

THE PREDICTION OF THERMOPHYSICAL PROPERTIES OF STEELS AND SLAGS

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ABSTRACT

The steel industry is increasingly using physically based models to simulate their production processes. These models rely on the use of high quality thermophysical property data. NPL has been involved for a number of years in the measurement of key thermophysical properties of alloys and slags. Most attention has been devoted to liquids and to those solid phases that crystallise from the melt. Typical properties include liquidus and solidus temperatures, fraction solid evolution and enthalpy release, density, thermal conductivity, viscosity and surface tension. Direct measurement is, however, expensive and effort recently has focussed on development of techniques for the prediction of such properties validated against experimental measurements on carefully targeted materials chosen such that they are representative of those used by industry.

In order to provide such information to engineers NPL has been developing *Virtual Measurement Systems* ie. software tools to predict how the processability properties of industrial high temperature liquids change as their composition and temperature vary.

INTRODUCTION

Over the last two decades mathematical modelling has become a well-established tool for improving both process control and product quality. These models have been applied to a wide variety of processes and industries such as the casting and foundry industry, steelmaking, secondary refining of non-ferrous metals, welding, spray forming, dip coating, metallic powder and ribbon production. The steel industry is increasingly using physically based models to simulate their production processes. The driving force for such modelling is improved productivity through lower energy costs, lower scrap losses, improved product quality, and product consistency. Model development has evolved to the point where one of the prime requirements is for accurate physical property data for the commercial alloys involved in these processes. For a variety of reasons, few experimental data are available for these models and the data that are available are often of questionable quality. This lack of data is an impediment to fully realising the potential benefits of process modelling.

In the UK, the Department of Trade and Industry has given NPL the role of developing reliable methods for the measurement of key thermophysical properties of alloys and slags necessary for the development of simulation models for high temperature metal processing and process control.

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Industry frequently needs to react quickly to combat specific problems in process control or product quality. It is, however, expensive to provide all the required data by direct measurement, especially in cases where the industrial liquid is highly corrosive or dangerous to handle in a laboratory environment. Even when experimental methods are available the production of accurate data is frequently time-consuming. Consequently, there is a need for the development of mathematical models to predict the thermophysical properties of alloys from their chemical composition and melting range, since frequently this is the only information available. However, accurate values may be estimated only if the data used in the model are based on reliable, traceable values for the material.

In order to provide such information to engineers and metallurgists NPL has been developing *Virtual Measurement Systems* i.e. software tools to predict how the processability properties of industrial high temperature liquids change as their composition and temperature vary. The key properties identified by industry are liquidus and solidus temperatures, fraction solid evolution and enthalpy release, density, thermal conductivity (for alloys), viscosity (for slags) and surface tension. The tools are based on models and critically assessed data developed and compiled at NPL and collaborating organisations and are being validated simultaneously via a programme of measurement on specific materials chosen such that they are representative of those used by industry.

These software tools have been aimed deliberately at the non-specialist engineer working in a foundry or similar industrial environment using a standard desktop PC. It was seen that a very simple and uncomplicated screen design was essential in order to allow them to be used routinely. Figure 1 shows the screen design for *Virtual Measurement System* for Steels.

