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Prediction of Properties of Metals Relevant to Process Simulation

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Abstract. Industrial metal processes, such as casting, primary production and welding are frequently simulated using physical models which require alloy properties including liquidus and solidus temperatures and fraction solid; properties associated with heat flow: enthalpy, heat capacity and thermal conductivity and properties associated with fluid flow: density, surface tension and viscosity. These properties are required both as a function of temperature and composition. In recent years, significant developments in the experimental methods for measuring these properties have occurred, but their measurement still remains difficult and expensive. These constraints have driven the development of methods for the prediction of the properties based upon the chemical composition of the alloy.

The paper describes a software program to predict properties of alloys based upon their chemical composition. The properties included are enthalpy, enthalpy of fusion, heat capacity, density, volume, fraction solid during solidification, solidification range, thermal conductivity, phases formed during solidification and viscosity. Most of the underlying models are based upon thermodynamic calculations using MTDATA, a software tool for the calculation of thermodynamics and phase equilibria developed at NPL. Transport properties such as thermal conductivity and viscosity are difficult to model and for example, thermal conductivity is estimated using empirical relationships. The program has been deliberately designed for the engineer who is not expert in thermophysical properties. The predictions will be compared with measurements for selected alloys.

Keywords. Casting, prediction, thermophysical properties.

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1 Introduction

Modelling is now a valuable tool to simulate liquid metal processes. The driving force for such modelling is improved productivity through lower energy costs, lower scrap losses, improved product quality, and product consistency. For example, casting manufacturers [1] routinely use modelling for studying statistical variation in a process; influencing the design of new parts; aiding process design such as efficient runners and risers for liquid metal; modelling the complete manufacturing sequence and thermal control in real time.

The relevant physical models have now developed to the stage where a major requirement is thermophysical property data for metals with the appropriate accuracy, in the liquid, liquid/solid and solid regions [2]. Often few experimental data are available and some data are of questionable quality. This lack of data is becoming an impediment to fully utilising these models.

Experiments to measure the thermophysical properties are time consuming, expensive, especially if the variation with composition within specifications is important and difficult to perform, particularly as some of these materials are reactive or volatile. To provide such information to engineers and metallurgists, NPL developed Virtual Measurement Systems. These are software tools to predict how the thermophysical properties of liquid and solid commercial alloys change as their composition and temperature vary. The key properties identified in consultation with representatives of the metals industry are liquidus and solidus temperatures, fraction solid evolution, enthalpy release, density and thermal conductivity with more limited interest in viscosity. The tools are based on models and compilations of critically assessed data [3].

These software tools are aimed deliberately at the non-specialist engineer working in industry using a standard desktop PC. The interface is simple with common standard alloy compositions selected from those provided. These can be modified to correspond to analysed compositions and the user can enter other compositions provided they lie within the composition range applicable to the program; compositions that can be entered are restricted to the range of the underlying data. The option is to input composition data in terms of mass or moles, with the main component able to balance to 100%. The other selections required are the temperature range; the number of temperature steps (related to quality of the prediction); and the cooling model which can be equilibrium or the Scheil [4] solidification model mainly used for aluminium and nickel alloys or a more sophisti-

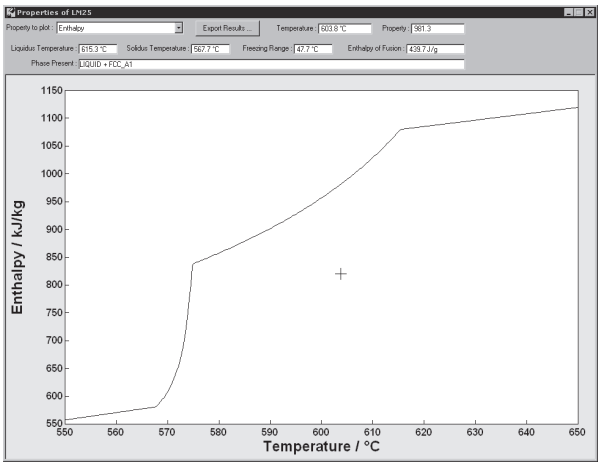

Figure 1. Typical results window showing the calculated enthalpy curve for the common aluminium alloy LM25 (Al-Si7Mg or A356). The liquidus and solidus temperature with the enthalpy of fusion are also shown.

cated cooling rate model for steels. All the properties modelled by the program are then calculated and can be displayed in a new window, for example Figure 1. The data can be easily exported directly to an Excel® spreadsheet, for further analysis or subsequent import into other software, such as a casting simulation program.

Beside the restrictions on appropriate composition ranges for the applicability of the models, warnings are also given where appropriate about the quality of a particular model. For example, the models for properties involving transport phenomena such as thermal conductivity and viscosity are not as well developed as those for enthalpy and density.

