The Physical Properties of Alloys in the Liquid and "Mushy" States[1]

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Data on the physical properties of alloys at high temperatures are urgently needed for the mathematical modeling of high-temperature processes such as casting, welding, secondary refining, dip melting, spray forming, and metal powder production. Data are required for those properties which are involved in heat and fluid flow in high-temperature processes. Levitated drop methods have been adopted to measure the surface tensions, densities, and enthalpies of commercial alloys, and rapid, transient methods have been developed to measure thermal conductivities to avoid the problem of convection. The results obtained for the properties of commercial alloys for the liquid and "mushy" states are discussed.

KEY WORDS: alloys; density; electrical resistivity; enthalpy; heat capacity; high temperatures; surface tension; thermal conductivity; thermal diffusivity; viscosity.

1. INTRODUCTION

Mathematical modeling of processes has proved to be a useful tool for the improvement of process control, product quality, and energy utilization. Process modeling has been found to be beneficial to a large variety of industrial processes, e.g., the casting and foundry industries, welding, secondary melting and refining, metal powder production, spray forming,

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dip melting, etc. These models have progressed to the stage today where one of the major requirements is the provision of accurate physical properties for the materials involved in the process. Property data are required for those properties involved in heat and fluid flow, *viz.*, melting range, heat capacity, enthalpy, enthalpy of fusion, thermal conductivity and diffusivity, emissivity, viscosity, density, and surface tension. The absence of data for commercial alloys reflects the difficulty associated with these measurements. This is a particular problem for high-melting point alloys such as steels, nickel- superalloys, and titanium alloys, where the results are affected by reactions between the sample and its container. Consequently, wherever possible, we have developed measurement techniques based on electro magnetic levitation to minimize errors from these sources. Such errors are particularly important when measuring surface tension (γ) since contamination with surface-active species such as oxygen call cause a dramatic decrease in surface tension (50 ppm O causes a decrease of 30 % in γ iron).

The experimental methods have been developed by using pure metals to calibrate the systems. However, commercial alloys frequently present more rigorous problems since they often contain (i) reactive elements (such as Ti, Hf, or Al) which form oxides, etc., in the form of particles or surface films which affect the measurements or (ii) surface active species (S, O) which can have a dramatic effect on the surface tension. Some of the problems encountered with the subsecond measurement of the surface tension, density, and thermal conductivity of commercial alloys are discussed below.

2. SURFACE TENSION MEASUREMENTS

The levitated drop method for measuring surface tension has been used in our laboratory for about 12 years. In this method, surface tension (γ) is determined from measurements of the natural oscillation of a levitated drop (ω_R) using the Rayleigh relationship [Eq. (1)], where m is the mass of the drop [1],

$$\gamma = 3\pi m \omega_R^2 / 8 \tag{1}$$

However, in practice a frequency spectrum is obtained which contains either three or five peaks and not the single frequency predicted by theory. Recent work [2] has established that oscillations of the drop also arise from both translational movements and the effect of magnetic pressure, which results in an asymmetrical drop. Cummings and Blackburn [3] derived ω_R from Eq. (2), where Subscripts 1–5 refer to the various peaks,

tr to the translational frequency, $Z_0 = g$ (the gravitational constant)$/2\omega_{tr}^2$, and a is the diameter of the drop:

$$\omega_R^2 = \tfrac{1}{5} \sum (\omega_1^2 + \omega_2^2 + \omega_3^2 + \omega_4^2 + \omega_5^2) - \omega_{tr}^2 \{1.9 + 1.2(Z_0/a)^2\} \qquad (2)$$

The translational frequency will be dependent upon both the mass of the droplet and the specific levitation facility. Consequently, collaborative work has been carried out betweent the NPL and the DLR [2] to derive the true value of the surface tension from levitated drop experiments.

2.1. EXPERIMENTAL PROCEDURE

In the NPL facility, the samples are levitated in a silica tube (typically 13-mm o.d.) placed inside a coil. The sample is raised in the coil with the aid of a BN push rod and levitated by applying the power to the coil, which is supplied by a 15-kW Radyne RF generator operating at 450 kHz. A flowing atmosphere of purified Ar + He, or Ar + He + H_2 is used to prevent oxidation of the samples. The temperature of the sample is adjusted by (i) altering the concentrations of H_2 or He in the gas mixture, since these have thermal conductivities much higher than that of Ar, or (ii) varying the power, which changes the position of the droplet in the coil such that a decrease in power causes an increase in temperature. The temperatures of the metal droplets are usually measured by an Ircon two-color (0.9 and 1.1 μm) pyrometer, but a Minolta-Land Cyclops 52 pyrometer operating at 0.65 μm was used for gold samples. The frequency spectrum is obtained by projecting the image of the drop onto a photodetector and analyzing the frequency content of the resulting electrical signal with a Wavetek dynamic signal analyzer. Further details are given elsewhere [2, 4].

