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THERMOTRANSPORT IN LIQUID ALUMINUM-COPPER ALLOYS

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16. ABSTRACT

A thermotransport study was made on a series of liquid aluminum-copper alloys which contained from trace amounts to 33 weight percent copper. The samples in the form of narrow capillaries were held in known temperature gradient of thermotransport apparatus until the stationary state was reached The samples were analyzed for the concentration of copper along the length Copper was observed to migrate to the colder regions in all the samples The heat of transport, Q* , was determined for each composition from a plot of concentration of copper versus reciprocal absolute temperature The value of Q* is the highest at trace amounts of copper (4850 cal/gm-atom), but decreases with increasing concentration of copper and levels off to 2550 cal/gm-atom at about 25 weight percent copper The results are explained on the basis of electron-solute interaction and a gas model of diffusion

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THERMOTRANSPORT IN LIQUID ALUMINUM-COPPER ALLOYS

INTRODUCTION

If a homogeneous single-phase liquid alloy is held in a temperature gradient, matter fluxes are usually generated and a concentration gradient will be created by the temperature gradient This phenomenon is called thermotransport, which can be characterized by a quantity called the heat of transport, denoted by Q* By definition, Q* of a species is the flux of heat in excess of enthalpy which is transported per unit flux of that species. The meaning of Q* has been described in earlier papers [1,2], especially Reference 1 Theoretically, the heat of transport is closely related to the dynamics of diffusion process and hence the results of thermotransport experiments help to understand the process of diffusion itself*. From a practical point of view, the heat of transport is a measure of the segregation that may be expected in an alloy when it is subjected to a temperature gradient. The amount of segregation will influence the physical properties of the alloy after solidification

Thermotransport studies made so far [1-4] have been primarily in dilute alloys which contained solute elements in amounts of a few parts per million Commercial alloys are generally more concentrated No systematic study of concentrated alloys seems to have been made so far It is the purpose of this work to study thermotransport in concentrated aluminum-copper alloys The aluminum-copper system was chosen for study because these alloys have wide applications They melt at relatively low temperatures, especially on the aluminum rich side, and hence can be studied over a wide range of temperatures Table 1 lists some parameters for aluminum and copper A copper atom is heavier than an aluminum atom and has a larger ionic radius. It also has a valence of one as compared with three for aluminum These factors tend to drive copper atoms to the colder regions in a thermotransport experiment [1]. Hence, the aluminum-copper system may be expected to exhibit a significant amount of thermotransport.

PHENOMENOLOGICAL BASIS FOR THE HEAT OF TRANSPORT

Thermotransport has been treated on the basis of the theory of thermodynamics of irreversible processes [5,6]. The approach to thermotransport used in the present work is described in Reference 1, in which an expression was derived for the heat of transport in relation to the temperature gradient and the concentration gradient at the stationary state The following expression is from Appendix 1 of Reference 1

$$\left(\frac{1}{\overline{V}_1 x_1} + \frac{1}{\overline{V}_2 x_2} \right) dx_2 = - \frac{1}{RT^2} \left(\frac{Q_2^*}{\overline{V}_2} - \frac{Q_1^*}{\overline{V}_1} \right) dT \tag{1}$$

where

Q_2^*, Q_1^* = heat of transport of solute and solvent respectively,

$\overline{V}_2, \overline{V}_1$ = partial molar volume of solute and solvent respectively,

*B N Bhat, Solute Diffusion in Liquid Metals, Marshall Space Flight Center, to be published as NASA Technical Report

TABLE 1. PARAMETERS FOR ALUMINUM AND COPPER

Element	Atomic Weight	Ionic Radius (Å)	Valence	Molar Volume at 700°C (ml)
Aluminum	26 98	0.51	3	11.4
Copper	63.55	0 96 0.72	1 2	7.25 (estimated)

x_2, x_1 = mole fraction of solute and solvent respectively;

T = absolute temperature,

and

R = gas constant.

