In Advanced Solidification Processes X, (Eds.: D. Stefanescu, J. A. Warren, M. R. Jolly and M. J. M. Krane), TMS, Warrendale, PA, **2003**, 669.

Modelling of the Thermo-Physical and Physical Properties Relevant to Solidification

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Abstract

The thermo-physical and physical properties of the liquid and solid phases are critical components in casting simulations. Such properties include the fraction solid transformed, enthalpy release, thermal conductivity, volume and density, all as a function of temperature. Due to the difficulty in experimentally determining such properties at solidification temperatures, little information exists for multi-component alloys. As part of the development of a new computer programme for modelling of materials properties (JMatPro) extensive work has been carried out on the development of sound, physically based models for these properties. Wide ranging results will presented for Fe, Ni, Ti, Al and Mg-based alloys, which will also include more detailed information concerning the density change of the liquid that intrinsically occurs during solidification due to its change in composition.

Introduction

The thermo-physical and physical properties of alloys are important input for almost all types of process modelling. At low temperatures such properties can be readily measured, although it may be a time-consuming and expensive procedure to obtain all relevant properties. Experimental measurement becomes far more problematical at high temperature and especially if the liquid phase is involved. To this end it is highly desirable to calculate thermo-physical and physical properties over the whole relevant temperature range for as wide a range of alloys as possible. The present paper describes a methodology to calculate properties such as density, thermal conductivity, specific heat (C_p), solidification shrinkage etc. for Al-, Fe-, Mg-, Ni- and Ti-based multi-component alloys. A significant advantage of the current method is that properties for each phase are calculated so fine detail can be obtained; for example the density change of the liquid during the solidification, which is governed both by an intrinsic change with temperature and by the composition changes that accompany solidification.

The property models that are described in the present paper have also been linked to the simulation of non-equilibrium solidification based on the Scheil-Gulliver (SG) model and also to an extended SG model (SGM) that accounts for fast diffusion of C and N in Fe-based alloys. Hence it is possible to directly input calculated values into casting simulation packages of all types.

The current work forms part of the development of a more generalised software package (JMatPro) for the calculation of a wide range of materials properties [1]. A feature of the new programme is that great store has been placed on using models that, as far as possible, are based on sound physical principles rather than purely statistical methods. Thus many of the shortcomings of methods such as regression analysis can be overcome. For example, the same model and model parameters are used for density calculations for all alloy types, whether it be for a commercially pure Al-alloy or a complex Ni-based superalloy.

The paper will discuss briefly the SG and SGM solidification models that directly calculate phase amounts, Cp, enthalpy and latent heat of solidification. Detail concerning the creation of a molar volume database that enables a variety of properties to be calculated, such as solidification shrinkage, density, thermal expansion coefficient, will then be presented. The calculation of thermal conductivity will also be discussed. Examples of the linking of the solidification models with the physical property calculations are made and properties calculated during solidification will be presented.

Background

Scheil-Gulliver (SG) and Modified Scheil Gulliver (SGM) Solidification Models

Recently the application of so-called 'Scheil-Gulliver' modelling via a thermodynamic modelling route has led to the ability to predict a number of critical thermo-physical properties for alloys such as Ni-based superalloys [2,3,4], Al-alloys [5,6] and cast irons [7]. Such calculations can be computationally very fast and readily used within solidification packages such as ProCAST [2]. The model assumes that solute diffusion in the solid phase is small enough to be considered negligible and that diffusion in the liquid is extremely fast, fast enough to assume that diffusion is complete. Such a process is quite simple to model using thermodynamic calculations based on the so-called CALPHAD method and has been described in a number of publications [2,6,8].

