

Theory and Practice of Computer Modeling of Phase Diagrams for Cast Irons

R.A. Harding

N.J. Saunders

IRC in Materials for

High Performance Applications

University of Birmingham

Edgbaston, Birmingham, ENGLAND

ABSTRACT

Although castings rarely solidify under equilibrium conditions, phase diagrams can be of considerable value for predicting the microstructural changes that occur during and after solidification. Unfortunately, experimentally determined phase diagrams are generally only available for simple binary and ternary alloy systems, which rarely correspond closely to industrial alloys, which may contain 10 or more elements. In recent years, various thermodynamics-based computer models have been developed, which enable phase diagrams to be predicted for multicomponent alloys, but, to date, their application to ferrous alloys has been mainly restricted to steels. In the present work, the existing modeling work has been extended to make it suitable for cast irons containing the following elements: Fe, C, Si, Mn, P, Ni, Cr, Mo, Cu, Nb, V, Ti, N and Mg.

This paper briefly outlines the principles involved in phase diagram modeling and provides examples of their practical application to cast irons. This includes prediction of precipitation hardening in cast irons and of the effects of using titanium-containing steel scrap in the manufacture of flake and spheroidal graphite cast irons. It has been possible to predict the competition between the formation of different carbides and graphite, the influence of the principal elements on the various carbide-graphite reactions, and the segregation developed during solidification and the formation of pinholes. The use of phase diagram modeling to predict physical property data for use in solidification modeling is also described.

INTRODUCTION

Phase diagrams are an important tool for metallurgists since they allow predictions to be made of the amounts and compositions of the phases that are present in a material at a given temperature under equilibrium conditions, and provide valuable information to help understand nonequilibrium processes. Their value is, however, limited by the fact that they are often only available for simple binary and ternary alloy systems, which rarely correspond closely to industrial alloys, which can often contain 10 or more elements. The effort required to produce phase diagrams for multicomponent systems is very large, and, in practice, phase equilibria are usually only determined for specific alloys, sometimes with variations for a specific element, for example C in a tool steel.

THEORETICAL BACKGROUND

The modeling procedure used has become known as the CALPHAD approach (CALculation of PHase Diagrams). It requires a mathematical description of the thermodynamic properties of the system of interest, in this case, a cast iron. If the phases are stoichiometric compounds (e.g., Fe₃C), the composition is defined and a mathematical formula is then used to describe fundamental properties, such as enthalpy and entropy. Where phases exist over a wide range of stoichiometries, which is the usual case for metallic materials, other mathematical models are used, which account for the effect of composition on the Gibbs energy. All types of models require input of coefficients that uniquely describe the properties of the various phases, and these coefficients are held in data bases.

Once the thermodynamics of the various phases are defined, an applications software package that performs a series of calculations based on the thermodynamic data is then used to calculate phase equilibria. This is usually done via a Gibbs energy minimization process. There are now a variety of such software packages available, which can perform complex multicomponent calculations. The Thermo-Calc package¹ developed at the Department of Materials Science and Engineering, Royal Institute of Technology, Stockholm, Sweden (KTH), was used in the present work. There are also various models available to describe the thermodynamic properties of phases that can be, for example, stoichiometric compounds, solution phases, gaseous species, ionic materials, intermetallic compounds, ceramic types, etc. Some of these are described.

Stoichiometric Compounds

The integral Gibbs energy of formation (ΔG) of a pure species or stoichiometric compound is given simply by the equation:

$$\Delta G = \Delta H - T\Delta S \quad (1)$$

where ΔH is the enthalpy of formation, T is the temperature and ΔS is the entropy of formation. Thermodynamic information is usually held in data bases using some polynomial function for the Gibbs energy, which, for the case of the Scientific Group Thermodata Europe,² is of the form given by Dinsdale:³

$$G_m - H_m^{\text{SER}} = a + bT + cT \ln T + \sum_2^n d_n T^n \quad (2)$$

The left-hand term is defined as the Gibbs energy relative to the Standard Element Reference state, where H_m^{SER} is the enthalpy of the element or substance in its defined reference state at 298.15 K. Letters a , b , c and d_n are coefficients and n represents a set of integers, typically taking the values of 2, 3 and -1 . Further thermodynamic properties, such as entropy, C_p , and enthalpy, can be obtained from Equation 2.

Solution Phases

For the case of a "solution" phase, where mixing of the various components takes place, its Gibbs energy (ΔG) can be written generally as:

$$\Delta G = \Delta G^\circ + \Delta G_{\text{mix}}^{\text{ideal}} + \Delta G_{\text{mix}}^{\text{XS}} \quad (3)$$

where ΔG° is the Gibbs reference energy arising from the contribution of the pure components of the phase, $\Delta G_{\text{mix}}^{\text{ideal}}$ is the ideal mixing term and $\Delta G_{\text{mix}}^{\text{XS}}$ is the excess Gibbs energy of mixing of the components. The various models that are used to describe the

thermodynamic properties of phases will not be considered in detail, but it is useful to briefly discuss some of the models that are available and where they are applied.

Ideal Solution Model

The simplest model is the ideal solution model, where interactions between components in the phase of interest are considered to be negligible (i.e., $\Delta G_{\text{mix}}^0 = 0$) and the Gibbs energy of the phase is given by just the reference energy and ideal mixing terms:

$$\Delta G = \sum_i x_i \Delta G_i^0 + RT \sum_i x_i \log_e x_i \quad (4)$$

where x_i is the mole fraction of component i , ΔG_i^0 defines the Gibbs energy of the phase in the pure component, i , and R is the gas constant. Ideal mixing is often assumed in the gas phase and this assumption can be quite reasonable, particularly at ambient pressures. However, in solid phases, the interactions between components are far more significant and cannot usually be ignored.