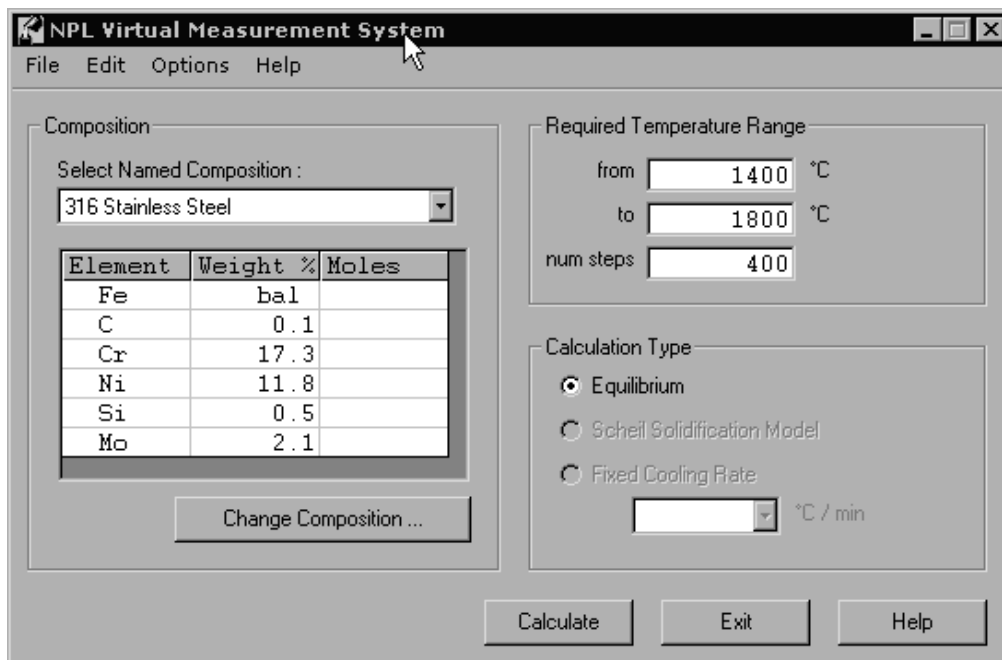


Figure 1 Typical screen layout for the *Virtual Measurement System* for Steels

The engineer selects the basic alloy specification of interest via a drop down menu. The composition of the steel is then displayed but can be modified if required. The engineer can then select the temperature range for the calculations and whether equilibrium, Scheil or a more complex cooling rate model is to be used. Use of the “calculate” button initiates the calculations. When the computer has completed the calculations the predicted values for a wide range of thermophysical properties can be displayed graphically.

Output can be sent to the printer or to spreadsheet packages such as Excel which allows calculated properties to be input easily into casting simulation packages such as MAGMASoft (99mag). In this paper the modelling underlying two such *Virtual Measurement Systems* will be described covering steels and slags. Other products have been developed covering aluminium alloys.

BASIS OF MODELS

Most methods for estimating thermophysical properties use as a starting point well defined standard reference data for the pure components (ie elements for steels or pure oxides in the case of slags). Such data for the components will differ from one phase to another and will also vary as a function of temperature. Therefore, for example, the molar volume of pure Fe will be different between the bcc phase (ferrite), the fcc phase (austenite) or liquid.

The composition dependence of a property is often modelled by:

$$\Omega^p = \Omega_1^p x_1 + \Omega_2^p x_2 + \Omega_3^p x_3 + \dots + \Omega_{theor}^p + \Omega_{excess}^p$$

where Ω^p represents the property Ω of phase p for the composition (x_1, x_2, x_3, \dots), usually expressed in terms of mole fraction. The property Ω_i^p is the value for the pure component i. For a number of properties, eg heat capacity, it may be sufficient to provide an acceptable estimate of the property in the multicomponent system just from data for the pure components especially if the experimental data are sparse or of limited accuracy. For other properties where experimental data are available it may be appropriate to add a correction term to compensate for the effect of any interaction between the elements on the property. This may contain a theoretical contribution Ω_{theor}^p eg for the molar Gibbs energy.

This approach requires that for each component, data are available for each property and for all the phases in which the component may dissolve. Furthermore these data must be available for a wide range of temperatures, eg perhaps represented in terms of some power series expression. In the case of iron, for example, it is necessary that volumetric data are available for the austenite, ferrite and liquid phases even for temperatures where the phase in question is not stable for pure Fe.

For other properties a more complicated approach may be necessary taking into account some knowledge about the internal structural characteristics of the material. For

example the thermodynamic properties of liquid oxides containing silica vary sharply over fairly narrow ranges of composition representing a marked change in the chemical structure of the melt. A proper representation of the thermodynamic properties must take account of this. In a similar way various crystalline phases ranging from carbides (eg $M_{23}C_6$) to spinels (eg magnetite or hercynite) where different elements occupy distinct crystallographic sites, can also show considerable complexity in terms of modelling.

CRITICAL ASSESSMENT OF DATA

The success of such predictive tools relies heavily on the quality of the data used in the models. In the long term the most successful approach is likely to be a highly systematic approach based on well-validated data for pure components, binary systems and multicomponent systems. This is the approach that has been used successfully for a number of years in the compilation of databases of thermodynamic data. The starting point is standard reference data for pure components in the various phases of interest. In the case of thermodynamic data for alloy systems there is now widespread use of the data developed by SGTE (91din).

