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# Diffusion couple preparation using cast coating technique

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A novel diffusion couple preparation technique suitable for the measurement of diffusivities in molten metals and semiconductors via the long capillary method has been developed. The so-called cast coating technique involves casting of a molten alloy, which contains the impurity element to be diffused, on top of the pure solvent rods. Planar, oxide and defect free interfaces were produced at the alloy/solvent junction of the diffusion couple following basic solidification principles and a controlled atmosphere. It was noted that the thermal properties of both the molten alloy and the mould were critical in determining the location and planarity of the diffusion couple interface. The Sn/Sn-1 wt% Au and Pb/Pb-1 wt% Au diffusion couples in conjunction with moulds machined from graphite, porous graphite and a machinable ceramic were chosen as a case study. © *2002 Kluwer Academic Publishers*

## Nomenclature

| | |
|---|---|
| $\alpha$ | Thermal diffusivity of mould |
| $B$ | Mould constant |
| $C_l$ | Specific heat of melt |
| $C_{md}$ | Specific heat of mould |
| $D_r$ | Runner diameter |
| $L_f$ | Latent heat of fusion |
| $L_r$ | Runner length |
| $k_{md}$ | Thermal conductivity of mould |
| $\rho_l$ | Density of melt |
| $\rho_{md}$ | Density of mould |
| $SA$ | Surface area |
| $T_l$ | Liquidus temperature |
| $T_p$ | Pouring temperature |
| $T_{md}$ | Mould temperature |
| $t$ | Time |
| $V$ | Volume |
| $W_c$ | Poured melt weight |

## 1. Introduction

The knowledge of diffusivities in liquid metals is of fundamental interest and is needed for many fields of engineering. The long capillary method is a widely used technique to determine the diffusion coefficients in molten metals [1–3]. This technique requires a diffusion couple composed of two sections of different compositions. The two sections are usually prepared separately and then joined together. It is essential that the interface between the two sections should be sharp to satisfy the boundary conditions of Fick's second law of diffusion and also be free of any oxide layers, inclusions, cavities or any other physical barriers. Hence, the ideal interface should be planar much like a grain boundary. It has often been difficult to meet all these requirements simultaneously in the past due to:

(i) In solid-solid diffusion couple preparation methods, two solids of different composition were polished and put together. Pressure was applied to the ends of the couple and the sample was welded together by heating to a suitable temperature [4]. In a different approach, one solid was just placed on top of the other [5]. It is obvious that an interfering oxide film is difficult to eliminate using these methods.

(ii) In the liquid-liquid methods, e.g., the more popular shear cell technique, the interface is inherently difficult to control to be sharp because of local liquid mixing [6–9].

A novel solid-liquid method called the cast coating technique for diffusion couple fabrication has been proposed and used recently by Zhu and Smith [10, 11] to meet those entire requirements above. Using these diffusion couples, a series of long capillary diffusion experiments with over fifteen different metallic solvent—solute systems have been carried out both in the terrestrial and microgravity environments under various projects sponsored by the Canadian Space Agency [12–15]. A schematics which involves the cast coating technique and the long capillary method for diffusion coefficient evaluation, e.g., gold diffusing in tin, is given in Fig. 1.

Three high purity solvent (e.g., tin) rods are placed in a graphite mould such that their top ends project slightly