Nonideal Solution Models

To deal with nonideal interactions, a further term is added to Equation 4, which becomes:

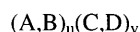
$$\Delta G = \sum_i x_i \Delta G_i^0 + RT \sum_i x_i \log_e x_i + \sum_i \sum_{j>i} x_i x_j \sum_v \Omega_{ij}^v (x_i - x_j)^v \quad (5)$$

The final term is based on a Redlich-Kister-Muggianu (RKM) equation, which considers the Gibbs energy of a multicomponent solution phase to be a product of the summated binary interactions and Ω_{ij}^v is an interaction parameter dependent on the value of v . In practice, the value for v does not usually rise above 3. Equation 5 assumes that higher order interactions are small in comparison to those that arise from the binary terms, but this may not always be the case. Ternary interactions are often considered, but there is little evidence of the need for interaction terms of a higher order than this. Various polynomial expressions for the excess term have been considered other than the RKM equation. However, all are based on predicting the properties of the higher-order system from the properties of the lower-component systems.

Equation 5 is extensively used in metallic systems for substitutional phases such as liquid, body-centered cubic (bcc), face-centered cubic (fcc), etc. However, for phases where components occupy preferential sites on crystallographic sublattices, such as interstitial solutions, carbides, ordered intermetallics, ceramic compounds, etc., simple substitutional models are not generally adequate and sublattice models are now becoming increasingly popular.

Sublattice Models

It is not possible within the scope of the present paper to go into detail concerning sublattice models, but it is instructive to consider a simple two-sublattice type. One of the earliest mathematical treatments of phases with distinct sublattice occupation was by Hillert and Staffansson,⁴ who considered the case of a phase with two sublattices. The sublattice occupancy is shown schematically:



where A, B, C and D are the components; u and v are usually integers and reflect the stoichiometry of the phase. ΔG° is written as:

$$\Delta G^\circ = y_A^1 y_C^2 \Delta G_{A:C} + y_A^1 y_D^2 \Delta G_{A:D} + y_B^1 y_C^2 \Delta G_{B:C} + y_B^1 y_D^2 \Delta G_{B:D} \quad (6)$$

where the site fractions y_A^1, y_B^1, y_A^2 and y_B^2 are given by the general equation:

$$y_i^S = \frac{n_i^S}{\sum_i n_i^S} \quad (7)$$

where n_i^S is the number of atoms of i on sublattice S and $\sum_i y_i^S = 1$. The ideal entropy of mixing is written as:

$$\Delta G_{\text{mix}}^{\text{ideal}} = RT[u(y_A^1 \log_e y_A^1 + y_B^1 \log_e y_B^1) + v(y_C^2 \log_e y_C^2 + y_D^2 \log_e y_D^2)] \quad (8)$$

The $\Delta G_{\text{mix}}^{\text{xs}}$ term (cf Eq. 3) considers the interactions between the components on the sublattice and can be quite complex (see for example Ansara et al.²). By considering that one of the sublattices is made up of interstitials and interstitial vacancies, phases such as austenite and ferrite can be modeled with high levels of accuracy. More recently, Sundman and Ågren⁵ both generalized and extended this model to take into account multiple sublattices, and their model has been used extensively in the present work.

RESULTS AND DISCUSSION

One of the main areas of the present work was to develop a data base suitable for cast irons that now includes the following elements:

Fe, C, Si, Mn, P, Ni, Cr, Mo, Cu, Nb, V, Ti, N, Mg

This was based on the Fe-data base (TCFe) developed at the KTH over the last 10–15 years, mainly for use in steels. As a result of the different emphasis of application, a significant number of binary and ternary interactions, which are quite critical to cast irons, had not been fully assessed in the original data base. Further, it had not been applied to any great degree to cast irons, so it was uncertain as to the accuracy that could be expected from it. A variety of published information, proprietary data⁶ and new work were, therefore, used to enable almost all of the binary interactions to be included and, where possible, the data base has been tested against experimental information on cast irons. It can be noted that, although the data base does not include sulfur, oxygen or rare earths, it has been found to perform extremely well for a variety of different cast iron types, ranging from simple gray cast irons to whiteheart malleable iron to more complex high Cr and P cast irons.

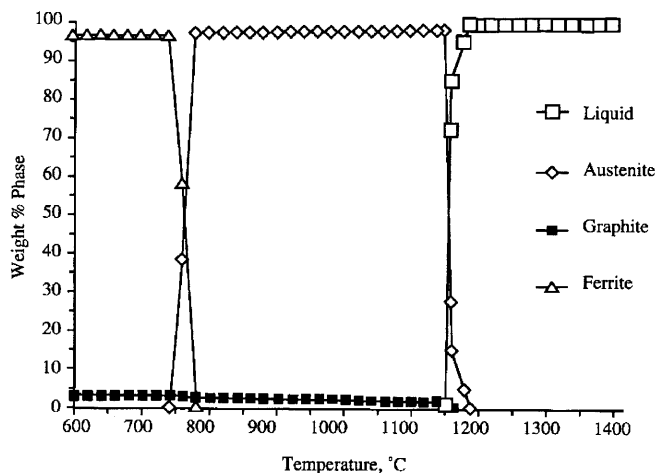


Fig. 1. Predicted phases in a gray cast iron of the following composition: 3.4% C, 2.0% Si, 0.75% Mn, 0.02% P, 0.1% Cr, 0.02% Mo, 0.2% Cu.

Application of Phase Diagram Modeling

The data base has been used to predict the effects of small additions of elements, such as titanium and nitrogen, on the formation of phases in flake and ductile cast irons, and examples of these are presented.

Calculations for Flake Graphite Irons

Calculations were carried out for a flake graphite cast iron of the following composition (wt%): Fe - 3.4% C, 2% Si, 0.75% Mn, 0.02% P, 0.1% Cr, 0.02% Mo and 0.2% Cu.

Figure 1 shows the calculated phase fractions as a function of temperature within the range 600–1400C. It shows that the iron is hypoeutectic, as would be expected from its carbon equivalent (CE) value, so that austenite is the first phase to form, and the remaining liquid then solidifies by a simple eutectic-type reaction to austenite and graphite. During cooling from 780 to 740C, the austenite transforms to ferrite with a subsequent slight increase in the amount of graphite, due to the lower solubility of C in ferrite. It should be stressed that the model predicts phases that will be present under equilibrium conditions and therefore predicts a ferritic matrix, rather than the pearlite that would normally be found in reality. However, it would be possible to halt temporarily the calculations just above the eutectoid temperature, suspend graphite from the calculations and then examine phase equilibria with cementite.

