

## Ferrous Phase Transformation Kinetics: A Combined Dilatometric-Calorimetric Approach

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### Abstract

Dilatometry and Differential Thermal Analysis (DTA) are often used to measure the kinetics of the phase transformations from austenite to ferrite and pearlite in C-Mn steels and other lean construction steels. It is, however, by no means straightforward to accurately obtain the relative amounts of austenite, ferrite and pearlite at each temperature from these measurements. The analysis of the dilatation curve is hampered by the changing atomic volume of the austenite due to carbon enrichment due to the formation of ferrite, which is poor in carbon. On the other hand, the results of the DTA analysis are significantly influenced by thermal-lag effects. This paper gives an overview of these two techniques for the determination of transformation kinetics. The importance of a combined analysis is stressed.

A PROFOUND KNOWLEDGE of the kinetics of the decomposition of austenite is essential for the production of high-quality homogeneous steel strips. Therefore a continuing endeavour to improve models is going on (e.g. [1,2]). In order to validate theoretical models, the development of the volume fraction of ferrite and pearlite as a function of time and temperature during the transformation as predicted by those models have to be compared to the fractions transformed as determined experimentally. Two techniques often used to obtain kinetic data are dilatometry and Differential Thermal Analysis. To obtain an accurate determination of the fraction as a function of time, the measured data should be meticulously interpreted.

Dilatometry is based on length changes that occur due to phase transformations. In the most frequently used

interpretation method it is assumed that the atomic volumes of the different phases have a linear temperature dependence. Compositional changes of the different phases, which occur due to partitioning, and which result in changes of the atomic volumes, are neglected. However, since during the austenite-to-ferrite transformation the remaining austenite enriches in carbon, the assumption on which this simplified dilatation analysis is based is not completely valid. For a correct analysis of the dilatation curve, the specific volumes of the different phases have to be taken into account.

In Differential Thermal Analysis (DTA) one measures, mostly in a cooling experiment, the temperature difference between a sample and a reference, caused by the transformation of the sample. During the transformation the transformation enthalpy is released. The DTA can thus be used to gain insight in the transformation kinetics. Due to the thermal resistance between the sample and the thermocouple and the heat capacity of the apparatus, however, any heat release results in a temperature effect that is spread out in time. This instrumental broadening is most commonly denoted as thermal lag [3]. In practice the effects of thermal lag are often neglected in the analysis of DTA results.

In this paper the two experimental techniques, dilatometry and Differential Thermal Analysis, will be discussed both from a theoretical and an experimental point of view. A comparison between the fractions transformed determined by either of both methods and the actual fraction transformed is made. The effects of simplified analyses will emerge. Furthermore the potential of a combined analysis is stressed.

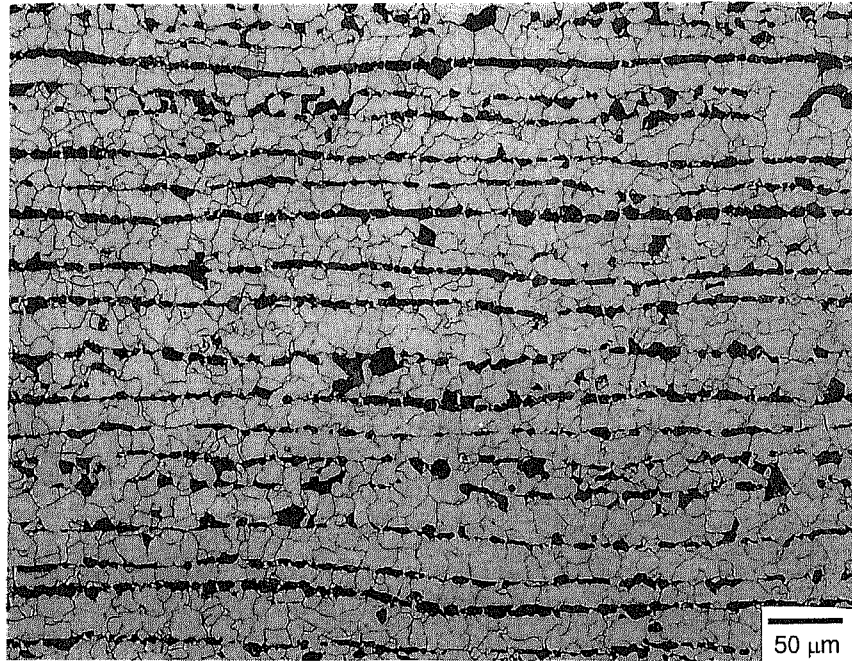


Fig. 1 - Ferrite/pearlite microstructure obtained after austenitising for 20 minutes at 1273 K and cooling down at 20 K/min.