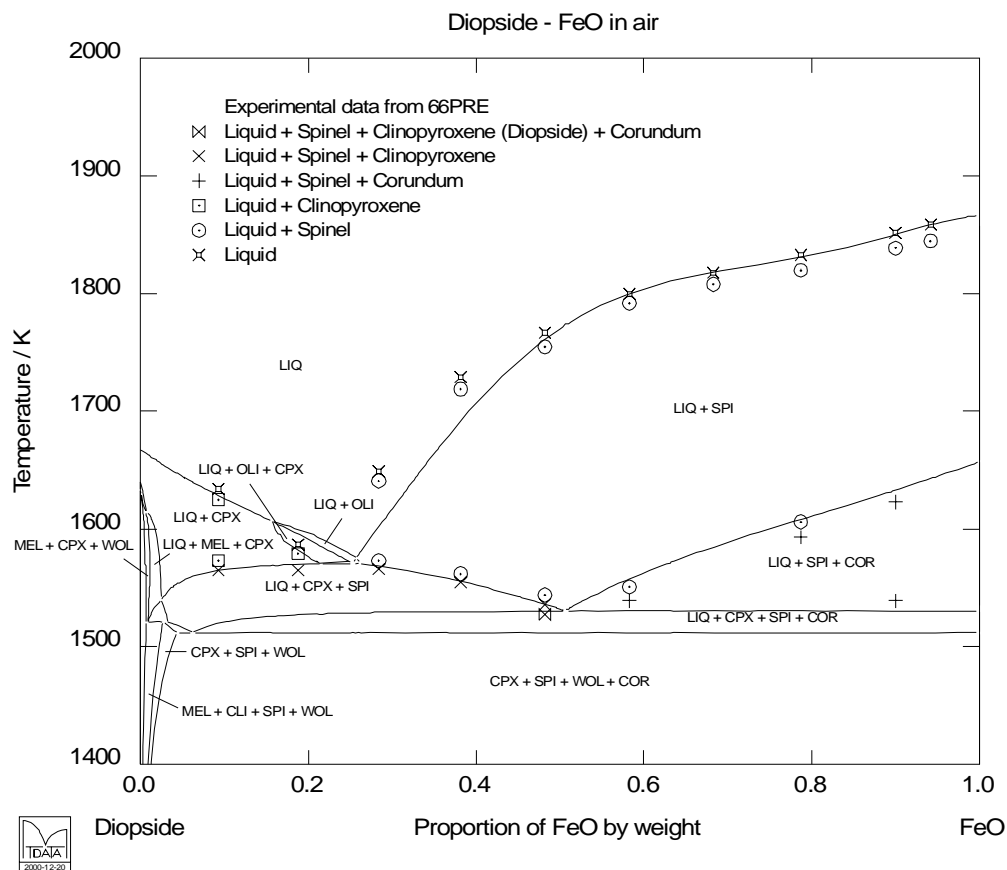


Fig 2 Calculated and experimental data for the CaO-MgO-Fe-O-SiO₂ system

Datasets can then be developed for key binary systems through a process of critical assessment whereby a set of model parameters is developed that represent the totality of the experimental information. Often, as in the case of thermodynamic

data, a number of different types of experimental data (eg enthalpies of mixing, activities, heat capacities, liquidus and solidus temperatures) may have to be taken into account simultaneously. The final set of model parameters is then defined through a complex constrained optimisation process. In a similar way critically assessed data can be derived for ternary and higher order systems by adjusting the agreement between any experimental information and predictions made from the model and parameters derived for the pure components and binary systems. Figure 2 shows an example of the agreement between calculation and experimental data obtained for the CaO-MgO-Fe-O-SiO₂ system.

CALCULATIONS OF PHASE EQUILIBRIA

One of the most successful uses of predictive modelling using computers has been in the field of the calculation of phase equilibria from critically assessed thermodynamic data. The success stems partly from the importance of an understanding of phase equilibria to materials processing but also to the sound theoretical basis underlying thermodynamics. This has led to the development of three major software products (MTDATA (90dav/din), ThermoCalc (85sun/jan) and FactSage (90eri/hac)) designed for the calculation of phase equilibria from stored critically assessed thermodynamic data. The basis behind the predictions made by such software products is the thermodynamic properties for various competing phases modelled as functions of temperature and composition. Then for an overall temperature and composition the amount and nature of the phases in equilibrium can be computed by minimising the Gibbs energy of the system. Using such techniques it is possible to gain an understanding of a number of very diverse industrial problems limited mainly by the availability of reliable databases containing critically assessed thermodynamic data.

