Some Thermal Properties of a Copper-Tin Alloy[1]

B. J. Monaghan,[2, 3] **J. G. J. Neale,**[2] **and L. Chapman**[2]

The thermal properties (heat capacity, thermal diffusivity, and electrical resistivity) of a Cu + 10 wt% Sn alloy in both solid and liquid phases have been reported. Using these values it was confirmed that the Lorenz relation is suitable for obtaining thermal conductivity from electrical resistivity in the liquid phase of this alloy. Also, the temperature differential $(d\lambda/dT)$ obtained from such an approach was in excellent agreement with the thermal conductivity values calculated from thermal diffusivity.

1. INTRODUCTION

Mathematical modeling is being increasingly used by the casting industry for process and product control and product innovation. The driving force for such modeling is improved productivity through lower energy costs, lower scrap losses, improved product quality, and product consistency [1]. There is an absence of reliable thermal conductivity data for the commercial materials used in the casting industry. This is a reflection of the difficulties in obtaining accurate experimental values, especially at high temperatures. The lack of reliable thermophysical data is a major impediment to realizing the full potential of current process modeling technology [1]. The need for reliable thermal conductivity data and thermophysical property data, in general, has been recognized by the Department of Trade and Industry, U.K., who has initiated a number of programs to improve measurement methods for thermophysical properties.

Mills et al. [2] reviewed the thermal conductivity data available in the literature for pure metals at temperatures around the melting point (both liquid and solid phases) and in the liquid phase. They concluded that the Lorenz relation which relates thermal conductivity to electrical resistivity could be used to calculate thermal conductivities from electrical resistivity data at the melting point and in the liquid phase region. While it has been shown that the Lorenz relation can be used to calculate the thermal conductivities of pure metals in the liquid phase, it is not clear whether this relation also applies for liquid–metal alloys.

Thermal conductivities of liquid metals are exceedingly difficult to measure. These difficulties include chemical reactivity (containment) problems at the high temperatures required for metallic systems and convectional (mass flow) heat transfer of the liquid. At high temperatures it is difficult to eliminate thermal instabilities in the measurement systems. Often these are enough to initiate convection. The thermal conductivity measurement techniques usually require a temperature gradient imposed on the sample or monitoring of the temperature response of a sample that has been perturbed by an energy pulse. These are much more difficult experiments to carry out than electrical resistivity measurements.

The relative simplicity of resistivity measurements and the fact that the measurements are independent of convective flow indicate that this technique may be a powerful tool in obtaining liquid–metal thermal conductivities. This is the driving force for this study, the aim of which is to establish whether the Cu + 10 wt% Sn alloy's thermal conductivity can be predicted from its electrical resistivity.

2. EXPERIMENTAL

A Cu + 10 wt% Sn alloy was prepared by melting electrolytic copper and pure tin in the appropriate amounts in a graphite crucible under argon in an inductively heated furnace. The compositions of the material used are given in Table I. The alloy's electrical resistivity was then measured. Samples for heat capacity measurements and thermal diffusivity measurements were then prepared from this "used alloy." The chemical composition

Table I. Sample Identification and Composition

NPL identifier	Material	Composition (wt%)
CGQ	Electrolytic Cu	99.98
ENP and ARY	Sn	99.9995

of the Cu + 10 wt% Sn alloy was analyzed both after the initial preparation and after the resistivity measurements. The analysis confirmed the alloy composition and that no losses and/or contamination of the sample were experienced due to processing or measurement.

2.1. Electrical Resistivity

The electrical resistivities (ρ) were measured using the NPL four-probe dc method as described in detail elsewhere [3], which is similar in principle and practice to the method developed by Mera et al. [4]. The electrical resistivity measurement system is calibrated prior to use on a sample of unknown resistivity by measuring triple distilled mercury at 293.15 +/−0.2) K, which has an electrical resistivity of $95.6 \times 10^{-8} \, \Omega \cdot m$ [5]. Where comparisons can be made with the recommended values of Iida et al. [6], the resistivity values obtained by this technique deviated by less than +/−1%.