## Experimental

The measurements discussed in this paper have been performed on a commercial steel, kindly provided by Hoogovens Research, containing as most important alloying elements, 0.136 wt.%C, 1.24 wt.%Mn and 0.02 wt.%Nb. The specimen were austenitised at 1273 K for 20 minutes before cooling down at a constant rate of 20 K/min. Figure 1 shows the ferrite/pearlite microstructure at the end of the experiment. From metallographic examination the fractions ferrite and pearlite are determined to be respectively 0.82 and 0.18.

## Differential Thermal Analysis

**Background.** A Differential Thermal Analyser determines the temperature difference between two identical cups positioned in a single oven, which is cooled at a constant cooling rate. The presence of a sample in one of the two cups results in a temperature difference between the two cups, which is proportional to the heat capacity of the sample. When the sample is steel, and in a certain temperature range transforms from austenite to ferrite, an additional heat flow, the transformation enthalpy, results in a larger temperature difference in the transformation range. The apparent specific heat  $\Phi$  at each temperature is given by

$$\Phi = f^\gamma \cdot c_p^\gamma + f^\alpha \cdot c_p^\alpha + f^p \cdot c_p^p + \frac{df^\alpha}{dT} \cdot \Delta H^{\gamma/\alpha} + \frac{df^p}{dT} \cdot \Delta H^{\gamma/p}, \quad (1)$$

where  $c_p^i$  and  $f^i$  are the specific heat and the volume fraction of phase  $i$ , respectively, and  $\Delta H^{\gamma/i}$  is the transformation enthalpy for the  $\gamma \rightarrow i$  transformation.  $\gamma$ ,  $\alpha$  and  $p$  stand for austenite, ferrite and pearlite, respectively. Since only these three phases occur, at any moment the relation  $f^\gamma + f^\alpha + f^p = 1$  holds.

The thermocouple attached to the sample cup does however not register the temperature instantaneously. A thermal resistance exists between the sample and the thermocouple. The experimentally observed heat capacity  $\Phi_m$  is therefore the actual apparent heat capacity  $\Phi$  smeared out in time according to [3]

$$\Phi_m = \Phi - \tau \cdot \frac{d\Phi_m}{dt}, \quad (2)$$

where  $\tau$ , the characteristic delay time, is given by the product of the resistance and the heat capacity of the system. A typical value for a standard DTA is  $\tau = 9$  s [4].

**Experiment.** The calorimetric data were obtained with a Perkin Elmer Differential Thermal Analyser. The sample measurements were corrected for instrumental influences by performing "baseline" measurements, i.e. experiments

using two empty cups. A measurement on sapphire is used as a reference to convert the observed temperature difference  $\Delta T_{\text{sample}}$  to the apparent specific heat by applying the ratio method [5],

$$\Phi_m = \frac{m_{\text{sapphire}}}{m_{\text{sample}}} \cdot \frac{\Delta T_{\text{sample}}}{\Delta T_{\text{sapphire}}} \cdot \Phi_{\text{sapphire}}, \quad (3)$$

in which  $m_{\text{sample}}$  and  $m_{\text{sapphire}}$  are the sample and sapphire masses, respectively. The specific heat of sapphire,  $\Phi_{\text{sapphire}}$ , is known as a function of temperature from literature [6]. The thus obtained specific heat for the steel under investigation is depicted in figure 2.

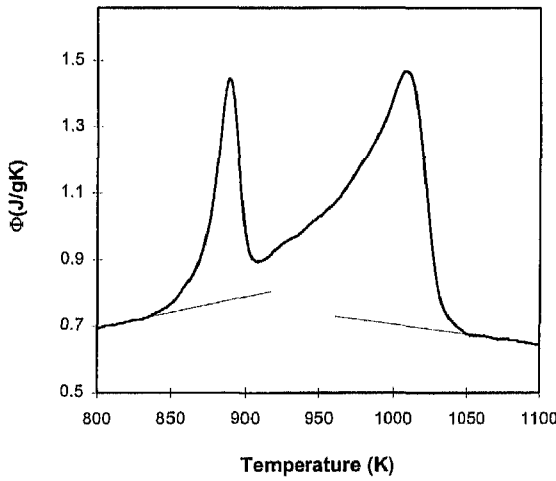


Fig. 2 - The experimental specific heat for the C-Mn-Nb steel. The straight lines give the extrapolations of  $c_p$  for the initial and the final phases.