2.2. Results and Discussion

A collaborative project involving the DLR, Köln, and, the NPL using the levitated drop method [2] has indicated that the surface tension values for gold, nickel, and iron obtained were

(i)   in excellent agreement with each other when processed using Eq. (2),

(ii) in agreement with recommended values obtained with conventional techniques, and

(iii) subject to an uncertainty of about $\pm 2\%$.

The surface tensions of more than 50 steels have been determined as part of an investigation into the causes of variable weld penetration in GTA/ TIG welding [5]. The surface tensions of steels are markedly dependent upon the concentrations of oxygen and sulfur impurities present. It was observed that for a low-sulfur (<40-ppm) steel the surface tension γ has a high value and exhibits a negative temperature coefficient ($d\gamma/dT$), where- as a high (>50-ppm)-S steel has a low value of γ and a positive ($d\gamma/dT$) value.

However, although it has been shown that O and S are equally surface active [5], it is the soluble O or S (denoted **O** or **S**) which affects the sur- face tension. Any oxygen or sulfur, in the form of a metal oxide or sulfide, has little effect on the surface tension, and since steels usually contain suf- ficient Al to reduce **O** to less than 5 ppm, the O content can be largely ignored. Providing that the steel does not contain relatively high levels of Ca, Mg, or Ce, the surface tension of the steel will be determined by the S content, which is close to the total S content for most steels. The surface tension at 1700°C and ($d\gamma/dT$) of 304 and 316 stainless steels [6] were both observed to be functions of the S contents, and it was found that ($d\gamma/dT$) for a mean temperature of 1700°C crosses from a negative to a positive value at about 40 ppm S, in good agreement with that predicted from thermodynamic calculations [7]. However, the latter also predicted that at 1430°C, ($d\gamma/dT$) = 0 would occur at around 10 ppm S.

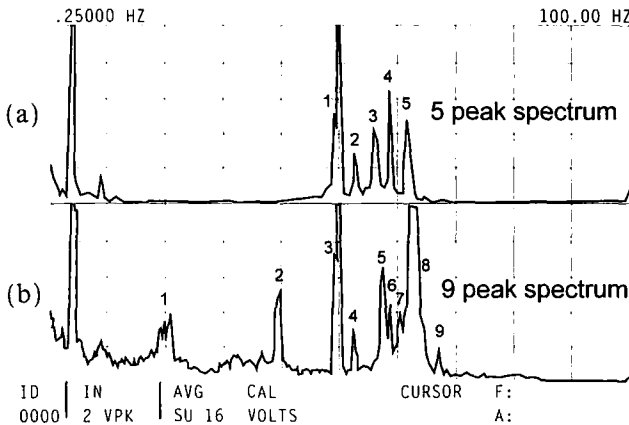Surface tension can be calculated to about 5 % accuracy by using Eqs. (3) to (5).

Fig. 1. Analyzer display showing typical (a) five-peak and (b) multi- peak spectra obtained with molten IN718.

$$\gamma_{1700} = 1150 \times 10^{-3} - 90.9 \ln(\% \ S_{total}) \tag{3}$$

$$d\gamma/dT = 1.51 \times 10^{-3} \times 0.268 \ln(\% \ S_{total}) \tag{4}$$

$$\gamma(T) = \gamma_{1700} + (d\gamma/dT)(T - 1700) \tag{5}$$

where γ is in $N \cdot m^{-1}$, $d\gamma/dT$ is in $N \cdot m^{-1} \cdot K^{-1}$, and T is in °C. However, problems have been experienced when measuring the surface tension of calcium-killed steels. The calcium reduces both soluble O and soluble S to very low levels, and it forms calcium aluminate or calcium aluminosilicate inclusions which form a thin film around the molten alloy. This solid film damps out any oscillations of the surface of the molten alloy surface and thus prevents measurements of the surface tension. The film melts around 1630°C, surface oscillations are observed, and hence surface tension values can be obtained for temperatures > 1650°C. The results obtained indicated that the surface tension results were consistent with those values obtained for the equivalent S content but were subject to considerably more scatter.