In deriving the above expression, it is assumed that the activity coefficient is constant This is justified in the present work because the values of the activity coefficients of copper in liquid aluminum-copper alloys, as calculated on the basis of other thermodynamic properties of aluminum-copper alloys [7], are nearly constant in the composition range studied here. The equation can be rearranged to yield the following expression,

$$d\left[\ln x_2 - \frac{\overline{V}_2}{\overline{V}_1}\ln(1 - x_2)\right] = \frac{Q^*}{R}\, d\left(\frac{1}{T}\right) \quad (2)$$

where

$$Q^* = Q_2^* - Q_1^* \frac{\overline{V}_2}{\overline{V}_1}$$

In the case of aluminum-copper alloys, $\overline{V}_2/\overline{V}_1$ is estimated to be 0.64. Dropping suffixes, one obtains,

$$d\left(\ln x - 0.64 \ln(1 - x)\right) = \frac{Q^*}{R}\, d\left(\frac{1}{T}\right) \quad (3)$$

where

x = mole fraction of copper which is considered solute.

In the case of very dilute alloys containing trace amounts of copper, expression (3) simplifies to

$$\frac{Q^*}{R}\, d\,\frac{1}{T} = d \ln x = d \ln c \quad (4)$$

where c = concentration of copper.

In a thermotransport experiment, if a column of liquid alloy is held in a known temperature gradient until the stationary state is reached, the logarithm of the resulting concentration along the length of the column is related to the corresponding reciprocal temperature through the factor Q*/R

EXPERIMENTAL

In the technique employed here, a thermotransport experiment consisted essentially in holding a column of liquid alloy of aluminum and copper of known composition in a known temperature gradient for a sufficiently long time for the stationary state to be attained. The experimental procedure is very similar to that described in Reference 1. The differences are accented in the following paragraphs

Thermotransport Apparatus

The apparatus designed for thermotransport experiments (Fig. 1) consists of two furnaces placed one above the other and controlled separately. The upper furnace is normally operated at higher temperature The controllers employ chromel-alumel thermocouples A steep temperature gradient is obtained by a water-cooled copper block between the two furnaces. The experiments are conducted in a quartz vacuum chamber which fits into the dual furnace assembly The samples are attached to the outside of a central quartz tube which houses the measuring thermocouple The temperature distribution along the axis of the inner quartz tube can be determined by properly positioning the thermocouple along the length of the tube Lateral temperature gradient can be determined by use of a side tube which occupies the same position as the sample The difference in the temperature between hot and cold ends can be controlled. In a typical profile the temperature dropped 100°C in a distance of 3 cm.