There are versions of the program to cover aluminium alloys, steels, copper alloys and solders, and a version for nickel superalloys is being developed. The concept of this program is also applicable to other classes of material provided that the thermodynamic data is available [5, 6].

2 Basis of Thermodynamic Models

2.1 Calculation of Phase Equilibria

One of the most successful uses of predictive modelling is in the field of the calculation of phase equilibria from critically assessed thermodynamic data. This success stems partly from the importance of an understanding of phase equilibria to materials processing but also from the sound theoretical basis underlying thermodynamics. This has led to the development of some major software products [3,7,8] designed for the calculation of phase equilibria from stored critically assessed thermodynamic data.

The basis for the predictions is thermodynamic models and data describing the Gibbs energy of the various phases in the system as a function of temperature, pressure and composition [9, 10]. By minimising the Gibbs energy of the overall system for a given temperature, pressure and composition, the amount of the phases in equilibrium and their compositions can be calculated, and hence the properties of the system determined.

2.2 Critical Assessment of Data

The success of predictive tools relies heavily on the quality of the data used in the models. One approach is based on well-validated data for pure components, binary systems and multicomponent systems and has been successfully used 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 [11].

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 (e.g. 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.

The thermodynamic databases used in the Virtual Measurement Systems also contain molar volume and expansivity data as an integral part of the thermodynamic models. Thus volume, and hence density, can be calculated directly through the derivative of the Gibbs energy with pressure. The use of this approach is described later.

The Virtual Measurement Systems are based around the core facilities of MTDATA, the phase equilibria software from NPL [3]. The package for aluminium alloys uses the thermodynamic database MTAL produced by NPL; a comprehensive thermodynamic database for commercial aluminium alloys, covering Al with additions of Si, Mg, Mn, Fe, Cu, Zn, Ti and B. The version of the program for steels uses as a basis the TCFE database developed by Thermo-Calc Software AB and the Royal Institute of Technology, Stockholm, although molar volume and expansivity data has been added to it to allow the calculation of density as described below.

3 Solidification Models

The simplest approach to modelling how the thermophysical properties change during solidification is to calculate the system at chemical equilibrium at every stage of the process. This assumes that there is complete diffusion in both the solid phases and the liquid, and is one limiting case. However in reality the approach to equilibrium is limited by diffusion of the various elements in the different phases present. The Gulliver–Scheil [4] model provides the other limiting case for solidification by assuming that there is complete diffusion in the liquid phase and no diffusion in the solid phases. Although this is still a simple model it is accepted to work well for aluminium alloys.

However neither of these models works well for steels. As for aluminium alloys the equilibrium model is unrealistic, but also due to the large variation in diffusion rates of the various elements in steels the Scheil model very significantly under predicts the solidus temperature. Therefore a more sophisticated model is being included to allow for this. The model chosen is one proposed by Brody and Flemings [12], which has been used with success by Hills and Duncombe [13] to model the solidification behaviour of steels. The model is similar to the Scheil model, but with the modification that fast diffusing elements, such as carbon, are maintained at equilibrium in the solid, and some back diffusion between the liquid phase and the solid is allowed.

Both these solidification models still use MTDATA phase equilibria calculations as their basis, and so the same range of properties are calculated from the thermodynamics, and not determined from the fraction solid calculations.

4 The Properties

The following section describes the basis of the model for each property together with an example of the prediction compared to experimental data.

4.1 Enthalpy; Liquidus and Solidus Temperatures; and Fraction Solid

These properties are directly calculated from the Gibbs energy minimisation used for determining phase diagrams described previously. Figure 2 shows the prediction of specific heat for the commonly employed casting alloy LM25 (alternative designations: Al-Si7Mg or A356) compared to measurements made using a single pan calorimeter [14]. This can be used to measure liquidus; solidus; and other transition temperatures, as well as the shape of the enthalpy curve. This technique gives better results than a conventional DSC, with improved resolution. This can be seen in Figure 2, which shows the results from the single pan calorimeter for an LM25 alloy, compared with the predicted

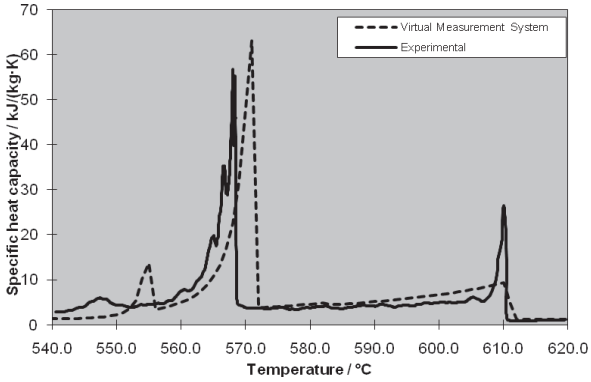

Figure 2. Comparison for heat capacity for LM25 between Virtual Measurement System using the Scheil model and experimental values from the single pan calorimeter.

results from the Virtual Measurement System, using the Scheil cooling model.