2.2. Heat Capacity

The heat capacity (Cp) of the Cu + 10 wt% Sn alloy was measured using a Stanton Redcroft differential temperature scanning calorimeter, Model DSC1500. Differential temperature scanning calorimetry (DTSC) is an established method [7] for obtaining heat capacity data for selected cooling (or heating) rates and has an associated error of +/−3% [1]. To make a DTSC measurement, three runs are carried out using (i) a platinum crucible plus sapphire spacer, (ii) a platinum crucible plus sapphire spacer and a calibrant, in this case, sapphire, and (iii) a platinum crucible plus sapphire spacer and the sample, all under identical conditions. The DTSC head is cooled (or heated) at a constant rate, and the signal is the temperature differential between the empty (or calibrant or sample) pan and the reference cell. The sapphire spacer is placed between the sample and the Pt cell to prevent any reaction between them.

2.3. Thermal Diffusivity

The thermal diffusivity (a) of the sample was measured using a Netzsch Laser Flash 427 instrument, which is a standard piece of equipment, the details of which are published elsewhere [7]. The measurement involves heating the front face of a disk-shaped sample using a high-intensity laser and monitoring the temperature rise on the back face. From the temperature rise, the thermal diffusivity can be calculated [8]. The method has an estimated uncertainty of +/−5% [2].

3. RESULTS AND DISCUSSION

3.1. Resistivity of the Cu + 10 wt% Sn Alloy

The results of the resistivity measurements on the Cu + 10 wt% Sn alloy are shown in Fig. 1. The measurements were made under three conditions: (i) cooling from the liquid, then stabilizing the temperature for 15 min prior to measurement, (ii) cooling from the liquid at cooling rates of approximately 1 and 6 K per min and (iii) heating from the solid after solidification at approximately 6 K per min. All three measurement regimes resulted in an identical resistivity-temperature curve.

The point of deviation from linearity in Fig. 1 is considered to be the liquidus temperature and has a value of 1282 K. All liquidus and solidus temperatures quoted in this paper are given in Table II. Above the liquidus temperature the resistivity increases linearly with increasing temperature. Below the liquidus temperature the resistivity decreases in a nonlinear manner. It is difficult to identify the solidus temperature of the alloy from this figure or whether the alloy has fully solidified. The calculated solidus temperature for this alloy is 1113 K [9]. The liquidus and all other calculated thermodynamic parameters presented in this paper were, unless otherwise stated, made using the NPL MTDATA thermodynamic package [9]. MTDATA uses internationally validated thermodynamic databases [9].

The nonlinear behavior of the resistivity below the liquidus point is to be expected since the resistivity in the two-phase region between the
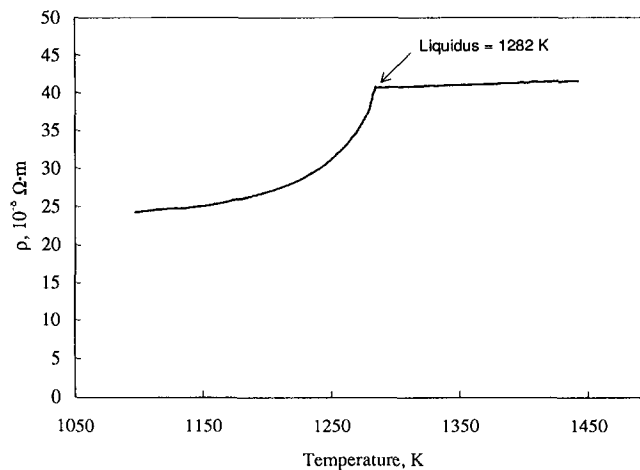

Fig. 1.   Resistivity versus temperature of the Cu + 10 wt% Sn alloy.

Table II. Solidus and Liquidus Temperatures for Different Techniques

Technique	Solidus temperature (K)	Liquidus temperature (K)	Temperature error (K)
Resistivity	—	1282	+/−4
DTSC	—	1278	+/−3
Laser flash	1072	1286	+/−8
MTDATA [9]	1113	1263	—

liquidus and the solidus will be affected by the changing composition of the alloy, in terms of the relative amount of both the liquid and solid alloy present and the solidifying species [10].

Although not observed, it would also be expected that the composition of the alloy below the liquidus, and hence the resistivity, would be affected by the different cooling rates. It can be concluded only that the lack of effect of cooling rate is a result of the change in cooling rate being too small to affect substantially the alloy's solidifying microstructure and, therefore, its resistivity.