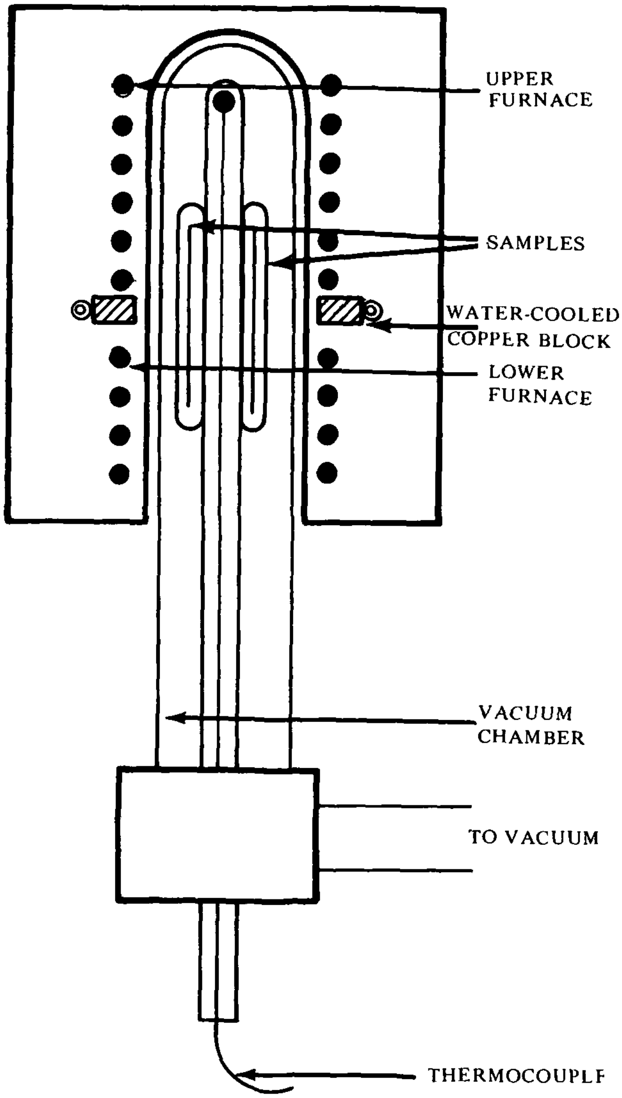

Figure 1. Thermotransport apparatus

Experimental Procedure

Preparation of Sample. The thermotransport experiments were conducted with aluminum that contained trace amounts, 5, 10, 15, 20, 25, and 33 weight percent of copper Aluminum metal and aluminum-33-percent copper eutectic alloy that were 99 999 percent pure were obtained from Materials Research Corporation. The eutectic alloy and pure aluminum were melted together in proper proportions under vacuum to yield alloys of desired composition. Those alloys which contained 15 percent or less copper were melted with requisite amounts of radioisotope Cu-67, which was obtained from Oak Ridge National Laboratory. The isotope is a gamma emitter with a half life of 61 hours

The samples consisted of graphite capillaries filled with these alloys. The capillaries had diameters of 0 238 cm, 0 159 cm and 0.13 cm respectively, were 5 cm long on the average, and were encapsulated in quartz tubes under a vacuum of approximately 10^{-5} torr

Diffusion Annealing The encapsulated samples were attached to the central quartz tube of the thermotransport apparatus and their positions with respect to the closed end of the tube were noted The tube was then introduced into the furnace assembly which was already at the operating temperature. The vacuum connections were made and the quartz chamber was evacuated The samples melted from the top first and a steady temperature gradient was attained in about an hour Experiments were conducted with 120° to 250°C difference between hot and cold ends. The variation in the temperature of the hot and cold ends was about ±3°C during a run The vacuum in the quartz chamber was approximately 10μm of mercury during the anneal

The time of anneal was 10 to 15 days, depending upon the length of the samples (the shorter samples required less time for reaching stationary state) At the end of this period, the samples were pulled out of the furnace assembly and allowed to solidify in air The process of freezing took less than half a minute

Analysis The metal was separated from the graphite capillaries and was thoroughly cleaned with polishing paper and then acetone and methyl alcohol The samples were cut into several sections of approximately equal lengths. The position of each section was noted. Each section was then analyzed Radiotracer analysis was made by use of a scintillation counter which used a 2π geometry NaI crystal Samples which contained 20 percent or more copper were analyzed by use of an atomic absorption spectrometer. In this technique, a weighed amount of sample was dissolved in a standard solution of HCl and H_2O_2 and brought to the correct volume The concentration of copper in this solution was compared with that of the standard by measuring the intensity of absorption spectra of both the solutions The error in the analysis of copper by either technique was estimated to be approximately 1 percent

Some Special Considerations

A few experiments were performed to ensure that the segregation obtained in thermotransport experiments was indeed due to temperature gradient and not due to other factors such as convection or sedimentation These special experiments are described below.

Convection causes mixing of components and decreases the amount of segregation This effect is a strong function of the diameter of the capillary. Thermotransport experiments were conducted with 0 238-, 0 16- and 0 13-cm diameter capillaries These experiments yielded essentially the same results This suggested that the observed segregation was not affected by convection.

Another factor which can influence segregation is sedimentation. A solute dissolved in a lighter solvent tends to concentrate at the bottom of a vertical capillary, thus contributing to the segregation caused by thermotransport To see if sedimentation was important in the present investigation, experiments were performed with a small negative temperature gradient in which the hot end was at the bottom and the cold end was at the top. The results showed that there was no measurable segregation in these samples Hence it was concluded that sedimentation did not materially affect the results of the present investigation.

RESULTS

In the radioactive samples, the concentration of solute in each section is proportional to its specific activity For the alloy containing trace amounts of copper only, it is not the actual concentration of the solute, but the relative concentration which is of interest The relative concentration of solute in each section (c/c_a) was obtained by dividing its specific activity (c) by the average specific activity in the whole sample (c_a). In the case of concentrated alloys the mole fraction of copper in section (x) was determined by use of the following expression,

$$x = x_a\left(\frac{c}{c_a}\right) \qquad (5)$$

where

x_a = average mole fraction of copper in the sample

In the samples which were not radioactive, the analytical technique yielded weight percent of copper in each section. This was converted to mole fraction.