The *Virtual Measurement Systems* are based around the core facilities within MTDATA for calculation of phase equilibria. The package for steels also contains the database TCFE, developed by TCAB and the Royal Institute of Technology, Stockholm and considered to be the most comprehensive and reliable database for steel systems available. The package for oxides contains a subset of a comprehensive database developed at NPL as part of an industrially funded project coordinated by MIRO (Mineral Industry Research Organisation) (95din/gis).

MODELLING OF SOLIDIFICATION

During a solidification process a number of different phases may be present at any one time eg the liquid and one or more crystalline phases. The simplest approach to model the process is to assume that the system is in chemical equilibrium, which can be computed provided the required thermodynamic data are available. This provides a limiting case for solidification. In reality equilibrium is limited by the different rates of chemical diffusion of the various elements in the different phases and it is appropriate to consider a more sophisticated model that allows for this. One such model is that proposed by Brody and Flemings, which has been used with some success by Hills (95hil/dun) for modelling the solidification behaviour of steels.

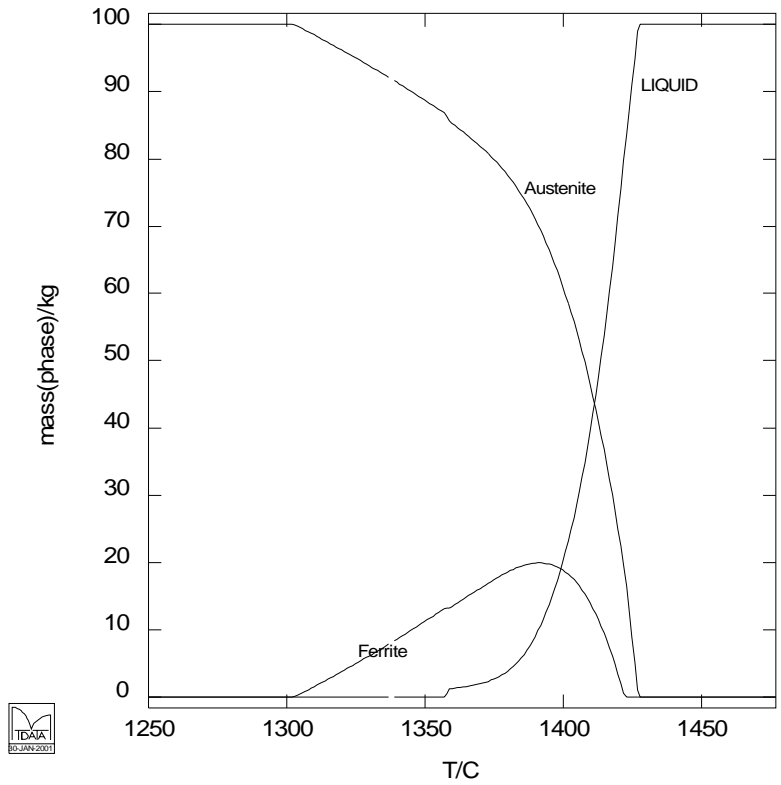


Figure 3 Calculated mass fraction of phases during solidification of a type 316 stainless steel assuming equilibrium conditions