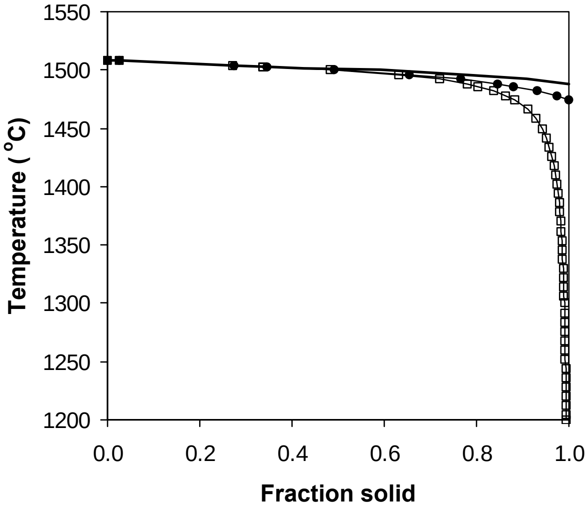

Figure 1. fraction solid vs. temperature curves for solidification of a 3310 steel calculated under (▬) equilibrium, (□) SG and (●) SGM conditions

It is known that some back diffusion will occur, but in many cases the "Scheil-Gulliver" assumption leads to good results for much of the solidification range and can be used to obtain high quality input for casting simulations [8]. For the case of steels, C and N diffuse rapidly in the solid state and it is possible to consider that complete back diffusion of these elements will occur. Such a model has been implemented in JMatPro by considering that C and N will diffuse sufficiently rapidly such that their composition in the growing austenite or ferrite phases will be equal to that of the solid at the growing solid/liquid interface. Within the current model, it is not yet possible to consider the solid state reaction between ferrite and austenite whereby the ferrite is consumed by the growing austenite in a peritectic reaction. However, the kinetics of this transformation may be slow enough such that it is reasonable to assume that the peritectic reaction is not completed during solidification. Having said this, it is clear that in many steels the SGM model provides results that are actually quite close to equilibrium where the full peritectic transformation is complete (Fig.1).

It will be seen later that the properties during solidification are intrinsically controlled not only by the properties of the liquid and solid phases themselves, but also by the fraction solid vs. temperature behaviour. Sharp deviations from smoothly changing behaviour are the result of discontinuities in the rate of solid transformed, which is amply demonstrated for a 356 Al-alloy, where sharp changes in fraction solid vs. temperature (Fig.2) cause sharp changes in the enthalpy vs. temperature plot (Fig.3).