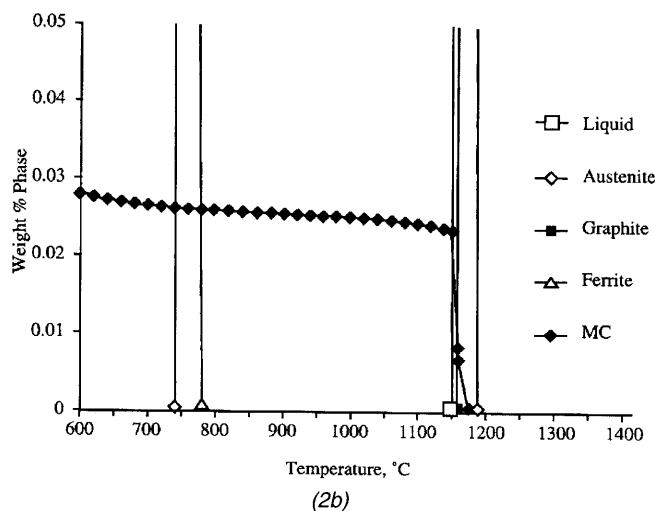
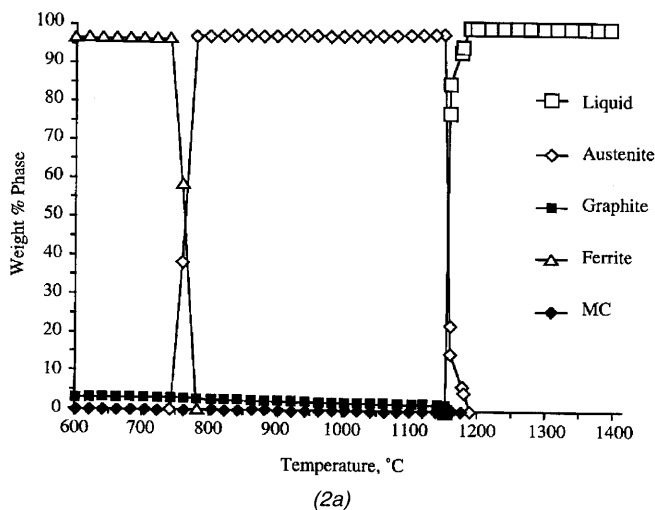


Fig. 2. Effect of adding 0.02% Ti on predicted phases in a gray cast iron having the base composition shown in Fig. 1; (b) is an enlarged section of (a).

When 0.02% Ti is added to the base iron, metallic carbide (MC) is formed during the eutectic transformation (Fig. 2a), but the eutectic temperature and eutectoid temperature range are basically unchanged. Figure 2b is an enlarged portion of the diagram and indicates that MC starts to form in the liquid, although the majority is formed during the austenite-graphite eutectic transformation. The phase diagram model enables the composition of all the phases present to be calculated, but, for the sake of brevity, these have not been included as figures. The MC phase formed in this case is TiC with a stoichiometry of almost 1:1.

The addition of a typical N content (50 ppm) to the above alloy has a profound effect on the behavior of the MC, and it is now better described as a carbo-nitride, Ti(C,N), with N being the predominant interstitial element. In this case, Ti reacts with N in the liquid to form predominantly TiN at 1389C, well above the eutectic temperature (Fig. 3). There is a transition in the behavior of the carbo-nitride at the eutectic where the C level increases at the expense of N, but this is quite a small effect. A further increase in Ti level to 0.05% results in the primary carbide liquidus rising to 1454C and a transitional behavior with respect to Ti(C,N). At the carbide liquidus, the stoichiometry is predominantly TiN, but, on cooling to temperatures close to the eutectic, it gradually changes to become predominantly TiC. The addition of N has little effect on the eutectoid transformation or its temperature.

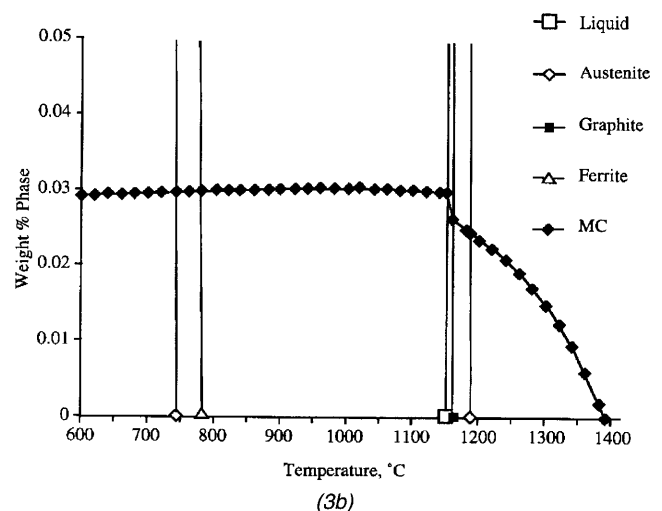
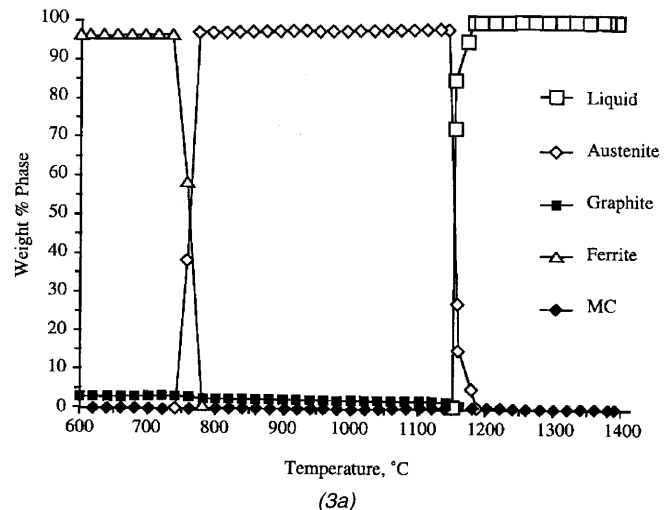


Fig. 3. Effect of adding 0.02% Ti and 0.005% N on predicted phases in a gray cast iron having the base composition shown in Fig. 1.