Since the position of each section was marked prior to analysis, the temperature of each section could be determined by comparing its position along the axis of the furnace assembly. The temperature was corrected for the lateral temperature gradient. Logarithm of relative concentration ($\ln c/c_a$) was then plotted against the reciprocal absolute temperature (1/T). Figure 2 is a typical plot for the sample containing trace amounts of copper

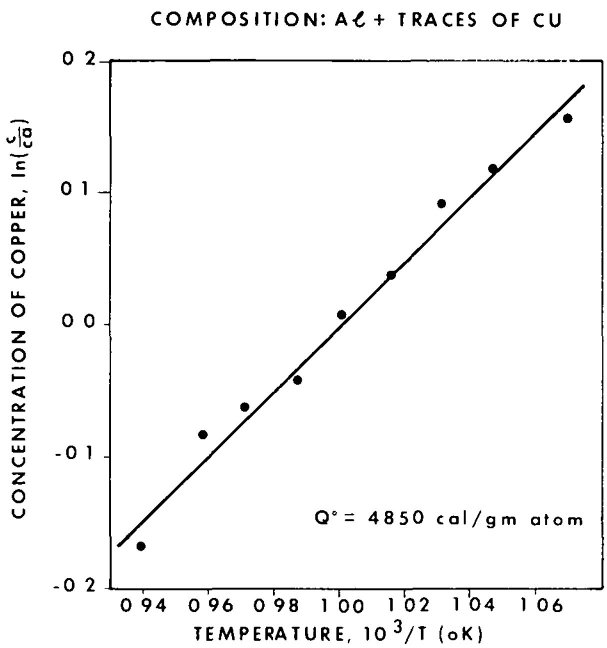

Figure 2 Thermotransport in aluminum-copper alloy containing trace amounts of copper

In the case of concentrated alloys, ln x-0.64 ln(1-x) was plotted against 1/T Figure 3 is such a plot for aluminum-33-percent copper alloy It is observed that the copper migrates to the colder regions The heat of transport can be determined from the slope of these curves by use of the expressions

$$Q^* = R\,\frac{d \ln (c/c_a)}{d(1/T)} \quad \text{for dilute alloys} \qquad (6)$$

and $$Q^* = R \frac{d\left[\ln x - 0.64 \ln(1-x)\right]}{d(1/T)}$$

for concentrated alloys (7)

Since no deviation from linearity can be delineated the plots of $\ln(c/c_a)$ versus $1/T$ and those of $\ln x - 0.64 \ln(1-x)$ versus $1/T$ are fitted with straight lines by use of a least mean square method. The slopes of the straight lines so obtained yield the values of the heats of transport, Q^*. The values of Q^* for at least three different samples of a given compositon were averaged to yield a mean value of Q^* for that composition. An error analysis was made for the experiments [8] and it was found that the principal errors arose from the measurements of temperature and analysis of copper A typical standard error in the value of Q^* is 15 percent.

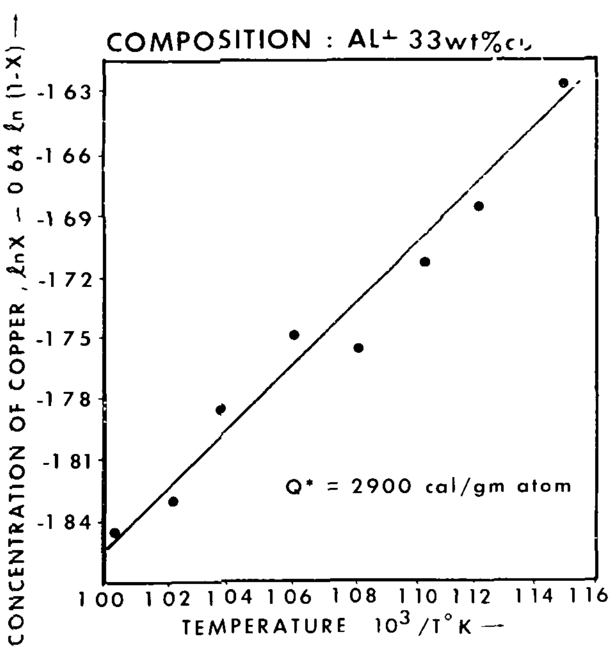

Figure 3 Thermotransport in aluminum-copper alloy containing 33 weight percent copper

Figure 4 is a plot of the heat of transport versus the concentration of copper. It is observed that Q^* is maximum (4850 cal/gm-atom) for the alloy which contained trace amounts of copper. The value of Q^* decreases rapidly with increasing concentration of copper and tends to level off to a value of 2550 cal/gm-atom at about 25 percent copper.