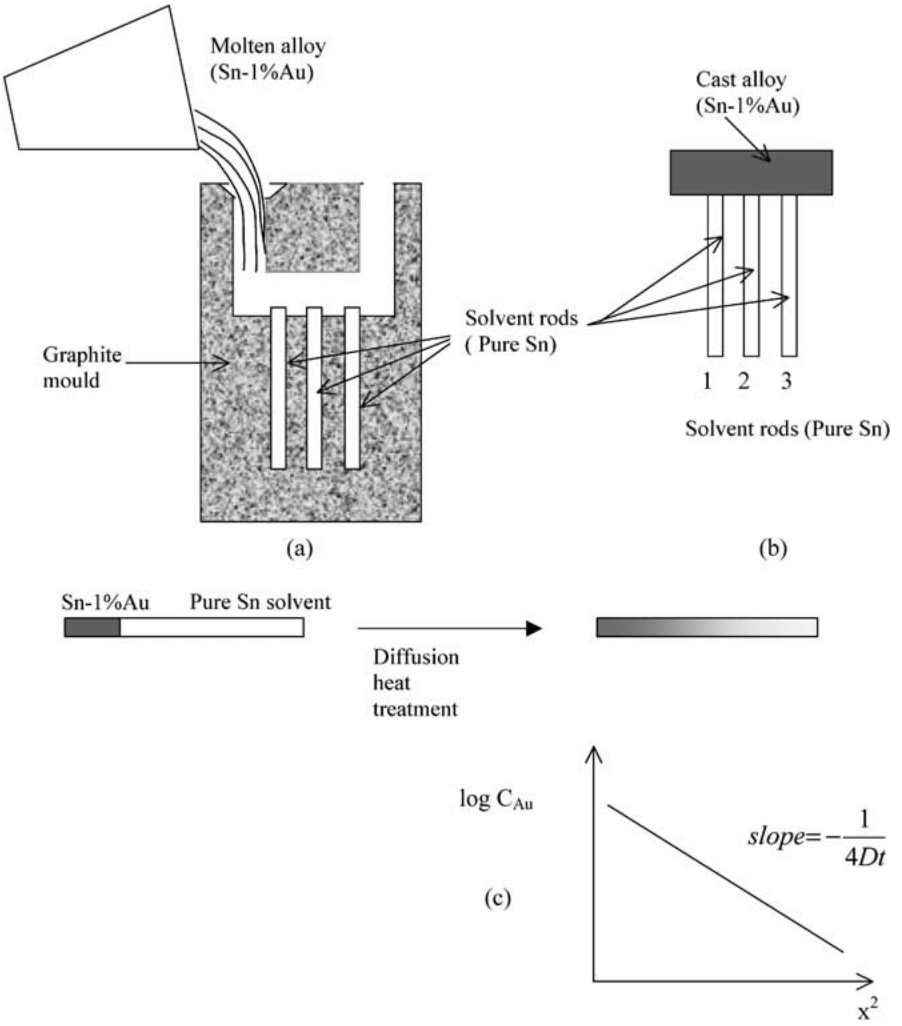

*Figure 1* The schematics of cast coating technique coupled with the long capillary method for diffusion coefficient measurement.

above the runner surface to react and form planar joints with the alloy half of the proposed diffusing couple as shown in Fig. 1a. The molten alloy which contains the impurity metal to be diffused, e.g., Sn-1wt% Au alloy, is poured down the sprue until the mould is filled and a casting is made on top of the three pure solvent tin rods, Fig. 1b. Following removal from the mould, three different diffusion couple samples can be cut off from the cast gallery. A typical diffusion couple result is sketched in Fig. 1c. It is then placed in a graphite crucible and sealed by a graphite end cap. The details of the specimen assembly and the long capillary method employed with the isothermal diffusion heat treatment and specimen quenching procedures have been provided earlier [10, 11]. The atomic absorption spectroscopy technique is usually used to measure the concentration distribution along the solvent rod after the diffusion treatment in order to avoid the errors of segregation effects with point analysis methods such as the electron microprobe. Finally, using Fick's second law of diffusion and a log $C$ vs (Distance)$^2$ plot, given in Fig. 1c, the diffusion coefficient $D$ of a particular solute, e.g., gold in tin at a particular temperature, can be calculated. The long capillary method probably still remains as the most common procedure to measure the diffusion coefficients. It has been claimed that significant errors can arise during heating and cooling between the melting point and the target point [6, 7]. However, the actual comparison of results obtained for the same alloy systems using the long capillary/quench technique and the shear cell method do not support this contention, i.e., the calculated $D$s being closely similar [8, 9]. The shear cell method can be advantageous for the systems that have large volume changes on freezing, or large differences in melting points [6–8].

## 2. Experimental procedure

Our previous experience [11, 15] and also the thermal and physico-chemical properties of some molten solids, particularly semiconductors, made necessary that:

(i) Both the alloy preparation and the diffusion couple fabrication should be carried out under a controlled neutral/reducing atmosphere in order to obtain a clean interface between the two parts of a diffusion couple.

(ii) A new mould design would facilitate the selection of the optimum thermal conditions needed to achieve a successful diffusion couple.