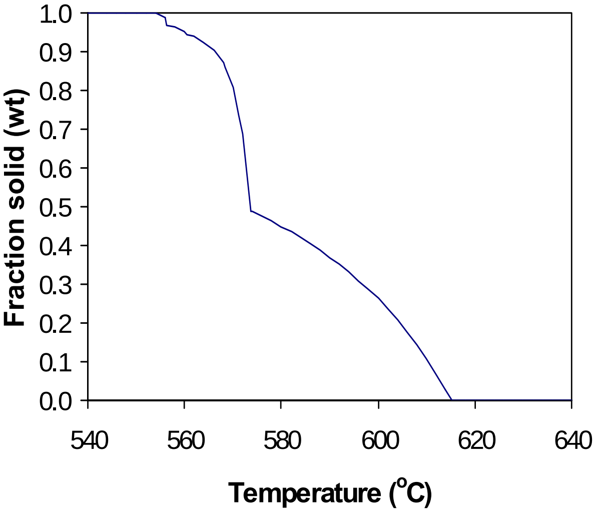

Figure 2. Fraction solid vs. temperature curve calculated for a 356 Al-alloy

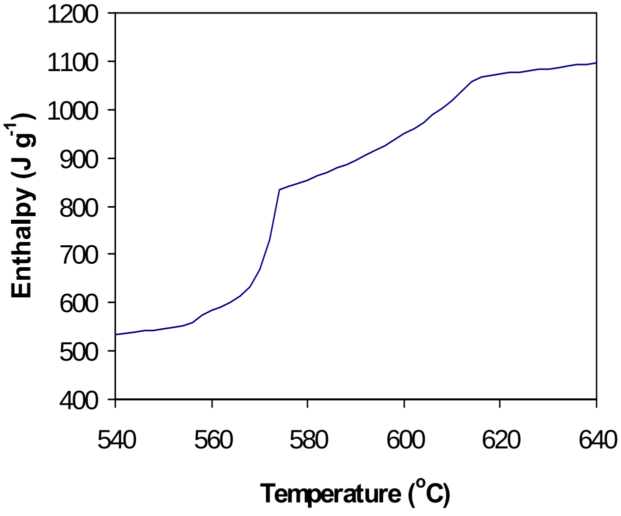

Figure 3. Enthalpy vs. temperature curve calculated for a 356 Al-alloy

At the completion of solidification, JMatPro retains information about the solid phases formed during solidification and extrapolates their properties below the solidus. Hence calculation of properties can be continued to low temperature and utilised with moduli calculations, which can also be obtained from JMatPro [1], to calculate residual stresses in castings.

The Calculation of C_p, Enthalpy and Latent Heat of Solidification

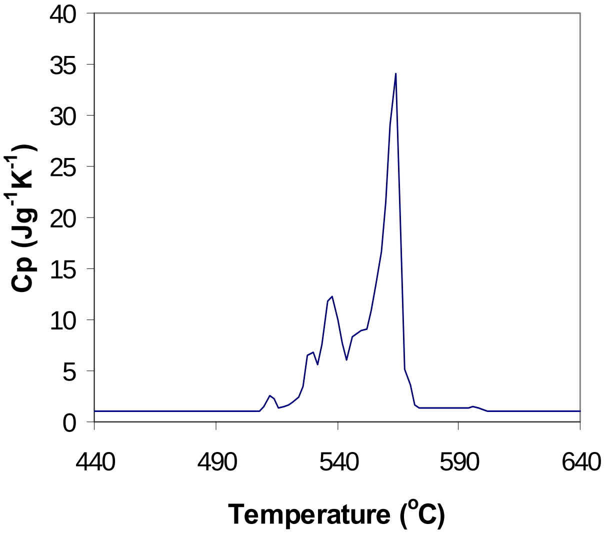

Figure 4. Cp vs. temperature calculated for a 339-1 Al-alloy during solidification

From the SG or SGM models, the CALPHAD methodology immediately provides results for enthalpy and C_p during the solidification process as well as the fraction solid transformed and amounts and compositions of each individual phase formed during solidification. When complex Al-alloys are cast, a wide range of phases can be formed, which leads to complex C_p behaviour see for example Fig.4 for a 339-1 Al-alloy. The enthalpies of both solid and liquid phases intrinsically change with temperature during solidification and the "full" enthalpy curve (see Fig.3) provides this quantity. Some casting packages utilise the latent heat, which is considered to be simply the heat that is evolved purely due to the liquid-solid transformation. This is also readily calculated.

Molar Volume Calculations

A major achievement of the JMatPro software project has been the development of an extensive molar volume database that can be linked to its thermodynamic calculation capability and hence provide volume data for the phases involved in the calculation. Presently, an extensive database of parameters exists for most of the major phases in Al-, Fe-, Mg-, Ni- and Ti-alloys and has been tested extensively in the solid state against lattice parameter measurements (both at room temperature and where available at high temperatures) and experimentally reported linear expansion data. Volume calculations are linked to the thermodynamic models such that, once a thermodynamic calculation is made, volume can be directly calculated.

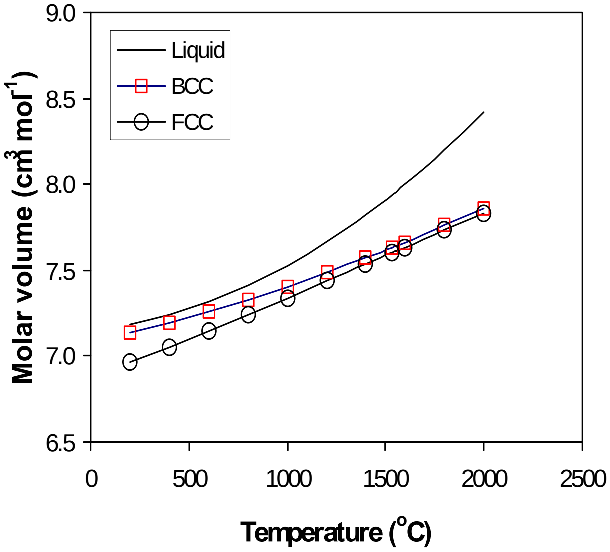

Figure 5. Calculated molar volumes for BCC, FCC and Liquid iron.