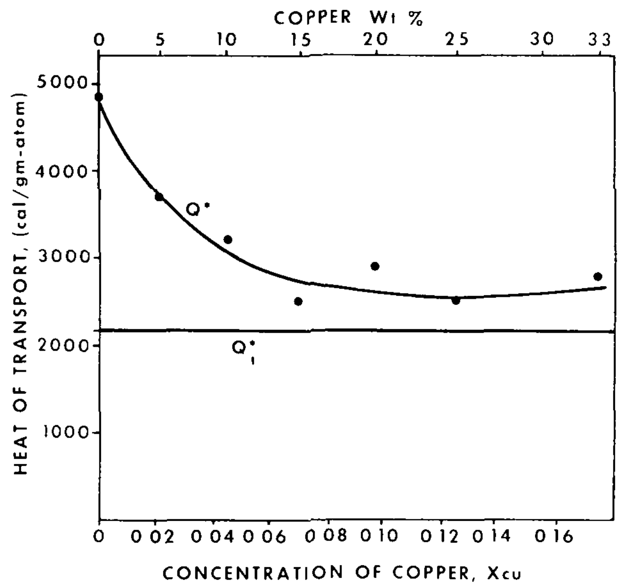

Figure 4 Heat of transport as a function of composition

DISCUSSION

The heat of transport has been discussed in detail from a kinetic point of view in Reference 1 According to the approach discussed in that paper the heat of transport Q^* may be considered to consist of two different contributions, namely

$$Q^* = Q_i^* + Q_e^* \tag{8}$$

where Q_i^* is the intrinsic contribution to the heat of transport. This contribution arises from the interaction between the ions themselves. The symbol Q_e^* represents the extrinsic contribution which can arise from (a) electrostatic fields created in the metal caused by the presence of temperature gradient and (b) interaction of the diffusing ion with the charge carriers which are electrons and/or holes

Intrinsic Heat of Transport

A value for the intrinsic heat of transport Q_i^* can be obtained from a gas model of diffusion in liquid metals and the method has been described in Reference 1. The Q_i^* is given by

$$\frac{Q_i^*}{RT} = K\left[\frac{m_2 - m_1}{m_2 + m_1} - 0.2\left(\frac{s_2^2}{s_{21}^2} - 1\right)x_2 + 0.2\left(\frac{s_1^2}{s_{12}^2} - 1\right)x_1\right] \tag{9}$$

where

m_1, m_2 = atomic mass of solvent and solute respectively;

x_1, x_2 = mole fraction of solvent and solute respectively,

s_1, s_2 = equivalent ionic diameter of solvent and solute respectively (equal to ionic diameters for rigid sphere model)

$$s_{12} = s_{21} = (s_1 + s_2)/2$$

and

$K = 2.2$ for liquid metals.

The value of the Q_i^* has been computed and plotted in Figure 4. It is observed that the value of Q_i^* is practically constant in the range of composition studied in this work. An average value of Q_i^* is

$$Q_i^* = 2200 \text{ cal/gm-atom} \tag{10}$$

Extrinsic Heat of Transport

Electrons are the main contributors to the extrinsic heat of transport in liquid metals and their contribution can be calculated by use of a method due to Gerl [9, 10]

$$Q_e^* = \frac{K_e T}{2}\left(\frac{m^*}{m}\right)^{-1/2}\left(E_F\right)^{-1/2} A_z(E_F)\left[1 + 2\left(\frac{d\,A/A}{d\,E/E}\right)_{E_F}\right] \tag{11}$$

where

K_e = electronic contribution to thermal conductivity,

m, m^* = rest mass and effective mass of electron;

z = effective charge on the diffusing ion

A_Z = resistivity scattering cross section of solute atoms for electrons,

E = energy of electrons,

and

E_F = Fermi level.