As part of a study of the comparative behavior of different carbide-forming elements, calculations were made for a flake graphite iron containing 0.005% N and 0.02% of either Ti, Nb or V. Figure 4 compares the phase fraction plots for these additions and shows that their carbo-nitride-forming effectiveness can be ranked $Ti > Nb > V$. Their relative behavior can be summarized as follows:

- Ti forms predominantly a nitride at a temperature well above the eutectic, whereas Nb forms predominantly a carbide during the eutectic transformation and V forms predominantly a nitride from the solid state.
- The C and N stoichiometry is a function of the Ti, Nb and V levels. As the latter increase, the carbo-nitride becomes increasingly C-rich. For example, as the V level is increased to 0.1%, the carbo-nitride becomes predominantly VC.
- None of the elements significantly affects the eutectic or eutectoid temperatures.

Some practical implications of these findings are as follows:

Trace Elements: Ti, Nb and V may be unintentionally present in cast iron, as a result of using microalloyed steel scrap as a charge material, and the modeling shows that all would result in MC in the as-cast condition. Figure 4 implies that, since the $Ti(C,N)$ is formed in the molten iron, it might be possible to eliminate some of it by decantation in the ladle or by the addition of a filter in the running system, but this would not be possible in the case of Nb and V additions.

Precipitation Hardening: This is a potential means of improving the properties of cast irons, especially ductile irons. Figure 4 indicates that it would be feasible to use vanadium for this purpose since MC present in the as-cast condition can be completely taken into solution by austenitizing at $\sim 960C$ and subsequently reprecipitated in a fine form (note that the solution temperature is dependent on the V and N contents). In contrast, Fig. 4 indicates that $Nb(C,N)$ would be only partly dissolved during austenitization and that $Ti(C,N)$ remains insoluble up to the cast iron liquidus, and both would, therefore, be unsuitable as precipitation-hardening elements in cast irons.

Pinholing Tendency: It is clear that Ti has a profound effect on the levels of N in the liquid. A calculation run for the base iron containing 0.005% N predicts the formation of N_2 gas below 1240C (Fig. 5). However, the addition of 0.02% Ti causes the levels of N in the liquid

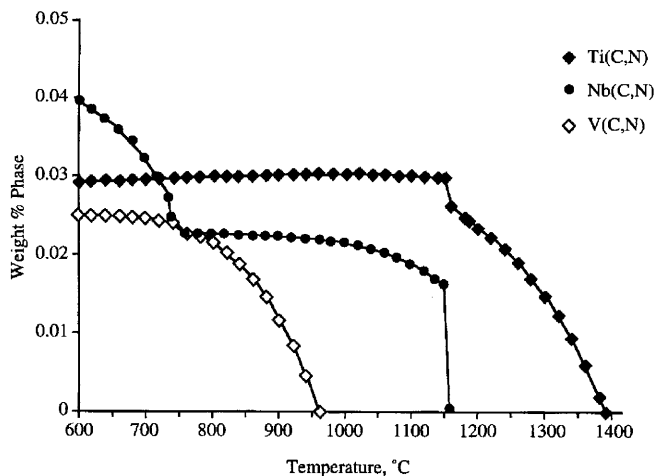


Fig. 4. Effect of adding 0.02% of Ti, Nb or V and 0.005% N to a flake graphite iron.

to decrease from 0.005% at 1400C to <7 ppm at the eutectic by the formation of $Ti(C,N)$. Calculations showed that the formation of equilibrium N_2 gas at 1 atmosphere (101.325 kPa) could be prevented by the addition of 0.0024% Ti. Of course, an overpressure is necessary to form a gas bubble, and this should be taken into account in any further analysis. The addition of Nb and V is far less efficacious with the minimum levels to prevent N_2 gas being 0.2 wt% and 0.87 wt%, respectively. In each case, the removal of N_2 gas is associated with formation of the carbo-nitride.

It can be noted that Fig. 5 shows that the model predicts that N_2 gas will also form during the eutectoid reaction. This is because the calculations are made for a pressure of 1 atmosphere, and the solubility of N in ferrite is much smaller than in austenite. There are insufficient elements such as Cr or Mo to tie up the N in a nitride until just below 620C, but, in reality, extreme overpressure is needed to form gas bubbles in the solid state and, therefore, N will stay in solution.

Calculations for Ductile Irons

Calculations were carried out for a ductile iron of the following composition (wt%): Fe - 3.4% C, 2.4% Si, 0.5% Mn, 0.04% Mg, 0.005% N.

The addition of Mg resulted in the following significant changes, which can be seen in Fig. 6:

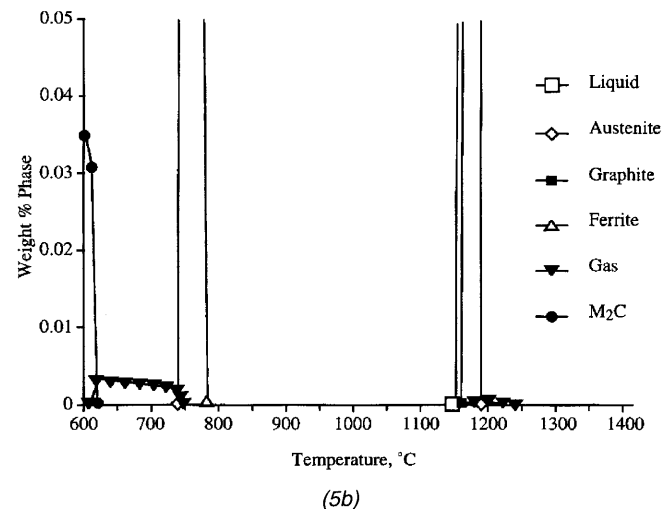
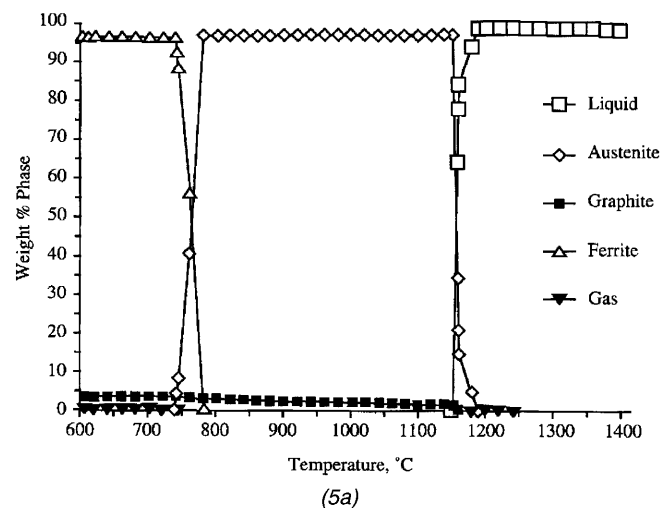
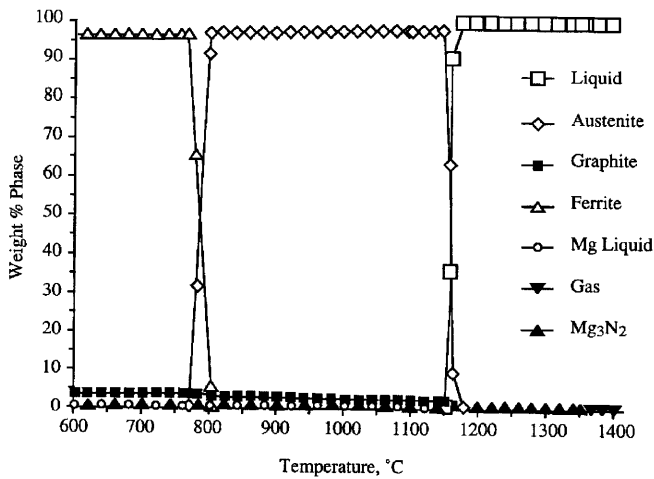


Fig. 5. Effect of adding 0.005% N on predicted phases in a gray cast iron having the base composition shown in Fig. 1.

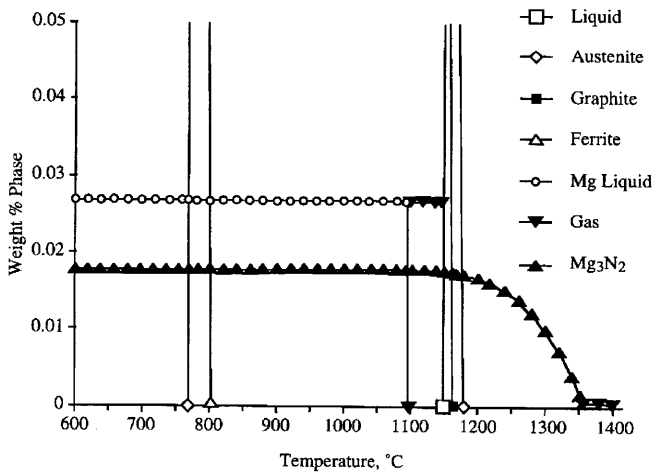
- Gas is formed at 1400C, which is predominantly N₂ but contains significant Mg.
- Mg₃N₂ is formed as a primary phase from the liquid.
- Low temperature N₂ gas formation is suppressed by the formation of Mg₃N₂.
- Mg gas is predicted to form during the eutectic transformation and to condense at a temperature below 1100C.

The first three effects are quite straightforward and are as might be expected, but the formation of Mg gas may be considered somewhat controversial. This can be explained by no allowance having been made for the possible reaction of Mg with O or S and insufficient N being present in the alloy to tie up all of the Mg. The latter has significant solubility in liquid Fe, but almost none in either ferrite or austenite. Therefore, when the alloy finally solidifies, the residual Mg left after reaction with N exceeds the solid solubility limit of Mg in austenite. At ambient pressures, this causes the formation of Mg gas at the eutectic, and this condenses to liquid below 1100C.

At pressures exceeding three atmospheres, the formation of gas is completely suppressed in favor of liquid Mg. This is in keeping with the phase diagram of Fe-Mg, which has a large miscibility gap in the liquid, and, under pressure, alloys solidify by a monotectic reaction that involves both Fe-rich and Mg-rich liquid. It is of interest to note that a number of theories have been made concerning the role



(6a)



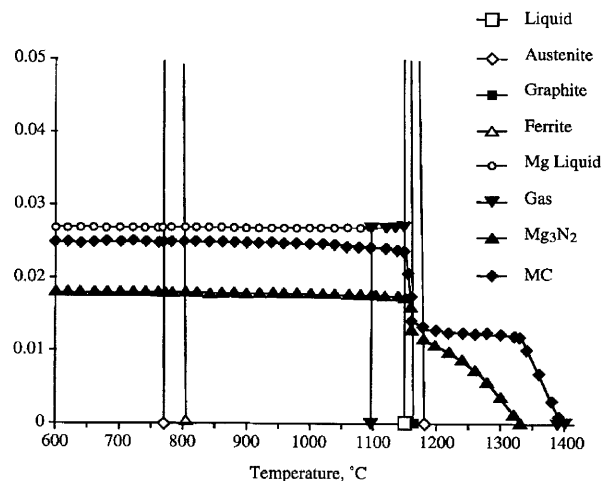
(6b)

Fig. 6. Predicted phases in a ductile iron of the following composition: 3.4% C, 2.4% Si, 0.5% Mn, 0.04% Mg, 0.005% N.