The solid information can be directly linked to calculations for the liquid phase by comparison with measured liquid densities to provide volume changes on freezing, which are quite well documented for pure elements. Fig. 5 shows a plot of the molar volumes of BCC, FCC and liquid Fe. The density of the liquid Fe has been evaluated from experimentally measured values reported in the literature [9,10,11,12] and combined with a model that extrapolates its properties to low temperatures.

The principle of the extrapolation method is based on the fact that the transition from the solid to liquid/amorphous state will be accompanied by an increase in volume associated with the larger volume of the liquid/amorphous phase in comparison to that of crystalline structure [13]. This means that the volume of the liquid should never reach that of the solid. We have also assumed that at a temperature close to the glass transition temperature, T_g, (assumed ~0.3T_m for metallic elements) the difference in volume will tend to reach a minimum and below T_g the volume difference will be fairly constant. We have found that quite simple temperature functions give both a good fit to the temperature dependence of the density at high temperatures and a reasonable low temperature extrapolation based on the above principle.

We have considered the volume of the liquid and solid phases in multi-component systems as being represented by simple mixture models, similar to those used to model thermodynamic excess functions in multi-component alloys [14]. In some alloys the stable crystal structure of the element in solid solution may be different to that of the solid solution itself. In this case we have assumed the molar volume of the metastable state is the same as that for the stable structure. We have invariably found that if there is a deviation from "ideal mixing" a volume contraction is involved and that the magnitude of contraction is strongly governed by the magnitude of the thermodynamic interaction.

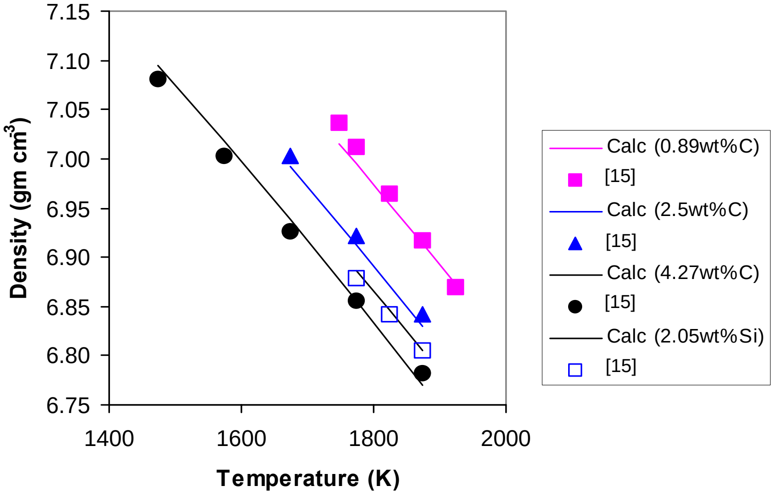

Figure 6. Comparison of calculated and experimentally measured densities of Liquid Fe-(C,Si) alloys

There have been few systematic investigations of alloying effects on the density of liquid alloys. An exception is the work of Lucas [15] who directly measured the density of pure Fe and a series of binary Fe-alloys as a function temperature and composition. Fig.6 shows the agreement with the calculated densities of Fe-C alloys as a function of temperature and composition. Also included are results for a Fe-Si alloy. For the sake of comparison there has been a slight adjustment to the experimental densities to take into account the evaluated density of pure liquid Fe, which in the present work is 0.039 g cm^{-3} higher than measured by Lucas [15].