The sign of Q_e^* is determined by the term in brackets in expression (11) If this term is positive, the effective scattering cross section of hot carriers is more than that of cold carriers, in which case the solute tends to segregate to the colder regions. This appears to be the case for copper in aluminum. If the effective scattering cross sections of hot carriers is sufficiently smaller than that of cold carriers, Q_e^* is negative and the solute tends to migrate to the hotter regions.

To calculate Q_e^*, it is necessary to know the values of electrical resistivity and thermoelectric power of aluminum-copper alloys as a function of composition No such data are available at the present time and a quantitative estimate of Q_e^* can not be made Qualitatively, however, it is possible to predict the behavior of Q_e^* as a function of composition. Following Gerl[9], the scattering cross section for electrons, A_Z is

$$A_Z \propto \frac{\partial \rho}{\partial x} \tag{12}$$

where $\partial \rho/\partial x$ is the resistivity concentration coefficient of solute. For a homogeneous binary alloy, resistivity will generally increase with increasing solute content up to a certain point and then decreases with further increase of solute [11,12]. Hence $\partial \rho/\partial x$ is largest at infinite dilution, decreases rapidly with increasing solute content, and becomes zero at some intermediate composition. This means that Q_e^* will be maximum at infinite dilution, will decrease rapidly, and will become zero at some intermediate composition. In comparison with the present experimental data, Q_e^* is found to be positive and the minimum in Q_e^* seems to occur at about 25-percent copper The value of the total heat of transport in that region is 2550 cal/gm-atom. This value is comparable to 2200 cal/gm-atom, which is the intrinsic heat of transport (Fig. 4) Hence Q_e^* appears to become less significant at higher concentrations of copper.

CONCLUSIONS

Thermotransport studies were made in liquid aluminum containing copper in amounts varying from trace amounts to 33 percent by weight Copper was observed to migrate to colder regions in all the alloys, yielding a positive heat of transport, Q*. The value of Q* is the highest at infinite dilution (4850 cal/gm-atom), but decreases with increasing copper content and levels off to 2550 cal/gm-atom, at about 25 percent. The results can be explained on the basis of gas model of diffusion and electron-solute interaction.

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Marshall Space Flight Center, Alabama 35812, May 1973

REFERENCES

1. Bhat, B N. and Swalin, R A. Thermotransport of Silver in Liquid Gold. Acta Metallurgica, vol. 20, Dec 1972, pp. 1387-1396.

2. Bhat, B.N and Swalin, R.A. Thermotransport of Solutes in Liquid Silver Zeitschrift fur Naturforschung, vol. 26a, no. 1, pp 45-47

3. Bhat, B.N and Swalin, R.A. Thermotransport of Cobalt in Liquid Silver Scripta Metallurgica, vol. 6, 1972, pp 523-528

4 Bhat, B.N., Murarka, S.P , and Swalin, R A Thermotransport of Beryllium and Mercury in Liquid Sodium. Scripta Metallurgica, vol. 7, 1973, pp. 523-528.

5. DeGroot, S R.: L'effet Soret N V Noord-Hollandsche Uitgevers Maatschappij (Amsterdam), 1945

6 DeGroot, S.R.: Thermodynamics of Irreversible Processes. North-Holland Publishing Co. (Amsterdam), 1961.

7 Hultgren, R., Orr, R.L., Anderson, P.D , and Kelley, K.K : Selected Values of Thermodynamic Properties of Metals and Alloys John Wiley & Sons, Inc , 1963, pp. 408-411

8 Bhat, B.N. Thermotransport of Solutes in Liquid Silver Ph D. Thesis, University of Minnesota, Minneapolis, Minnesota, 1971.

9 Gerl, M.: Contribution au Calcul des Forces Agissant sur une Impurete d'un Metal Soumis a un Gradient de Temperature. Journal of Physics and Chemistry of Solids, vol. 28, 1967, pp 725-36.

10 Gerl, M Calcul des Forces Agissant sur une Impurete d'un Metal Soumis a un Gradient de Temperature. Centre D'etudes Nucleaires de Saclay. Rapport CEA-R3096, December 1966

11 Howie, R A and Enderby, J E . The Thermoelectric Power of Liquid Ag-Au. Philosophical Magazine, vol. 16, 1967, pp. 467-476.

12. Faber, T E The Resistivity of Liquid Alloys Advances in Physics, vol. 16, no. 64, 1967, pp 637-650.

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