**Analysis.** To obtain the fractions ferrite, pearlite and austenite as a function of temperature, Eq. 1 has been solved at each temperature. A correction for the contribution of the thermal lag is not included in the analysis in order to show its effect. Since there is no direct way to analyse the simultaneous formation of two successive steps. In the high-temperature range (that is: for temperatures higher than that of the onset of the pearlite peak at approximately 900 K) one can assume  $f^p = 0$ . For lower temperatures  $f^\alpha$  is assumed to be constant. In general, the pearlite start temperature is easily recognised in the DTA curve (see figure 2). In order to solve Eq. 1, the  $c_p$  values and the  $\Delta H$  values have to be known. The specific-heat values of the different constituents are determined by extrapolating the experimental data from high and low temperatures (see figure 2). The transformation enthalpies used for the calculation are calculated with the thermodynamical database programme Thermocalc. These enthalpies are

scaled in order to get a total fraction transformed austenite of 1. Furthermore there is an intrinsic problem resulting from Eq. 1. The change in ferrite or pearlite fraction,  $df^i/dT$ , can only be determined if  $f^\alpha$  and  $f^p$  are known. Therefore a sequential analysis from the high temperature region downwards is performed. Starting from  $f^\alpha = f^p = 0$  at high temperature, at each temperature interval the change in the fractions,  $df^i/dT$  is calculated from Eq. 1, using the previous values for  $f^\alpha$  and  $f^p$ .

## Dilatometry

**Background.** All substances have their own specific lattice parameters and their own linear expansion coefficients. Dilatation measurements and their interpretation are based on these two facts. A phase change will in general result in a density change, and therefore if during heating of a sample a phase transformation occurs it will give rise to an observable dilatation that is different from the linear expansion effect.

As previously described in a theoretical treatment on this subject [7] the atomic volume  $V$  averaged over the whole sample can be written as

$$V(T) = f^\gamma \cdot V^\gamma(T, x_C^\gamma) + f^\alpha \cdot V^\alpha(T) + f^p \cdot V^p(T), \quad (4)$$

in which  $V^i$  denotes the atomic volume of phase  $i$  and  $x_C^\gamma$  is the carbon content of the austenite. To calculate the fractions austenite, ferrite and pearlite from experimental data using Eq. 4 assumptions have to be made, as was the case in the analysis of the DTA data, considering the temperature ranges during which ferrite and pearlite form. Using the same assumptions as were made for the analysis of the DTA data, analytical expressions can be drawn up for the fraction fractions ferrite and pearlite:

$$f^\alpha = \frac{V_0 \cdot \left( \frac{\Delta V}{V_0} + 1 \right) - V^\gamma}{V^\alpha - V^\gamma}; \quad (5a)$$

$$f^p = \frac{V_0 \cdot \left( \frac{\Delta V}{V_0} + 1 \right) - V^\gamma + f^\alpha \cdot (V^\gamma - V^\alpha)}{V^p - V^\gamma}. \quad (5b)$$

In these equations  $\Delta V = V - V_0$  is the experimentally observable quantity, with  $V_0$  the atomic volume at room temperature.

**Experiment.** The dilatation measurements were performed on a Bähr deformation type dilatometer. A Pt-10%Rh/Pt-thermocouple was spot-welded onto the surface of the sample, which was 10 mm long and had a diameter of 3 mm. Anvils of fused silica were used. To correct for instrumental errors reference measurements were performed on a platinum sample. Using the starting length of the platinum sample and its linear expansion coefficient  $\alpha$ , given by

$$\alpha = 0.0013 \cdot 10^{-6} \cdot T \text{ K}^{-2} + 8.568 \cdot 10^{-6} \text{ K}^{-1}, \quad (6)$$

the length of the platinum specimen at each temperature can be calculated. The correction factor as a function of temperature follows from the comparison of the calculated and the measured platinum length at each temperature.

In the experiment the relative length change,  $\Delta L/L_0$ , is determined. This quantity is converted into the relative volume change  $\Delta V/V_0$  by

$$\frac{\Delta V}{V_0} = 3 \cdot \frac{\Delta L}{L_0} \quad (7)$$

Since  $\Delta L/L_0$  is small (usually less than 1%) the second and third order terms have been neglected in deriving Eq.7.