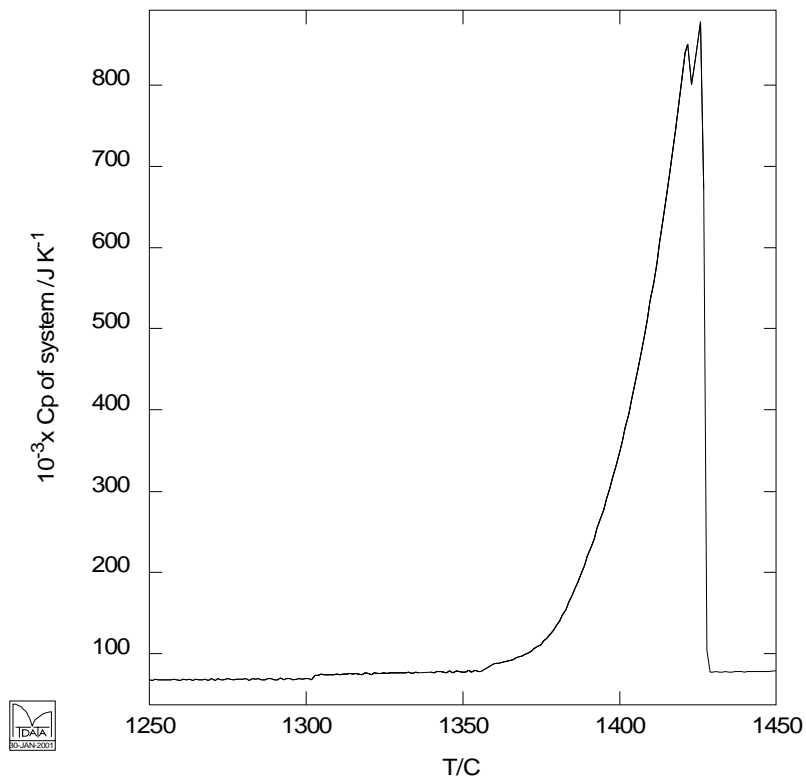


Figure 4 Calculated heat capacity associated with the solidification of a type 316 stainless steel assuming equilibrium conditions

Figure 3 shows the calculated mass fraction during solidification of a 316 type stainless steel assuming that all the phases are in thermodynamic equilibrium. The liquidus temperature is predicted to be 1425°C. The solidus temperature is very sensitive to the amounts of impurities such as sulphur and phosphorus and those elements like manganese which form stable intermetallic compounds with them. This effect is expected to be even more pronounced when a model taking into account the cooling rate is used. Austenite (fcc) is predicted to be the first crystalline phase to appear from the melt although ferrite (bcc) begins to solidify soon after.

This is reflected in the calculated heat capacity curve (Figure 4) which shows a double maximum corresponding to the appearance of the two crystalline phases. Figure 5 shows the equivalent enthalpy curve from which the enthalpy of fusion can be derived.

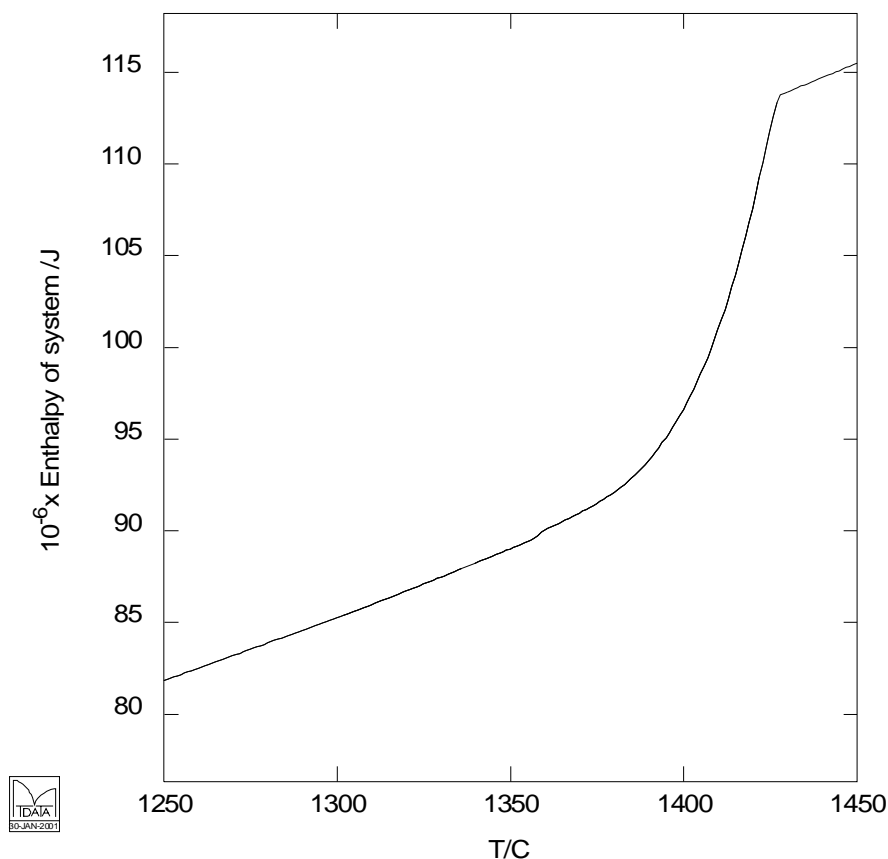


Figure 5 Calculated enthalpy associated with the solidification of a type 316 stainless steel assuming equilibrium conditions