The surface tension of a nickel-based superalloy, IN 718, has also been determined. These alloys form a nickel–chromium oxide film which melts around 1720°C and thus prevent oscillations at temperatures < 1720°C. The frequency spectra obtained from these samples frequently contained the usual five peaks (Fig. 1a) but, on other occasions, contained seven or nine peaks (Fig. 1b). The surface tension–temperature relation for IN 718 is
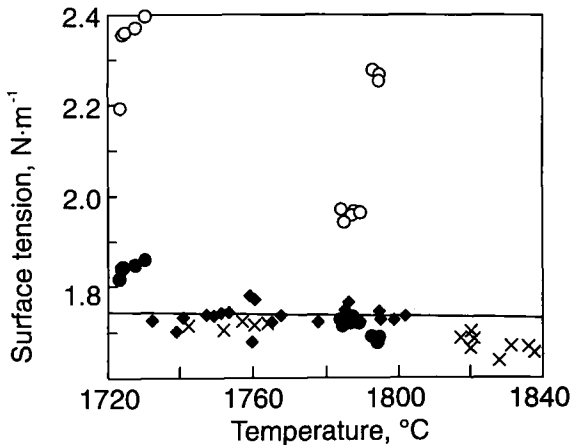

Fig. 2. Surface tension of IN 718 as a function of temperature. (X, ◆) Values obtained from five-peak spectra; (○) values from seven- or nine-peak spectra using the five most prominent peaks; (●) values calculated using all (seven or nine) peaks.

shown as a solid line in Fig. 2 and was obtained using only five peak spectra. A second sample of IN 718 with a nominally higher S content was also examined; the usual five-peak spectra, together with the five most prominent peaks of the seven-peak spectra, were used to obtain surface tension values with Eq. (2).[4] The results shown in Fig. 2 indicate that the surface tension values obtained in this way exhibited a large amount of scatter. However, when ω_R was derived using all seven or nine peaks [Eq. (6)], the results were much more consistent (Fig. 2). It is not known whether the values obtained at 1720°C, shown in Fig. 2, are genuine, since it is possible that the surface oscillations may have been affected by the high viscosity of the aluminosilicate film in the proximity of the solidification temperature. Further work is required to determine the surface tension at this temperature. The cause of the further splitting has not been established. Almost certainly the film will tend to sit preferentially at the base of the sample and the splitting may be a consequence of this behavior.

$$\omega_R^2 = \tfrac{1}{9} \sum (\omega_1^2 + \omega_2^2 + \omega_3^2 + \omega_4^2 + \omega_5^2 + \omega_6^2 + \omega_7^2 + \omega_8^2 + \omega_9^2)$$

$$- \omega_{tr}^2 \{1.9 + 1.2(Z_0/a)^3\} \tag{6}$$

3. DENSITY MEASUREMENTS

3.1. Experimental Procedure

Densities were obtained using the levitated drop method. In these experiments the volume of a molten, levitated drop of known mass was determined by photographing the drop simultaneously in three directions through an optically flat, square cross-sectioned tube. The film taken from above was then projected onto graph paper and examined to identify those times where the drops appear to be circular and, thus, can be assumed to be axisymmetric. The corresponding images taken from the side are then projected onto graph paper and traced, and the volume of the drop is determined by summing the volumes of revolution taken along the axis of symmetry. The magnification factor was obtained by calibrating the system with a ball bearing of known diameter at 25°C. The mass of the drop was remeasured at the end of the experiment to determine any weight losses due to vaporization. The temperatures were calibrated by comparison of the values recorded for the melting point of pure metal samples with the recommended values for those materials.

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[4] In practice, smaller peaks were observed at higher and lower frequencies and were ignored in these calculations.

3.2. RESULTS

The densities (e) of molten iron and copper have been measured and it was found that the experimental values were about 1% higher for Cu and 2% lower for Fe than the recommended values [8]. This could be due to

(i) changes in the magnification factor due to the temperature dependence of the refractive index of the gas surrounding the sample,

(ii) problems associated with the edge detection of the image of the drop,

(iii) improvements in the synchronization of the cameras for the copper measurement, or

(iv) uncertainties in the recommended values which are probably about $\pm 1\%$.