3.2. The Heat Capacity of the Cu + 10 wt% Sn Alloy

The results of the DTSC heat capacity measurements for a number of cooling runs are given in Fig. 2. Cooling the alloy (read Fig. 2 from right to left) from the liquid, it can be seen that a large amount of energy is evolved at 1278 K. This is considered to be the liquidus point. On further cooling, the energy released diminishes until the temperature reaches 1063 K, where another energy peak is encountered. From the phase diagram given by Hansen [11] and reactions predicted from MTDATA [9], it is likely that this peak represents a peritectic reaction and the left side of this peak represents a complete solidification temperature with a value of 1053 K. The Cp of the liquid phase was found to be independent of the temperature, with a value of $0.505 \, \text{J} \cdot \text{g}^{-1} \cdot \text{K}^{-1}$.

3.3. The Thermal Diffusivity of the Cu + 10 wt% Sn Alloy

The laser-flash thermal-diffusivity results are given in Fig. 3. It can be seen that the thermal diffusivity increases nonlinearly with increasing temperature up to the solidus point (start of the shaded area) and increases linearly with temperature in the liquid region (to the right of the shaded area). The shaded area represents the two-phase liquid–solid region.
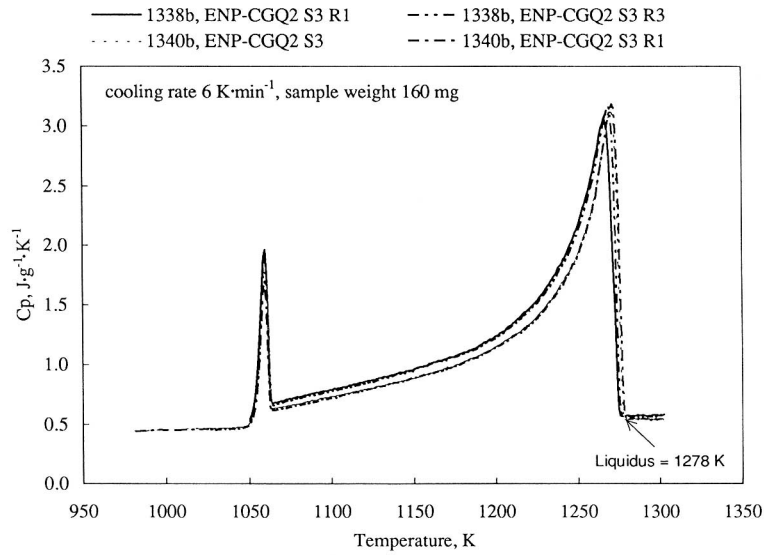
—— 1338b, ENP-CGQ2 S3 R1   — · — 1338b, ENP-CGQ2 S3 R3
· · · · · 1340b, ENP-CGQ2 S3   — · — · 1340b, ENP-CGQ2 S3 R1

Fig. 2. Heat capacity of the Cu + 10 wt% Sn alloy on cooling.
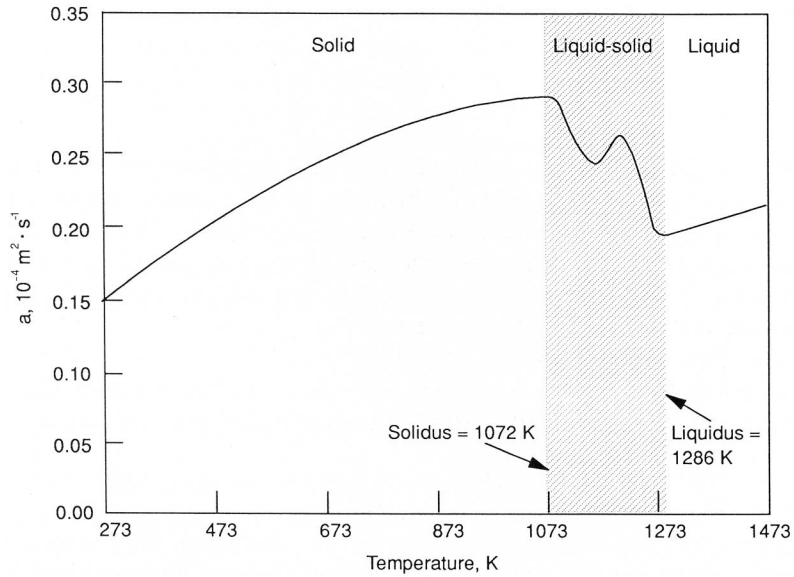

Fig. 3. Thermal diffusivity versus temperature of the Cu + 10 wt% Sn alloy.