The dilatation curve, after correction for instrumental errors, is presented in figure 3.

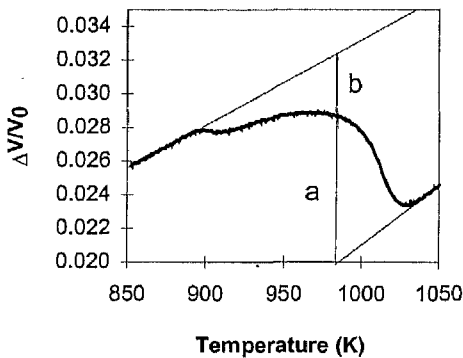


Fig. 3 - The dilatation curve and the extrapolated dilatation lines for the initial and final phases. The fraction transformed austenite is given by  $a/(a+b)$ .

**Analysis.** It is well known that during the first stages of the austenite-to-ferrite phase transformation of Fe-C alloys the remaining austenite enriches in carbon due to lower carbon solubility of ferrite. As was shown by Onink *et al.* [8] the lattice parameter of austenite is strongly dependent on the carbon concentration. In figure 4 the significance of the concentration dependence is

illustrated. The atomic volumes of austenite, ferrite and pearlite are depicted. For the atomic volume of pearlite a constant ratio between the ferrite and cementite volume fractions is assumed (0.86/0.14). The austenite volume is calculated taking into account the carbon enrichment of the austenite due to the ferrite formation occurring in the temperature range between 1020 K and 900 K. It is evident that if the changing carbon concentration of the austenite is neglected –which would correspond with an extrapolation from the high temperature regime to lower temperatures– a totally different austenite atomic volume results.

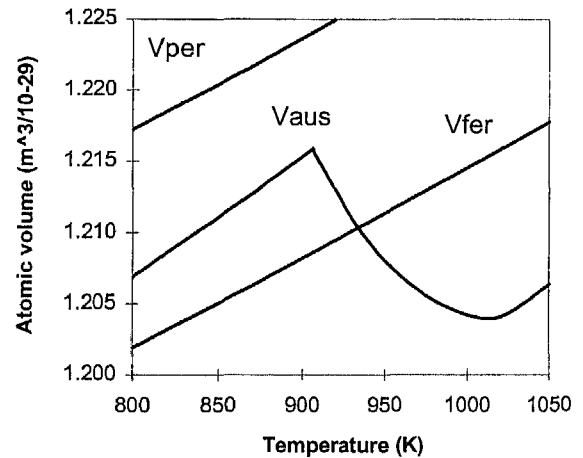


Fig. 4 - The atomic volume of austenite, ferrite and pearlite as function of temperature, taking into account a changing carbon concentration of the austenite.

In order to come to a correct analysis, Eqs. 5 should be solved for each temperature, taking into account the effect of the carbon enrichment of the austenite. However two problems occur.

First, to calculate  $V^\gamma$  the carbon concentration of the austenite should be known. The austenite enrichment however depends on the austenite and ferrite fractions present, according to

$$x_C^\gamma = \frac{x_C^0 - f^\alpha x_C^\alpha}{1 - f^\alpha}, \quad (8)$$

in which  $x_C^0$  is the overall carbon concentration and  $x_C^\alpha$  is the carbon concentration in ferrite, which is assumed to be constant. This problem can be solved using an iterative calculation.

The second problem however is more fundamental. As can be seen in figure 4 the  $V^\gamma$  and  $V^\alpha$  curves intersect due to the carbon enrichment of the austenite. From error-analysis theory it follows that

$$\sigma_{f^{\alpha}}^2 = \left( \frac{V_0}{V^{\alpha} - V^{\gamma}} \right)^2 \cdot \frac{\sigma_{\Delta V}^2}{V_0} + \left( \frac{V^{\alpha} + V_0 \cdot \left( \frac{\Delta V}{V_0} + 1 \right)}{(V^{\alpha} - V^{\gamma})^2} \right)^2 \cdot \sigma_{V^{\gamma}}^2 \quad (9)$$

In this equation  $\sigma_j$  gives the experimental inaccuracy for the property  $j$ . Note that the inaccuracy in  $V^{\gamma}$  is due to the inaccuracy in  $f^{\alpha}$  (Eq. 8).

The implication of Eq. 9 is that even a small error in the determined relative volume change results in large errors in the fraction determined. To overcome this problem no satisfactory solution has been found yet.