A knowledge of the temperature coefficient (de/dT) is necesary to calculate buoyancy forces. The principal advantage of the levitated drop method is that it can be used over a large temperature range and is thus capable of giving accurate values of (de/dT) providing the effect of gas temperature on the magnification factor can be quantified. Information obtained from the densities of pure metals will be used to determine these magnification factors for different specimen temperatures, and then values of the densities and (de/dT) for various commercial alloys will be determined.

The problems of the oxide film formation should not have a large effect on density measurements for industrial alloys. Preliminary experiments have been carried out on aluminium alloys that form a protective film of Al_2O_3 which remains solid up to 2050°C . These oxide films form whenever the partial pressure is greater than 10^{-20} bar, thus it is virtually impossible to avoid some oxide formation. Preliminary experiments showed that it was possible to obtain axisymmetric drops for drops with oxide coatings. Densities could be obtained for alloys by correcting for the density differences between the metal and the oxide; this could be done by sectioning the drop and carrying out microscopical measurements to determine the mean thickness of the oxide film.

4. THERMAL CONDUCTIVTY

4.1. Introduction

Even at room temperatures it is difficult to eliminate convective contributions to the thermal conductivity of liquids when using steady-state

methods. It has been our objective to obtain reliable values of the thermal conductivity (λ) of molten metals and alloys for the modeling of heat flow, but at high temperatures, the eradication of convective contributions has proved very difficult, as it is difficult to maintain accurate temperature control at the high temperatures used for processing molten metals.

Transient techniques have become the preferred method for determination of the thermal conductivities of liquids since they are essentially free of convective contributions. Two transient techniques are being developed in our current research program, *viz.*, the transient hot-wire method (THW), which is sometimes known as the "line source technique," and the laser pulse method. In the hot-wire method a current is applied to a thin metallic wire (which acts both as a heating element and as a resistance thermometer) for about 1 s and the temperature of the wire is monitored continuously [9]. The thermal conductivity can be calculated from the reciprocal of the slope of the temperature rise as a function of ln(time). The onset of convection can be seen as a departure from linearity of this plot, and experiments have shown that convection can be initiated at times of less than 1 s [9]. When measuring thermal conductivities of liquid metals by the THW method, it is necessary to insulate the metallic probe electrically from the molten metal sample. This requires the development of a stable insulating coating which provides electrical insulation even at the high temperatures associated with molten metals.

The laser pulse method is more robust and involves the monitoring of the temperature transient of the back face of a disk-shaped liquid sample after a laser pulse has been applied to the front face. Since the energy pulse used in this method is much larger than that used in the THW method, and experiments typically take 3 or 4 s, there is the possibility of convective contributions to the thermal diffusivity values recorded. Consequently, the coated THW method has been investigated as a way of quantifying any convective contribution to the results obtained in the laser pulse method.

Thermal conductivity data are also needed for the "mushy" phase (i.e., between T_{liquidus} and T_{solidus}) of commercial alloys. One major problem is that when a pulse of energy is applied in either the laser pulse or the THW method, some of the energy is used to melt the alloy, thereby giving an erroneous value for the thermal conductivity of the "mush". To obtain values for the mushy region, it was decided to make electrical resistivity measurements, since a recent survey [10] has shown that the Wiedemann–Franz–Lorentz (WFL) rule provides reliable values (within 10%) for the thermal conductivities of pure metals in the vicinity of the melting point. Support for this approach is provided by thermal conductivity values calculated from electrical resistivity measurements for aluminium alloys which were found to be in good agreement with values derived from laser pulse experiments [11].

4.2. Experimental Procedure

4.2.1. Thermal Conductivity

The procedure used for the THW measurements on liquid metals is similar to that reported by Powell [9], except an oxidized alumel wire was used instead of a platinum element. The alumel wire was initially oxidized by heating in air for 30 min at 800°C, but more recently, an alternative procedure has been used to promote the formation of Al_2O_3 at the expense of other oxides such as NiO. This procedure involves oxidizing the wire at higher temperatures ($> 1300°C$) at low partial pressures of oxygen ($< 10^{-14}$ atm.), for much longer periods of time (up to 48 h).

4.2.2. Electrical Resistivity Measurements

The electrical resistivities for the molten and mushy regions of alloys were obtained using the four-probe method [12].