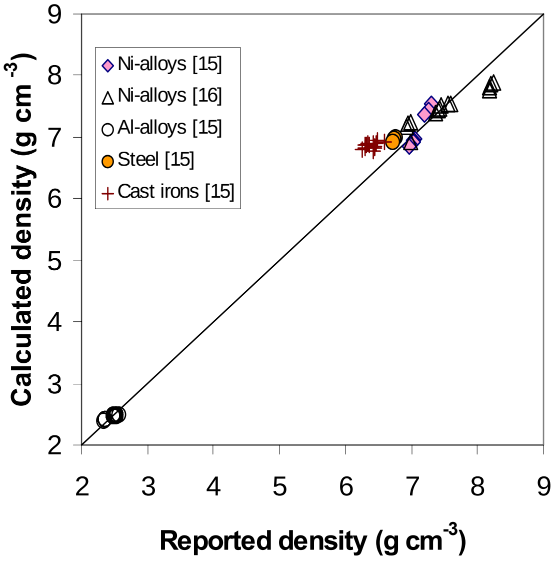

Figure 7. Comparison of calculated and reported densities for various multi-component alloys

There are very few such direct measurements available for the density of multi-component alloys and, therefore, the authors are slightly wary of comparing calculations with estimates based on indirect correlation. However, it is instructive to compare calculated values with those reported in the open literature and Fig.7 shows such a comparison. Two main sources of information have been used. (1) from the Auburn solidification design centre [16], which are mainly estimations and (2) from literature citations by Sung et al. [17] for Ni-based superalloys. In the latter case it is not always clear if density has been directly measured or estimated in some other way. In the main there is good agreement except for the Ni-based superalloy PWA1484 and cast irons where there is a clear discrepancy (~10%) between calculated densities and reported values. For the case of PWA 1484 the present result is rather similar to that found by Sung et al [17], who concluded that re-measurement was probably necessary for this alloy. For the case of cast irons the Auburn group provide only estimated values. Based on the direct measurements of Lucas for Fe, Fe-C and Fe-Si alloys, all as a function of temperature, it is difficult to see that such low reported values for the density of liquid cast irons are accurate. In this case, we believe the current calculations provide answers that are more consistent with actual behaviour.

It is now possible to combine the SG and SGM models with the volume database to make calculations for solidification of various alloys. Fig.8 shows the calculated shrinkage for a 718 Ni-based superalloy on casting. It should be noted that there are two parts to the shrinkage. There is the natural shrinkage that occurs on cooling of the liquid and solid phases and also the shrinkage that occurs due to the liquid to solid transformation itself. Note that for this case, and subsequent solidification calculations, properties are also calculated below the solidus.

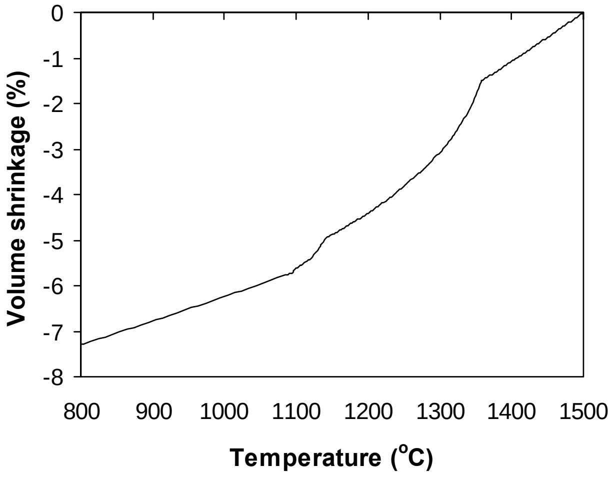

Figure 8. Calculated volume shrinkage for a 718 Ni-based superalloy during solidification

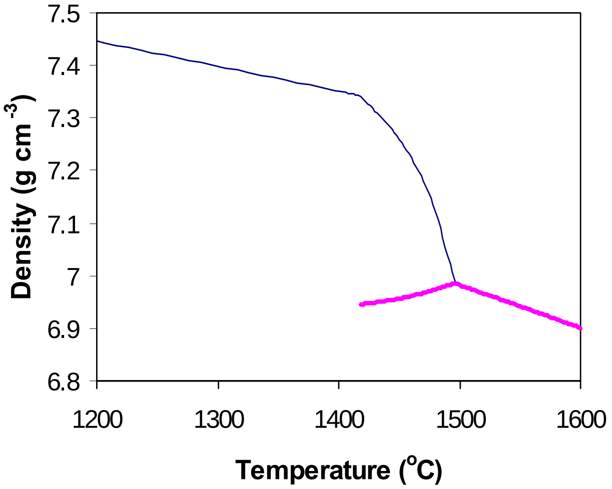

Figure 9 Calculated density of a 1353 steel during solidification. Bold line shows density of the liquid

