunnen leveren hebben en zeer korte pulsduur. Hierdoor worden in het compact na schokgolf passage tevens sterke ontspanningsgolven geïnitieerd, welke bij hun interactie tot trekspanningen en daardoor scheuren leidt. Om toch een hoge schokgolf druk, met behoud van de langere pulsduur te bereiken, is er een nieuwe cilindrische configuratie ontworpen en getest. In deze nieuwe configuratie wordt een schuin detonatie front in een springstof met een lagere detonatiesnelheid geïnitieerd door een omringende laag springstof welke een hoge detonatiesnelheid heeft. Door deze hoeksverandering t.o.v. de buiswand en het convergeren van het schuine detonatie front wordt een sterkere schokgolf in het poeder gegeneereerd. Door de lange pulsduur wordt de intensiteit van de ontspanningsgolven verminderd en daarmee de kans op radiële scheuren. Bovendien is met deze twee-laags configuratie de druk d.m.v de springstoffen en de mate van detonatie convergentie eenvoudig te sturen.
NAWOORD

Dit promotieonderwerp is het resultaat van een samenwerking tussen de vakgroep Anorganische Chemie en Thermodynamica (ACT) van de TU Delft en het Prins Maurits Laboratorium van TNO te Rijswijk. Bij het laatste is het onderzoek uitgevoerd aangezien het werken met explosieven aan strikte veiligheidsnormen en speciale faciliteiten is gebonden.

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Erik Carton, dd. 8 december 1997
CURRICULUM VITAE


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