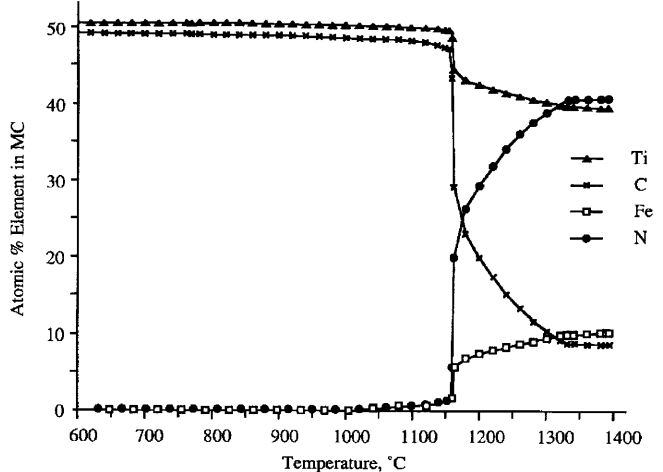
of Mg in the nodularization of graphite, and there is clear evidence⁷ for the presence of Mg halos around graphite nodules. The latter is in clear agreement with the prediction here. However, whether this has any effect on nodularization must still be considered doubtful, as preliminary calculations with the data base modified to include S have shown that S levels in the liquid are reduced by some three orders of magnitude with the addition of Mg, which is much more in keeping with accepted wisdom.

The addition of Ti to the ductile iron results in competition between Mg₃N₂ and Ti(C,N) formation in the liquid state, as can be seen in Fig. 7a. There is a large change in the stoichiometry of Ti(C,N) as a result of this competition (Fig. 7b), since much of the available N is taken by Mg₃N₂. The formation of Mg gas and liquid is not affected by the addition of Ti. It is interesting to note that almost 50% of the Ti(C,N) is now formed at the eutectic and that it basically forms as a carbide. Calculations were carried out to determine the changes brought about by the addition of 0.01–0.1% of Ti combined with 0.005–0.02% of N. For a fixed Ti content, an increase in the N content was found to lead to:

- an increase in the gas content of the molten iron;
- an increase in the amount of Mg₃N₂;
- an increase in the amount of M(C,N);
- a reduction in the amount of Mg vapor found at the eutectic.



(7a) phases formed



(7b) composition of MC

Fig. 7. Effect of adding 0.02% Ti to a ductile iron having the base composition shown in Fig. 6.

With increasing levels of Ti and low levels of N₂, there is an increasing amount of C-rich M(C,N) formed at the eutectic. However, as the Ti level increases, the presence of high N₂ levels in the ductile iron may lead to the formation of a substantial amount of TiN while the iron is still molten. This suggests that there is scope to make deliberate additions of nitrogen to molten irons of high titanium content with the intention of forming TiN, which could be removed from the iron by separation in the furnace or ladle or by passing the iron through a ceramic filter placed in the running system of the casting.

Segregation During Solidification

Thermo-Calc was used to calculate the nonequilibrium solidification of a flake graphite iron using the Scheil assumption of no back diffusion of the elements in the solid state. In steels, this assumption is known to provide erroneous results, as C rapidly diffuses in austenite. This means that equilibrium is maintained with respect to C, and some back diffusion must be accounted for to provide the necessary equilibrium constant composition profile in the dendrite arm. However, most cast irons are basically eutectic alloys, and C is in equilibrium with graphite during the eutectic transformation. This means that the composition profile of C in austenite remains almost constant during the transformation, and effectively little or no back diffusion will occur anyway. It is, therefore, concluded that the Scheil calculation should provide reasonable predictions for fraction solid (f_s) vs. temperature plots, heat evolution and segregation patterns.

Thermo-Calc performs a Scheil simulation very straightforwardly, and the process can be envisaged as follows (Fig. 8): A liquid of composition C_0 is cooled to a small amount below its liquidus to T_1 . It precipitates out solid with a composition C_1^{sol} and the liquid changes its composition to C_1^{liq} . However, on further cooling to T_2 the initial solid cannot change its composition and is effectively isolated.

A local equilibrium is then set up where the liquid of composition C_1^{liq} transforms to a liquid of composition C_2^{liq} and a solid with composition C_2^{sol} , which is precipitated onto the original solid of

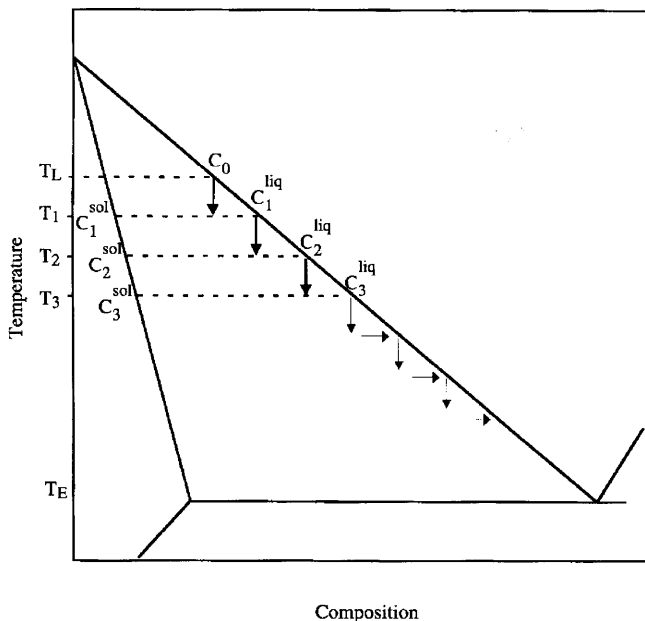


Fig. 8. Solidification based on Scheil assumption of no back diffusion.

composition C_1^{sol} . This process occurs again on cooling to T_3 , where the liquid of composition C_2^{liq} transforms to a liquid of composition C_3^{liq} and a solid with composition C_3^{sol} , which grows on the existing solid. This process occurs continuously during cooling and when the partition coefficient, $k^{sol/liq} < 1$, leads to the solid phase, becoming lean in solute in the center of the dendrite and the liquid becoming more and more enriched in solute as solidification proceeds.

Figure 9 shows a plot of f_s vs. temperature calculated using the Scheil simulation for the flake graphite iron (FG Iron Calculation) with 0.02 wt% Ti and 0.005 wt% N, and compares this with the equilibrium behavior of the alloy. The Scheil plot closely follows the equilibrium behavior for 70–80% of the solidification but, in the last 10%, deviates from equilibrium quite markedly. This is partly due to the segregation of elements, such as Cr, Mn and Mo, to the interdendritic liquid, but the very low final freezing temperature is due to the P segregation, which leads to the formation of small amounts of phosphide eutectic, as is often observed in practice. It is also possible to calculate the latent heat/ C_p of solidification that can be used in the preparation of datafiles for solidification software packages such as PROCAST or MAGMASOFT. This is discussed in the Calculation of Specific Heat section.