Fig.9 shows a plot of density vs. temperature for a HSLA steel calculated using the SGM model. In this plot we have also shown the density of the liquid in the mushy zone, where the liquid density decreases as C partitions to the liquid. Testing with various alloys shows that the density change can be quite varied and is, as expected, strongly controlled by partitioning of the various elements to the liquid. In Ni-based alloys interesting effects are observed when heavy elements such as Re, W and Ta are involved because while Ta strongly partitions to the liquid, W and Re are invariably depleted. It is therefore possible to manipulate the alloy concentration to provide either an increase in density or a decrease during solidification.

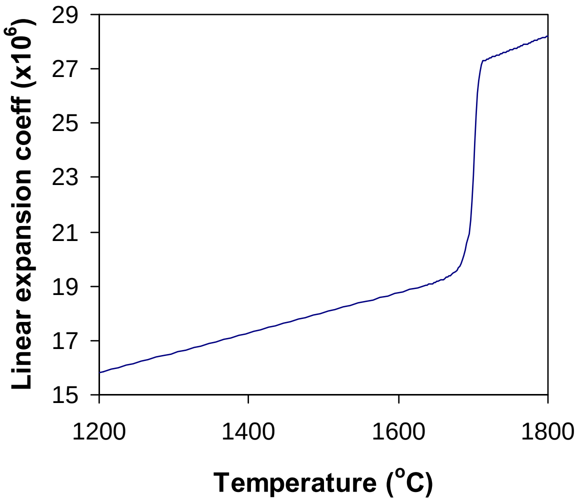

Figure 10. Calculated linear expansion coefficient for a Ti-6Al-4V alloy

It is also possible to extract the linear expansion coefficient and this is shown for a Ti alloy (Fig.10). Physical property information is extremely difficult to obtain experimentally for liquid Ti-alloys due to their highly reactive nature. The modelling route supplies a powerful alternative method to producing thermo-physical and physical properties.

Thermal Conductivity Calculations

The calculation of thermal conductivity is more problematical in that it is a more complex physical phenomenon. There are sharp changes on alloying in the solid state and the behaviour in terms of mixing models is more difficult to match. On alloying, a “bath tub” shape is often seen, where the thermal conductivity falls sharply in the dilute range and then forms a fairly flat plateau in the concentrated region [18]. The current mixing models have been able to match this behaviour to a reasonable extent and extensive validation of solid state multi-component alloys shows good results [1].

Because of the dearth of information concerning the thermal conductivity of binary liquid alloys we cannot directly assess coefficients for alloying effects in the liquid. However, information does exist for thermal conductivity in the liquid state in pure elements and we have evaluated parameters using this information [19,20] as a first basis. Fig.11 shows the calculated thermal conductivity in Al-Mg solid alloys with measured [21] thermal conductivities for the Al and Mg solid solutions shown for comparison. In this case we have assumed that the thermal conductivity of the FCC and HCP forms is the same and can be represented using one curve. A “bath tub” curve is clearly seen, but of interest is that an “ideal” extrapolation of the liquid thermal conductivity at this temperature provides thermal conductivities rather close to those in the plateau region. To obtain the usually observed result in metals, in that the thermal conductivity of the liquid is less than that of the liquid, only a small negative interaction coefficient is needed. We have invariably found this result in our assessment work and have evaluated interaction terms based on this principle.