4.3. Results and Discussion

4.3.1. Thermal Conductivity

Preliminary measurements of thermal conductivity on mercury and gallium have been obtained using the THW method with the alumel probe. The results of Hg are shown in Fig. 3, along with those reported by other investigators. Thermal conductivity values obtained in this study tend to be lower than most of those reported in the literature. This is consistent with
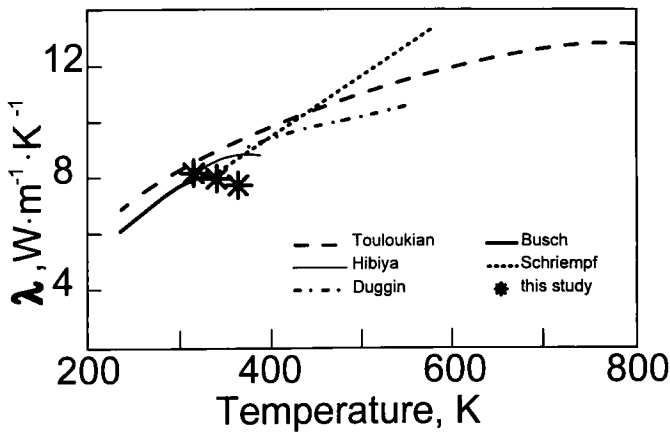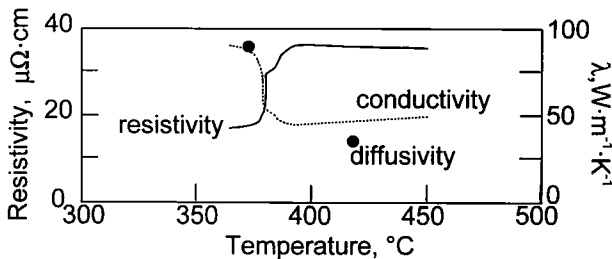

Fig. 3.   The thermal conductivity of Hg as a function of temperature.

the fact that values obtained with the steady-state techniques may contain contributions from convection. The different $d\lambda/dT$ values observed in the mercury data may not be real and could be a result of problems associated with the characterization of the alumel probe prior to use. It was decided that mercury data should be considered for use as one of the calibrants for the THW alumel probe for use in liquid materials. Attempts were made to measure the thermal conductivity of liquid Al–Si commercial alloys. Unfortunately, the molten liquid attacked the coated alumel probe and the electrical insulation was lost. Consequently, new coatings are being developed by

(i)   using different oxidizing conditions for the alumel wire (see Section 4.2.1) and

(ii) applying sol-gel techniques to provide a stable coating.

4.3.2. Electrical Resistivity

Electrical resistivity measurements have been carried out on mercury to calibrate the system and to determine the cell constant. The mercury resistivity value used was 95.6 m$\Omega \cdot$ cm at 26°C. The apparatus was then checked by measuring the electrical resistivity of gallium. The results were found to be within 1% of the recommended values [13]. The electrical resistivity of a commercial zinc alloy in both the liquid and the mushy regions was then measured (cooling from liquid); the results are shown in Fig. 4. As expected, the resistivity of the alloy increased on melting. Also, as expected the large change in resistivity on going from liquid to solid occurred over a temperature range, as opposed to the invariant melting

Fig. 4. The electrical resistivity and thermal conductivity of a Zn commercial alloy as a function of temperature. ($\bullet$) Thermal conductivities (λ) calculated from thermal diffusivity measurements; (—) electrical resistivity measurements; ($\cdots$) thermal conductivities calculated from resistivities by the WFL rule.

temperature of a pure metal. The resistivity exhibited a negative tempera-
ture dependence. The different resistivity–temperature slopes going through
the mushy region are considered to be a result of the effects of different
cooling rates on the microstructure, which affects the resistivity.

The thermal conductivity values derived from the resistivity measure-
ments using the WFL relation were compared with those obtained from laser
pulse thermal diffusivity measurements at apparent solidus and liquidus
points and are shown in Fig. 4. The heat capacity and density values used
to convert thermal diffusivity to thermal conductivity were calculated by
the NPL METALS model. It can be seen that there is some discrepancy
between the two sets of results. While the thermal conductivity of the alloy
calculated from the diffusivity measurement just prior to melting agrees
very well, just after melting the agreement is poor. This may be attributed
to uncertainties in the density data used in the calculation, small differences
in the heat capacity, and experimental uncertainties associated with the
measurements of thermal diffusivity ($\pm 10\%$) and electrical resistivity
($\pm 5\%$).

ACKNOWLEDGMENT

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