The currently accepted method of analysing dilatation curves is therefore the best method available. This method consists of extrapolating the dilatation curve from the high and the low temperature regions to the temperature region of interest. The fraction transformed austenite is then determined from the quantities  $a$  and  $b$  indicated in figure 3, according to

$$f^{\alpha} + f^p = \frac{a}{a+b} \quad (10)$$

This corresponds to neglecting the carbon enrichment of the austenite.

It should be noted that at the temperature and stage of transformation at which  $V^{\alpha} = V^{\gamma}$ , the experimental curve of  $\Delta L/L_0$  as a function of temperature displays a maximum.

## Results: Ferrite and pearlite fractions

Figure 2 presents the measured apparent heat capacity curve and the extrapolated ferrite and austenite heat capacities. For the determination of the fractions transformed with Eq. 1, 907 K was used as pearlite start temperature. This temperature corresponds to the minimum in the  $c_p$  vs. temperature curve. The resulting ferrite and pearlite fractions are shown in figure 5. The transformation enthalpies were scaled in order to achieve a final fraction ferrite of 0.82, as observed by light microscopy (figure 1). It was found that  $\Delta H^{f/\alpha} = -52.8$  J/g and  $\Delta H^{p/\alpha} = -85.6$  J/g. Analysis of series of other experiments have shown that although the absolute values of  $\Delta H$  can differ from one measurement to the other, the obtained fractions austenite, ferrite and pearlite reproduce quite accurately.

The result of the determination of the fraction transformed austenite (according to Eq. 10) from the dilatometer experiment is also shown in figure 5.

## Discussion

To compare the results of both methods with the actual fractions, the fractions transformed found in the experiments are used to calculate the dilatation curve. To be able to calculate the dilatation of the transformation curve found from the dilatation measurement a decision has to be made concerning the pearlite start temperature. In this calculation the pearlite is allowed to form as soon as the remaining austenite has reached the eutectoid carbon concentration. Due to the rapid ferrite formation according to the dilatation analysis, this already happens at 959 K. The two calculated dilatation curves and the measured curve itself are depicted in figure 6.

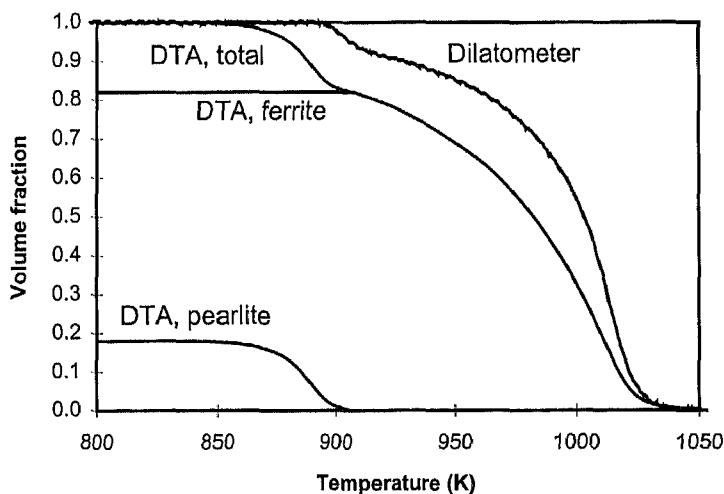


Fig. 5 - Volume fraction of ferrite and pearlite and the total fraction transformed as determined by DTA and dilatometry.