Although for the major peaks there is a small difference in temperature between the experimental results and the prediction, which is probably due to undercooling, there is detail seen in the experimental curve that would be missing from a conventional DSC trace. This detail is also seen in the predicted curve, showing the technique's value in validating the model.

4.2 Density

There are some simple approaches to modelling the density of alloys, such as one described by Miettenen [15] for carbon and low alloy steels. This approach fitted the data to a power series of the form:

$$\rho = \rho_{\mathrm{Fe}} + \sum k_i C_i, \tag{1}$$

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. A similar model for nickel superalloys has been described by Sung [16].

Approaches like this, however, take 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 as different phases formed during the solidification will have different densities, and as their fractions change the overall density of the material can change in a much more complex way than is allowed for in these models.

The approach adopted within the Virtual Measurement Systems is to include molar volume and expansivity information as an integral part of the thermodynamic database. Therefore volumes, and hence densities, are calculated as part of the phase equilibria, i.e. the differential of the Gibbs energy with respect to pressure, and so as the fraction of

phases change during solidification the overall density will change to reflect this. For instance as intermetallic phases, with a very different density to the matrix, precipitate their effect on overall density will be seen; for example in nickel superalloys with the Ni_3Al phase. This approach allows the possibility of predicting the complex change in density during solidification as the amount and compositions of the phases change.

A valuable technique developed to measure density is the piston dilatometer [17]. Due to the design of the piston this technique can cope with liquid alloys as well as solid, and so can measure the density of the alloy during the liquid/solid region. The variation of density of LM25 with temperature measured using this technique is shown in Figure 3 compared with the prediction from the Virtual Measurement System. Also shown are the recommended values from Mills [18]. The agreement is good, within 1%, particularly as the predication is completely independent of the experimental values. It can be seen that the model has the same variation through the liquid/solid region as shown by the experimental values showing the benefit of modelling density in this way.

4.3 Thermal Conductivity

The thermal conductivity of liquid metals is difficult to measure accurately since the measured heat flux frequently contains contributions from convection. It is also likely that the convection effect associated with liquid thermal conductivity measurements at high temperature is more pronounced due to the complications of attaining thermal stability at such temperatures. Due to these problems the laser flash technique, for example Monaghan [19], is frequently used to measure the thermal diffusivity (a) which is directly related to the thermal conductivity (λ) through:

$$\lambda = aC_p\rho, \tag{2}$$

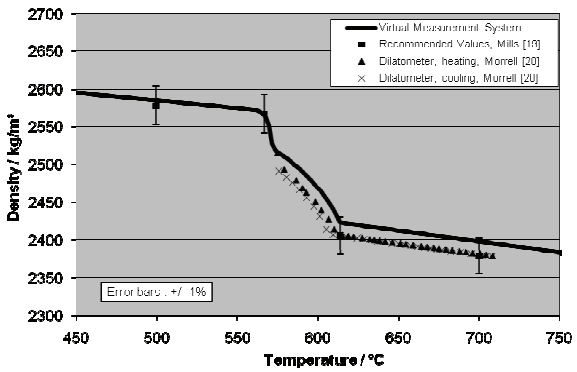

Figure 3. Comparison of Virtual Measurement System prediction for density of LM25 with recommended experimental values [18] and piston dilatometer results [17].

where C_p is the heat capacity and ρ the density. Measurements using the laser flash technique are extremely fast (<0.1 s) and as such are less susceptible to problems associated with convection. Experimental data for the thermal diffusivity of certain liquid iron alloys are available although a detailed study of the effect of carbon on the thermal diffusivity has yet to be carried out.

When experimental data are unavailable an alternative approach is to use the Wiedemann–Franz–Lorenz (WFL) rule relating thermal (λ) and electrical (σ) conductivities:

$$\lambda = L_0 T\sigma, \tag{3}$$

where L_0 is a constant with a theoretical value of $2.445 \times 10^{-8}\,\mathrm{W}\cdot\Omega\cdot\mathrm{K}^{-2}$ and T is the temperature in Kelvin. At high temperatures the principal mechanism for thermal conduction in liquid metals is the transport of electrons. Although phonon (or lattice) conduction can make a significant contribution at lower temperatures, a review by Mills et al. [20] concluded that electronic conduction is the dominant mechanism for temperatures around the melting point for the metallic elements. Consequently, the rule can be used with some confidence to predict thermal conductivities of molten alloys, and is the approach taken in the Virtual Measurement Systems.