In this shaded area, it is difficult to make laser-flash thermal-diffusivity measurements, as the measurement changes the state of the material being inspected. The laser pulse that is used to supply the energy to the sample is adsorbed in the fusion reaction of the metal alloy, melting the alloy and producing an apparently low thermal-diffusivity measurement. Szelagowski et al. [12] modeled this effect by coupling both the mass-flow and the heat-flow equations. Their analysis confirmed the above problem but suggested that under certain conditions thermal diffusivity measurements in the two-phase region could be made. It is the authors' intention to try the Szelagowski [12] approach at some future date.

3.4. Thermal Conductivity of the Cu + 10 wt% Sn Alloy

As mentioned previously, there is an absence of reliable thermal conductivity data for the commercial alloys used in the casting industry [1, 2] and it is difficult to make thermal conductivity measurements of liquid metals with traditional steady-state or pulse methods. In contrast, accurate electrical conductivities are simpler to obtain experimentally and, more importantly, are unaffected by convection. Therefore, the Lorenz relation offers a powerful alternative to obtaining thermal conductivities of liquid metal alloys should it be proven.

The Lorenz [6] relation relates thermal conductivity (λ) to electrical resistivity (ρ) by Eq. (1),

$$\lambda = \frac{L_o T}{\rho} \tag{1}$$

where T is the temperature in kelvins and L_o is a constant with a value of 2.445×10^{-8} W·Ω·K^{-2} [6] and, therefore, may be used to obtain liquid thermal conductivities that are unaffected by convection. The Lorenz relation is valid only if the heat conduction in the metal is carried by electrons. This is likely to be the case near or above the melting point of a metal where the metal is in a highly energized state.

The liquid thermal conductivities calculated from the Lorenz relation are shown in Fig. 4. For comparison, also shown in Fig. 4 are the thermal conductivity values calculated from the measured thermal diffusivity (a) data by Eq. (2),

$$\lambda = aCpd \tag{2}$$

where d is the density. Data used for converting the thermal diffusivity values to thermal conductivity were (i) C_p calculated for both the solid and
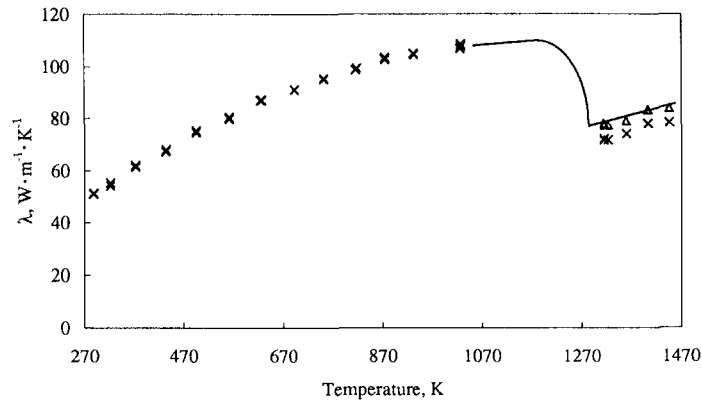
Fig. 4. Comparison of thermal conductivity of the Cu + 10 wt% Sn alloy calculated via the Lorenz relation (—) with those calculated from thermal diffusivity using MTDATA C_p calculations ($\times$) and thermal diffusivity using the measured C_p from a DTSC ($\triangle$).

the liquid phases from MTDATA [9], (ii) measured C_p DTSC data for the liquid phase, and (iii) density calculated for both solid and liquid phases from the Metals Model [13].

The density is calculated in the Metals Model using an empirical relation based on partial molar volumes [13]. The thermal diffusivity data in the two-phase region in Fig. 3 have not been converted to thermal conductivity as, for reasons outlined earlier, there are too many uncertainties in the data.

In Fig. 4 it can be seen that the thermal conductivities calculated from the Lorenz relation in the liquid region compare well with those calculated from the thermal diffusivity values. The largest difference is approximately 10% between the thermal conductivity calculated from thermal diffusivity using MTDATA C_p values. The thermal conductivity values calculated using the measured C_p are in better agreement with those calculated using the Lorenz relation. The discrepancy between the thermal conductivities calculated via the Lorenz and those converted from thermal diffusivity using the measured C_p values lies within the combined uncertainties of the measurement methods. What is also of note is that the $d\lambda/dT$ of all the liquid thermal conductivities is the same. In terms of heat-flow modeling, this parameter is as important as the absolute value of the thermal conductivity.