ESTIMATION OF DENSITIES

Miettinen (94mie/lou, 97mie) has studied the densities of a range of carbon and lower alloy steels and fitted the data to a power series expression of the form:

$$\rho = \rho_{Fe} + \sum k_i C_i$$

where ρ_{Fe} is the density of pure Fe, k_i describes the effect of the solute i and C_i is the composition of the solute in weight percent. Figure 6 demonstrates the success of Miettinen's approach albeit for a limited composition range of steels

Miettinen's approach, however, takes no account of the way in which the phase equilibria change as the material is cooled. This limits the extent to which the model can usefully be applied. The approach adopted within the *Virtual Measurement Systems* is to include molar volume and expansivity information as an integral part of the thermodynamic database. In principle this would allow computation of phase equilibria for different pressures although this is unlikely to be of much interest for the casting industry. Because ferrite, austenite and liquid phases have such different densities this allows the possibility of predicting the complex change in density during solidification as the amount and compositions of the competing phases change.

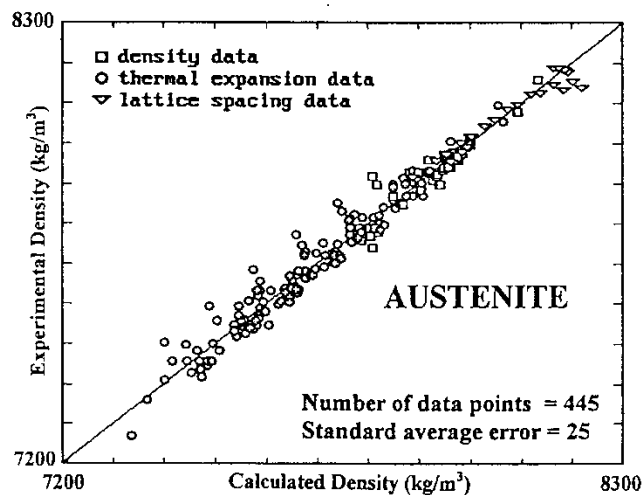


Figure 6 Fit of experimental data for the density of austenitic steels by Miettinen

ESTIMATION OF VISCOSITIES

For the current *Virtual Measurement Systems* it was decided to restrict consideration of viscosity to the products concerned with slags and glasses. This was decision was based not on the availability of good models but rather on the basis of industrial need.

The approach we favour is that developed by Seetharaman et al (94see/du, 94du/byg1, 94du/byg2, 97ji/du, 98ji/du, 98ji) based upon an equation derived from absolute rate theory proposed by Glasstone et al (41gla/lai):

$$\eta = K \exp\left(\frac{\Delta G^*}{RT}\right)$$

where ΔG^* is the Gibbs energy of activation and R is the Gas Constant and K is a constant of proportionality.

For this model A is given by:

$$K = \frac{hN}{V_m}$$

where h is the Planck constant, N the Avogadro number and V_m the molar volume of the alloy at the appropriate temperature.

For metallic melts Seetharaman et al suggested that ΔG^* is related closely to the Gibbs energy of mixing in the liquid at the appropriate temperature through the equation:

$$\Delta G^* = \sum x_i \Delta G_i^* + \Delta^m G_{mix} + 3RTx_1x_2$$

where ΔG_i^* is the Gibbs energy of activation for each of the pure components i and $\Delta^m G_{mix}$ is the Gibbs energy of mixing. Seetharaman (94see/du) applied this model to a number of binary alloy systems with good success and used it to extrapolate in multicomponent systems.

For slags Seetharaman has recommended using a modified Temkin approach to represent the composition dependence of this activation Gibbs energy. This is similar in form, although not identical, to the ionic liquid model used by Sundman et al (85hil/jan) for the thermodynamic properties of slags. Figure 7 shows the agreement between calculated and predicted viscosities for a number of multicomponent slags.