Figures 10a–10f show the concentration of various elements in the liquid as a function of fraction solid transformed. In terms of segregation profiles, the predicted behavior is as would be expected in practice with Mo, Cr and Mn strongly segregating to the liquid, Cu being rather neutral and Si segregating to the dendrites. There is a change in behavior of the Cr, Mn and Cu profiles in the last 1–2% transformation associated with the formation of Fe_3C , as mentioned earlier. Both Cr and Mn are Fe_3C stabilizers and preferentially partition to it, while Cu, which is not, behaves in the reverse fashion. The Ti profile in Fig. 10f is rather different to the other elements and shows a change in its partitioning at around the 70–80% transformation point. This is not so easy to explain, but appears to result from a change in stoichiometry from being predominantly TiN in the initial stage of solidification to being almost completely TiC in the last stages of solidification. It should be noted that the initial Ti level is less than 0.02%, and this is because some Ti(C,N) was present at the start of the austenite solidification.

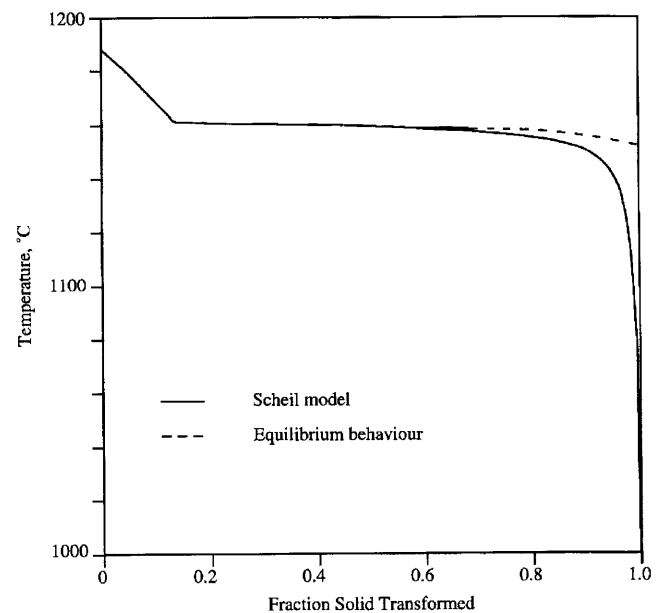


Fig. 9. Prediction of fraction solid as a function of temperature for the base gray iron containing 0.02% Ti and 0.005% N.

Calculation of Specific Heat

As well as calculating f_s and composition profiles during solidification, it is also possible to calculate the latent heat evolution and subsequently derive relationships for specific heat (C_p) as a function of temperature. These are important input parameters for solidification modeling. An example of a C_p calculation will now be briefly described.

The latent heat evolution was calculated during the Thermo-Calc Scheil simulation, and Fig. 11a shows the result for a flake graphite iron containing 0.02 wt% Ti and 0.005 wt% N. The total heat evolved was calculated to be almost exactly 250 J g^{-1} . The rate of heat evolution changes markedly at the graphite eutectic and then slows considerably during the final stages of solidification. A C_p function was then derived by calculating the heat evolved between each isothermal step of the calculation and dividing by the temperature step to give the average C_p during each step. The plot of C_p vs. temperature is then given as a step function and shown in Fig. 11b.

The effect of the alloy solidifying as a white iron was achieved in Thermo-Calc by simply removing graphite from the calculation. Solidification then takes place by a eutectic reaction with cementite at an undercooling of some $30\text{--}40^\circ\text{C}$ below the graphite eutectic. The equilibrium range of transformation was calculated to be $1150\text{--}1160^\circ\text{C}$ for the graphite eutectic and $1110\text{--}1126^\circ\text{C}$ for the metastable cementite eutectic. It can be noted that the temperature range of the graphite eutectic transformation is almost half that for the cementite eutectic.