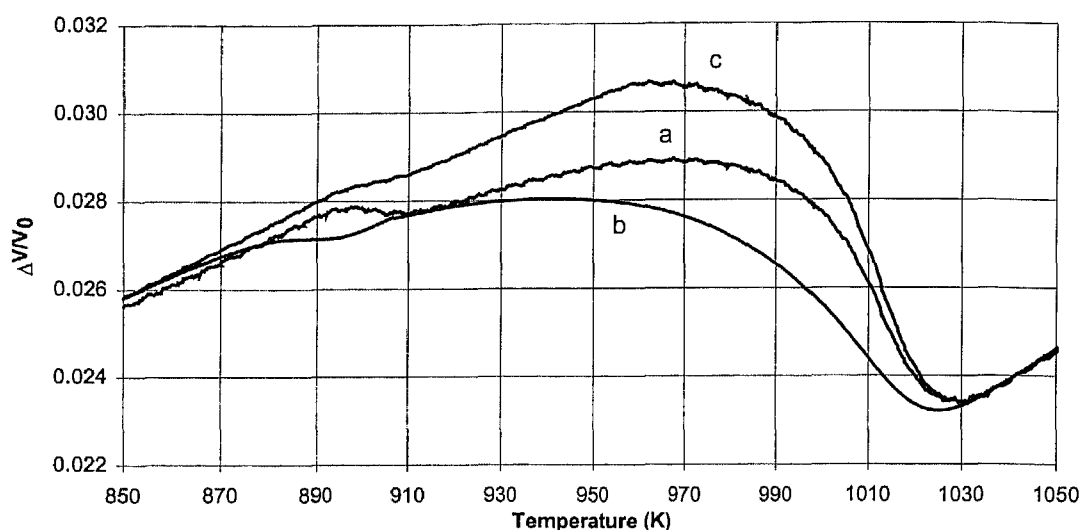


Fig. 6 - a) The experimental dilatation curve. b) The calculated dilatation curve using the ferrite and pearlite fractions obtained by means of DTA (fig. 5). c) The calculated dilatation curve using the fraction transformed obtained by means of dilatometry (fig. 5).

It can be concluded from figure 6 that the transformation rate of the sample as found from the DTA measurement is too low. This is caused by the effect of thermal lag. In the cooling experiment, the heat effects are smeared out in time towards lower temperatures. The ferrite fraction extracted from this measurement is therefore spread out to lower temperatures as well. A more accurate analysis of the DTA data, taking the thermal lag effect according to Eq. 3 into account, is currently being developed.

It is clear that the fraction transformed obtained with the simplified dilatation analysis overestimates the transformation kinetics. This can be understood when bearing in mind that due to the extrapolation of the austenitic dilatation the austenite atomic volume is underestimated. The fraction ferrite determined from Eq. 10 (with  $f^p = 0$ ) will therefore be too large. Another drawback of this dilatation analysis is the prediction of the fractions of ferrite and pearlite that are formed. Looking at the dilatometry curve in figure 5, the point of inflection at approximately 910 K is expected to indicate the start of the pearlite transformation. Although this temperature is in agreement with the minimum in the DTA-curve of figure 2, this would lead to the false conclusion that 95% ferrite is formed. This is caused by the implicit assumption that the atomic volume change of the austenite-to-ferrite transformation equals the atomic volume change of the austenite-to-pearlite transformation.

For an accurate analysis of the dilatometry results it is necessary to develop a more sophisticated approach than the currently used tangent method. A first improvement should be the analysis in two stages; ferrite formation and pearlite formation, taking into account the difference in dilatation due to the pearlite formation and due to the ferrite formation. The border between these two stages can be accurately determined from DTA measurements, because of the high sensitivity of the DTA for the pearlite formation as can be seen in figure 2. Secondly, the carbon content of austenite, which is changing as the transformation proceeds, should be taken into account. In order to overcome accuracy problems due to Eq. 9, additional information on the transformation rate, for instance from DTA measurements, should be incorporated in the analysis.

## Conclusion

Two methods for determining phase transformation kinetics are presented. It is shown that if during a calorimetric measurement the effect of thermal lag is neglected the experimentally determined transformation rates are too low. Furthermore, it is shown that Differential Thermal Analysis is very effective in indicating the pearlite formation. Observing the large deviations between the actual fractions transformed and those obtained by the simplified dilatometry analysis, the need for an improved analysis for partitioning transformations is evident. The improved analysis should

consist of a treatment in two stages, taking into account the carbon enrichment of the austenite.

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### References

1. R.C. Reed, H.K.D.H. Bhadeshia, *Mat. Sci. Techn.* 8, 421-435 (1992)
2. M. Enomoto, *ISIJ Intern.* 32, 297-305 (1992)
3. W.F. Hemminger, H.K. Cammenga, *Methoden der Thermischen Analyse*, Springer-Verlag Berlin, Heidelberg (1989), p. 189
4. G.P. Krielaart, S. van der Zwaag, *Mat. Sci. Techn.* in press (1997)
5. R.F. Speyer, *Thermal Analysis of Materials*, Marcel Decker, Inc. New York (1994), p.80
6. J.D. Cox, *Pure and Appl. Chem* 40, 419-421 (1974)
7. T.A. Kop, J. Sietsma and S. van der Zwaag, to be published in the *Proc. of the Euromat-97 Conference*, Maastricht, 1997
8. M. Onink, F.D. Tichelaar, C.M. Brakman, E.J. Mittemeijer and S. van der Zwaag, *Z.Metallk.* 87, 24-32 (1996)