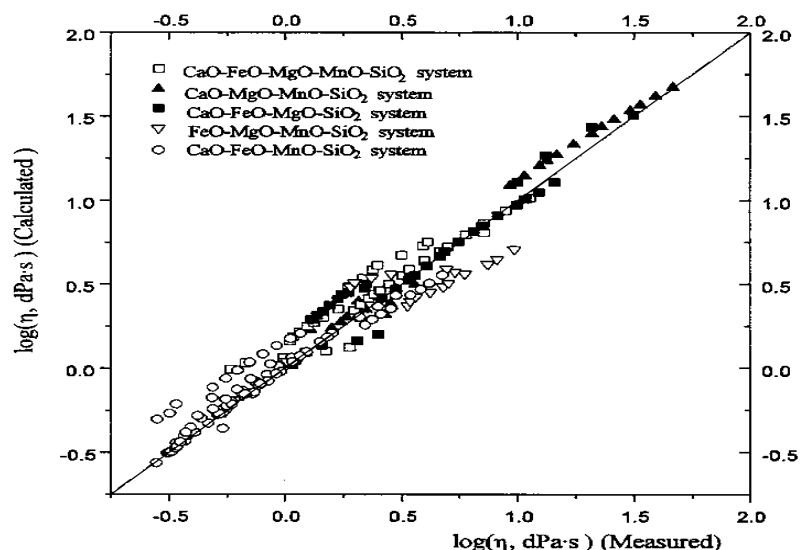


Figure 7 The agreement between calculated and predicted viscosities for a number of multicomponent slags using the model of Seetharaman et al (98ji).

A number of other models have been developed to estimate the viscosity of slags from the temperature and its composition (69wat/fer, 74cap/kau, 81lan/ros, 81mcc/ape1, 81mcc/ape2, 87koy/nag) although those by Riboud (81rib/rou), Urbain (81urb/cam) and Ling Zhang (97zha/jah) seem to have widest applicability.

THERMAL AND ELECTRICAL CONDUCTIVITIES

Thermal conductivities of liquid metals are difficult to measure accurately since the measured heat flux frequently contains contributions from convection and these difficulties become increasingly important at the high temperatures. In recent years it has been shown that transient techniques provide the most accurate values for liquid alloys since they minimise contributions from convection.

At high temperatures the principal mechanism for thermal conduction in liquid metals is due to the transport of electrons. Although phonon (or lattice) conduction can make a significant contribution at lower temperatures, a recent review (96mil/kee) concluded that electronic conduction is the dominant mechanism for temperatures around the melting point. Consequently, the Wiedemann-Franz-Lorenz (WFL) rule relating thermal (λ) and electrical (σ) conductivities can be used with confidence to predict thermal conductivities of molten alloys. The WFL relation is shown below where L_0 is a constant with a theoretical value of $2.445E-8 \text{ W}\Omega\text{K}^{-2}$ and T is the temperature in kelvins.

$$\lambda = L_0 T \sigma$$

The electrical conductivities (unlike thermal conductivities) should not be affected by convective flows in the molten metal pool. Consequently, it should be possible to calculate thermal conductivities for molten alloys from the electrical conductivity values. Iida and Guthrie (89iid/gut) have reported electrical conductivity data for molten binary alloys and the values indicate that most alloys exhibit relatively small (< 10%) negative departures from linearity. ie.

$$\sigma_{T_{liq}} = \overline{\sigma}_1 x_1 + \overline{\sigma}_2 x_2 + \overline{\sigma}_3 x_3 \dots\dots$$

For solid alloys, thermal conductivities calculated from this approach are much larger than those obtained experimentally because both electronic and phonon (or lattice) conduction are important at lower temperatures. This is particularly true for steels and it is therefore sensible to consider the electronic and lattice effects separately. Electrical and thermal conductivities are also significantly reduced by the presence of dislocations and non-metallic inclusions and these are affected by both the heat treatment and mechanical treatment of the sample. An empirical procedure has been devised by Mills et al (00que/din) to represent the two separate contributions.

An alternative approach was developed by Miettinen (97mie) who expressed the thermal conductivity for solid and liquid phases by:

$$\lambda = \lambda_{Fe} + \sum k_i C_i$$

where, λ_{Fe} is the thermal conductivity of pure iron, k_i describes the effect of the solute i and C_i is the composition of the solute in weight percent. In the solid liquid region for carbon and low alloy steels Miettinen has assumed that the thermal conductivity can be expressed as:

$$\lambda = (1 + A_{mix})f^L\lambda^L + (1 - f^L)\lambda^S$$

where λ^L and λ^S are the thermal conductivities of liquid and solid states and A_{mix} is a constant value parameter describing the effect of liquid convection upon the thermal conductivity.

A more sophisticated approach has been developed by Spittal et al (99spi/rav, 99rav/bro) who derived numerical methods for predicting an effective thermal conductivity in solid/liquid regions as a function of fraction solid using a finite difference method applied to the known morphologies of the mushy zone. It was concluded that the thermal conductivity will be highly anisotropic especially if the liquid and solid thermal conductivities are very different or if the proportion of primary arm material is high in columnar dendrites.

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