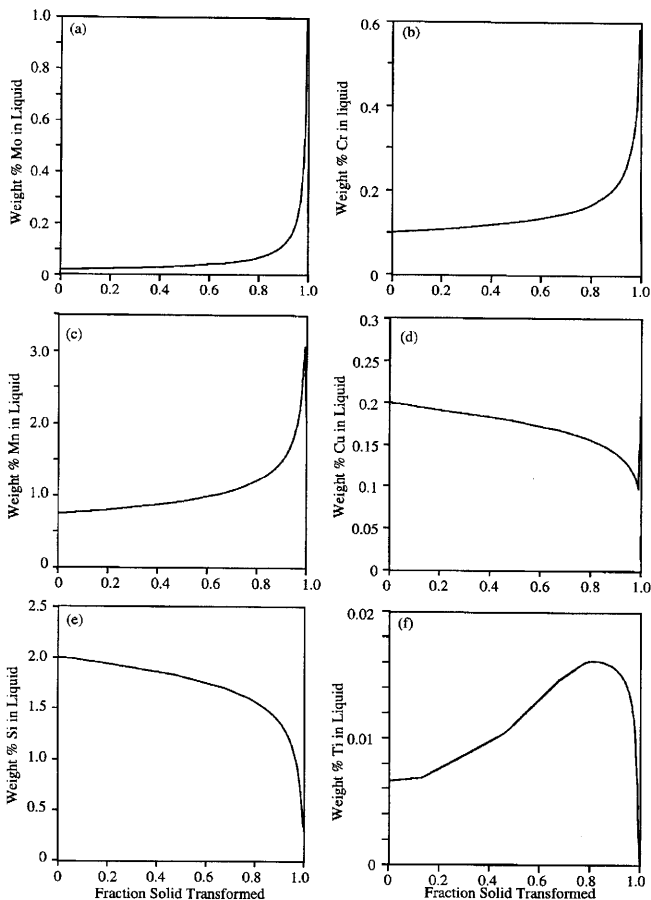


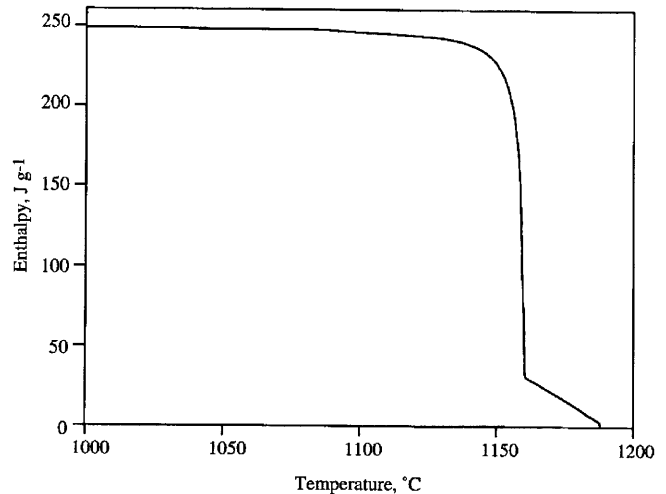
Fig. 10. Segregation in a flake graphite iron containing 3.4% C, 2.0% Si, 0.75% Mn, 0.02% P, 0.1% Cr, 0.02% Mo, 0.2% Cu, 0.02% Ti and 0.005% N.

Figure 11b compares the C_p plots for the Scheil simulation of carbidic and graphitic solidification. It is interesting to note that, although the latent heat for white solidification (240 J g^{-1}) is only 5% different from that for gray solidification, the specific heat plots appear significantly different. The peak height for gray solidification is twice that for white solidification because the rate of transformation of the graphite eutectic is substantially faster than that of the cementite eutectic. The rate of heat evolution is then higher and the C_p during the transformation will therefore be increased. Although the peak for the cementite transformation is smaller, it is actually broader, and this accounts for much of the apparent difference in heat evolution.

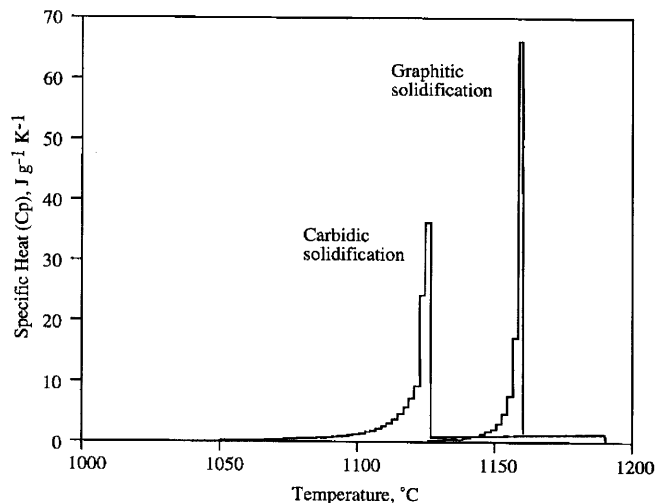
CONCLUSIONS

A thermodynamic data base for Fe-based alloys has been used to predict phase diagrams for flake and spheroidal graphite irons containing various amounts of Ti, Nb, V and N.

1. For a typical gray cast iron containing 3.4% C, 2% Si, 0.75% Mn, 0.02% P, 0.1% Cr, 0.02% Mo and 0.2% Cu, the main conclusions are as follows:



(11a) predicted enthalpy for gray solidification



(11b) predicted latent specific heat for carbidic and graphitic solidification

Fig. 11. Example of prediction of thermal property data for a flake graphite iron containing 0.02% Ti and 0.005% N.

- Trace amounts of Ti (0.02%) lead to the formation of TiC in the molten iron.
 - The simultaneous addition of 0.02% Ti and 0.005% N leads to the formation of Ti(C,N) at temperatures below 1389C. Increasing the Ti content to 0.05% results in the formation of Ti(C,N) at temperatures below 1454C.
 - The addition of Nb leads to the formation of predominantly a carbide during the eutectic transformation, whereas V forms predominantly a nitride in the solid state.
 - Under equilibrium conditions, pinhole formation in a gray iron containing 0.005% N will be prevented by the addition of 0.0024% Ti or 0.2% Nb or 0.87% V.
2. For a typical SG cast iron containing 3.4% C, 2.4% Si, 0.5% Mn, 0.04% Mg and 0.005% N, the main conclusions are as follows:
- The presence of 0.04% Mg leads to the formation of not only Mg₃N₂ but also Mg gas or liquid, the latter confirming the known poor solubility of Mg in Fe.
 - The addition of increasing levels of Ti to an SG iron of fixed N content leads to increasing amounts of M(C,N) and a reduction in the amount of Mg₃N₂, while the addition of increasing amounts of N to an SG iron of fixed Ti content leads to increasing amounts of both M(C,N) and Mg₃N₂.
3. Although the use of Ti to counteract the pinholing tendency of high N content is well-established, the present modeling indicates

that it should be possible to exploit the same reaction to reduce the Ti content of cast irons. The deliberate addition of N will form solid Ti(C,N) particles in the liquid, and it should be possible to remove these by decantation in the furnace or ladle or by a ceramic filter in the running system. This would then enable foundries to use the Ti-containing steel scrap that they are reluctant to use at present.

ACKNOWLEDGMENT

The authors wish to acknowledge the financial support for part of this work from the EC-funded CRAFT project reference BRE 2-CT 94 - 1565.

REFERENCES

1. Sundman, B., *User Aspects of Phase Diagrams*, ed. F. Hayes (The Institute of Metals, London, 1991), p 130.
2. Ansara, I., Sundman, B. and Willemain, P., 1988, *Acta Metall.*, 36, p 977.
3. Dinsdale, A.T., 1991, *CALPHAD*, 15, p 317
4. Hillert, M. and Staffansson, L.-I., 1970, *Acta Chem. Scand.*, 24, p 3618.
5. Sundman, B. and Ågren, J., 1981, *J. Phys. Chem. Solids*, 42, p 297.
6. Saunders, N., unpublished research.
7. Itofuji, H., 1992, *Cast Metals*, 5, p 6.