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 [21] have reported electrical conductivity data for molten binary alloys and the values indicate that most alloys exhibit relatively small (<10%) negative departures from linearity, so it can be calculated simply from composition, i.e.

$$\sigma_{T_{\mathrm{liq}}} = \overline{\sigma_1}x_1 + \overline{\sigma_2}x_2 + \overline{\sigma_3}x_3 + \cdots. \tag{4}$$

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.

For solid aluminium alloys the electrical resistivity at 298 K is calculated from the composition using constants derived from a numerical analysis of experimental data. The WFL rule is then used to calculate the thermal conductivity at 298 K, and the thermal conductivity for the alloy then varies linearly between this value and that at the solidus temperature. The thermal conductivity of the solid alloy at the solidus temperature is taken as twice the thermal

conductivity of the liquid alloy at the liquidus temperature. This is the same ratio as for pure aluminium. Values for the liquid/solid region for the alloy are calculated using the values at the liquidus and solidus temperatures, and the calculated fraction solid. The values of thermal conductivity calculated using this model are for fully annealed material, and the actual values could be significantly lower depending on the microstructure of the alloy. Therefore as no account is taken of the microstructure the predictions of this model can only be a rough guide, and if an accurate values are needed for solid aluminium alloys they would need to be measured. An example of the predicted results for LM25 is shown in Figure 4, compared with recommended experimental values from Mills [18].

A more sophisticated approach has been developed by Spittal [22, 23] 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.

4.4 Viscosity

Models for viscosity are much less developed than some of the properties considered previously. A brief review of some of the potential models is available [24]. From a review of binary data for the viscosity of Al alloys, Dinsdale and Quested [25] concluded that increasing concentrations of Ti; Ni; Cu; Cr and Mn raised the viscosity compared to single phase Al, whereas Si lowers the viscosity. The reported data for Zn and Mg shows more complicated behaviour. They also concluded on the basis of the quality of input data it is probably better to describe the viscosity of aluminium alloys with fairly simple models such as:

$$\eta = x_{\mathrm{Al}} \cdot \eta_{\mathrm{Al}} + \sum x_i c_i , \qquad (5)$$

where c_i is the coefficient of viscosity/concentration for element i; x_i is the mole fraction of element i and η_{Al} is the viscosity of aluminium at the required temperature.

Using an oscillating cup technique [26], the viscosities of Al-Si-Mg alloys were measured and the results were compared with a simple model based on fitting the binary data, Figure 5. It can be seen qualitatively that the ordering with increasing Si is shown but the predicted temperature dependence is poor.

5 Conclusions

1) There are advantages of calculating reliable thermophysical data needed for simulation of metal processes compared to experimental measurement.

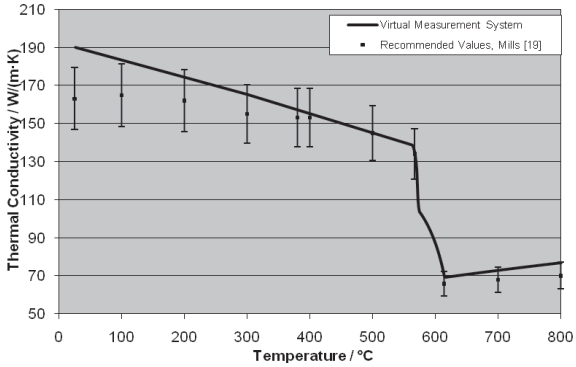

Figure 4. Thermal conductivity of LM25, comparison between the Virtual Measurement System; prediction and recommended experimental values from Mills [18].

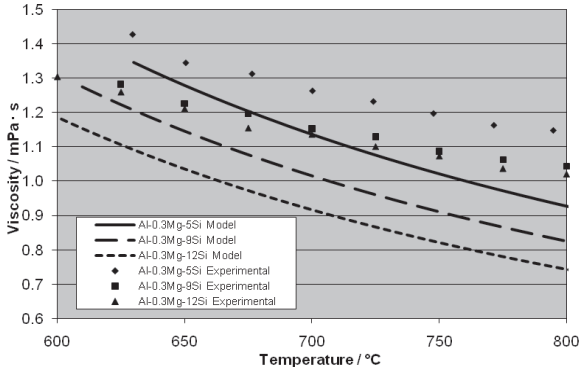

Figure 5. Viscosity of some Al-Si-Mg alloys. Comparison between Virtual Measurement System prediction and values measured at NPL using an oscillating viscometer.

2) Calculated properties such as fraction solid; enthalpy (specific heat) and density derived from modified thermodynamic models are probably sufficient for many applications.

3) Calculated transport properties such as viscosity and thermal conductivity are not calculated using existing simple models with the same success and there is a need for improved models.

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