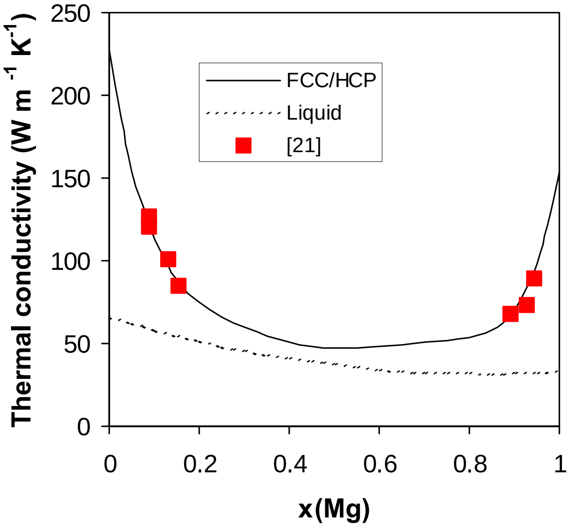

Figure 11. Calculated & experimental thermal conductivities of Al-Mg alloys at 100℃.

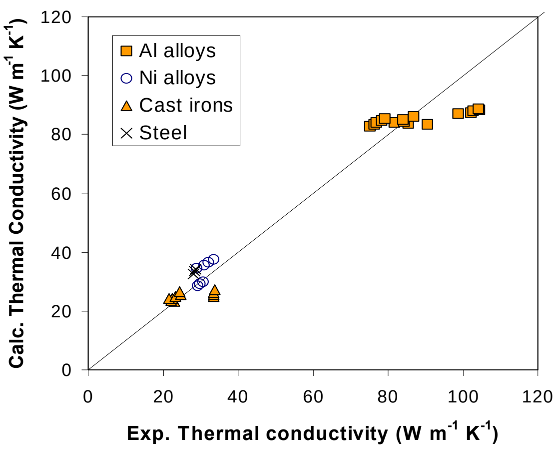

Figure 12. Comparison between calculated & experimental [16] thermal conductivities in multi-component alloys

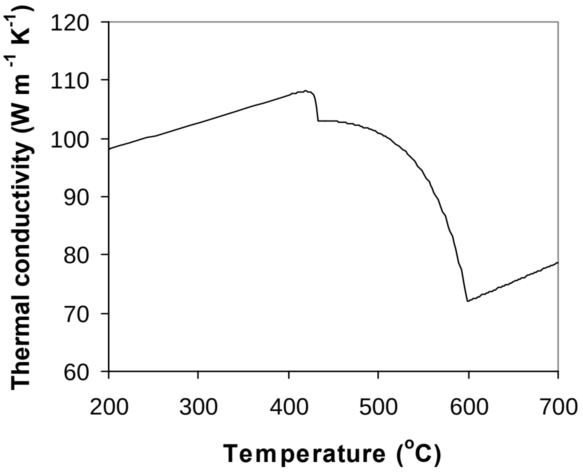

Figure 13. Calculated thermal conductivity of an AZ91 Mg-alloy during solidification

Where results are available for multi-component liquid alloys good agreement is usually found. Fig.12 shows comparison with results from the Auburn University centre for materials measurements for various cast irons, steels, Al-alloys and Ni-base superalloys. The agreement is rather good, except for a 201 Al-alloy. In this case we rather trust the calculated values because one might generally expect the thermal conductivity to decrease when alloy elements are added in dilute solution. This is the case for A201 whose main addition is ~2at% Cu and to match experiment would require a quite sharp increase in thermal conductivity on alloying. An example of thermal conductivity during solidification is shown for a Mg-alloy, AZ91 (Fig.13).

Summary and Conclusions

Models have been developed for the calculation of the various thermo-physical and physical properties of metallic alloys at solidification temperatures. Comparison with reported experimental behaviour is generally very good. Where significant discrepancies occur clear questions arise as to the validity of the experimental result. The present paper describes calculations for fraction solid, enthalpy, Cp, thermal conductivity, density, linear expansion coefficient and volume shrinkage during solidification. Using known relationships between various properties it is also possible, from the results shown here, to calculate electrical conductivity, electrical resistivity and thermal diffusivity. Work is currently undergoing to model viscosity that will complete a very comprehensive set of properties of value to process modellers of all types. A further, significant advantage of the approach described here, is that it is possible to obtain important properties for each phase individually. For example, the density of the liquid phase during the solidification process is automatically calculated.

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