The deviations between the thermal conductivities may result from failings in the Lorenz relation or errors associated with the resistivity, thermal diffusivity, heat capacity, and density values. This small deviation

demonstrates that, for this alloy at least, the thermal conductivity of the liquid phase can be calculated from the resistivity.

3.5. Liquidus and Solidus Temperatures

The apparent liquidus and solidus values obtained with the different techniques are no surprise. It is the authors' experience that no two techniques for measuring the liquidus/solidus give the same answer. Possible reasons for these discrepancies are as follows: (a) *Material composition*—Are all the techniques measuring exactly the same composition of material? (b) *Nonequilibrium solidification*—many materials exhibit undercooling, particularly in "clean" environments with no nucleation sites. Scheil solidification [14] (microsegregation) results from solute rejection during solidification. The cooling rate can have a significant effect on microsegregation [14]. This is a major problem, as each piece of equipment imposes different heat transfer conditions on the sample, and while the ideal set of experiments will all be done at the same cooling rate, they are seldom exactly the same, particularly for samples of different geometry. (c) *Instrument effects*—(i) time constants can have an effect; (ii) the laser flash technique hits the sample with a burst of energy, which will likely melt some metal when the sample is close to the solidus; and (iii) most thermocouples have an uncertainty of approximately $+/-4$ K at best at high temperatures.

4. CONCLUSIONS

The Lorenz relation is suitable for calculating thermal conductivity from electrical resistivity in the liquid region for the Cu + 10 wt% Sn alloy. The Lorenz relation is suitable for calculating $d\lambda/dT$ from electrical resistivity–temperature data.

ACKNOWLEDGEMENT

REFERENCES

1. P. N. Quested, K. C. Mills, R. F. Brooks, A. P. Day, R. Taylor, and H. Szelagowski, *Proc. 4th Int. Conf. Solid. Process.* (Dept. Eng. Mater., University of Sheffield, Sheffield, 1997), pp. 143–150.
2. K. C. Mills, B. J. Monaghan, and B. J. Keene, *Int. Mater. Rev.* 41:209 (1996).

3. B. J. Monaghan, *Int. J. Thermophys.* **20**(2): (1999).
4. Y. Mera, Y. Kita, and A. Adachi, *Technol. Rep. Osaka Univ.* **22**:445 (1972).
5. A. Roll and H. Motz, *Z. Metallk.* **48**:272 (1957).
6. T. Ilda and R. I. L. Guthrie, *The Physical Properties of Liquid Metals* (Clarendon Press, Oxford, 1993), pp. 226–242.
7. K. D. Maglic, A. Cezairliyan, and V. E. Peletsky (eds.), *Compendium of Thermophysical Property Measurements Methods* (Plenum Press, London, 1992), Vol. 2, pp. 519–545.
8. L. Dusza, *High Temp.-High press.* **27**:467 (1995).
9. R. H. Davies, A. T. Dinsdale, J. A. Gisby, S. M. Hodson, and R. G. J. Ball, *Proc. Conf. Appl. Thermodyn. Synth. Process. Mater.* (ASM/TMS, Rosemont, IL, 1994).
10. R. Cahn and P. Hassen, *Phys. Met.* (North-Holland, Oxford, 1996), Vol. 1, pp. 670–844.
11. M. Hansen and K. Anderko (eds.), *Constitution of Binary Alloys* (McGraw–Hill, London, 1958), pp. 633–637.
12. H. Szelagowski, R. Taylor, J. D. Hunt, and P. N. Quested, *Proc. 4th Int. Conf. Solid. Process.* (Dept. Eng. Mater., University of Sheffield, Sheffield, 1997), pp. 151–154.
13. K. C. Mills, A. P. Day, and P. N. Quested, *Symp. New Frontiers Mater. Sci. Related Eng. Appl.* (Nottingham University, Nottingham, 1995).
14. K. Fisher, *Fundamentals of Solidification* (Trans. Tech. Publ., Aedermannsdorf, 1992), pp. 117–161.