The systems examined here were Sn-Au, Pb-Au, Bi-Mn, Bi-In, Sb-In and In-Sb which contained either 1 wt% of the impurity or its eutectic content. Both the solvent rods and alloys were prepared from at least

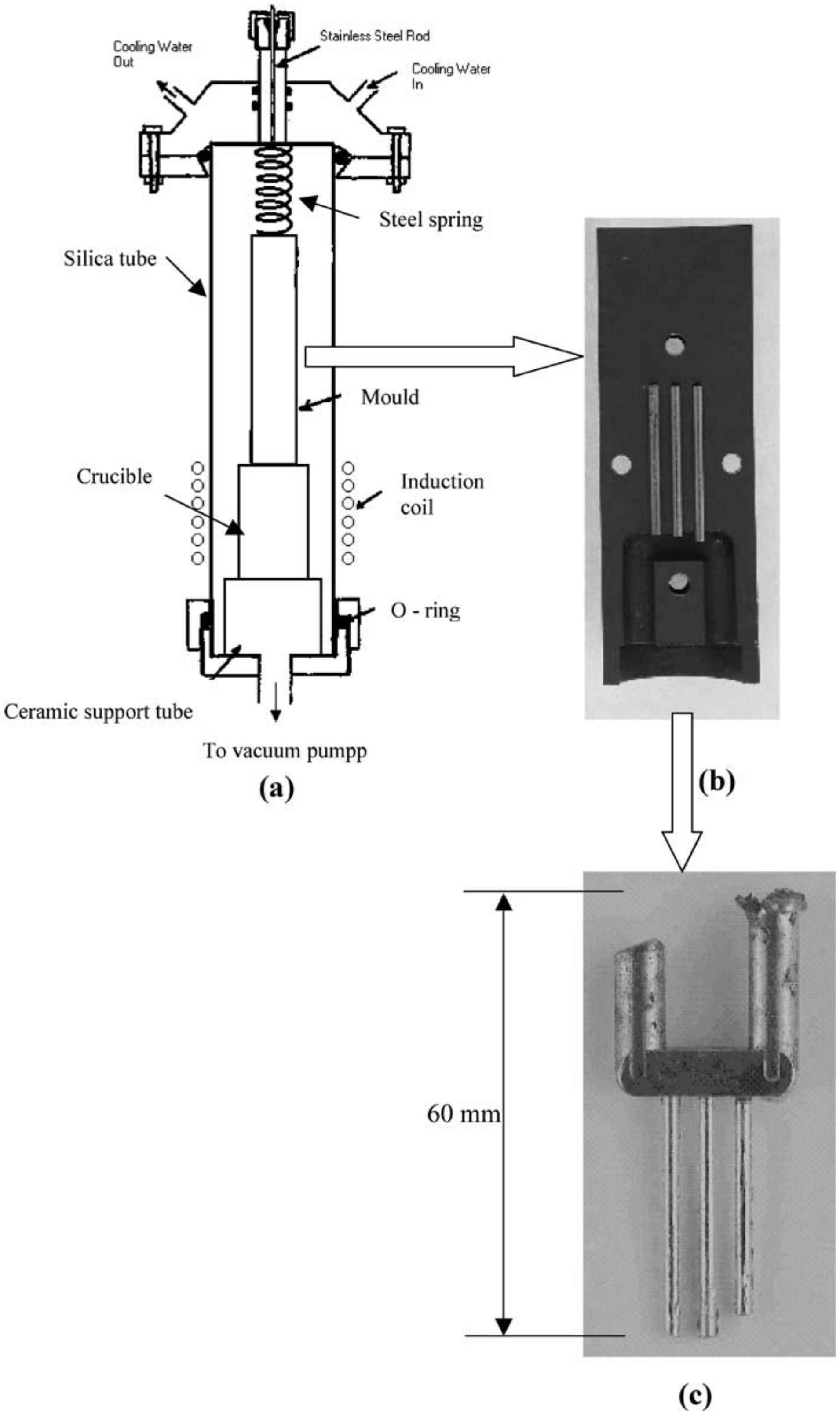

*Figure 2* The details of casting coating technique. (a) Vacuum induction furnace set-up. (b) Graphite mould and solvent rods. (c) Cast coated solvent rods.

99.999% purity components either in sealed Vycor tubes or in a vacuum induction casting furnace. The cast coating technique for diffusion couple preparation described in Fig. 1a and b was carried out in an experimental set-up shown in Fig. 2. In this, a 2.5 kW high frequency induction furnace, which can be tilted up to 180 degrees, has the mould and crucible assembly positioned inside a silica tube that was connected to a vacuum pump and could be back-filled with high purity argon. The melting crucible was machined from high purity graphite whereas the mould used could be either graphite, machinable ceramic or porous graphite. The porous graphite contained approximately 50% microporosity and the machinable ceramic, called Rescor 902, was produced by Cotronics Corporation, N.Y., U.S.A. All three materials had rather different thermal

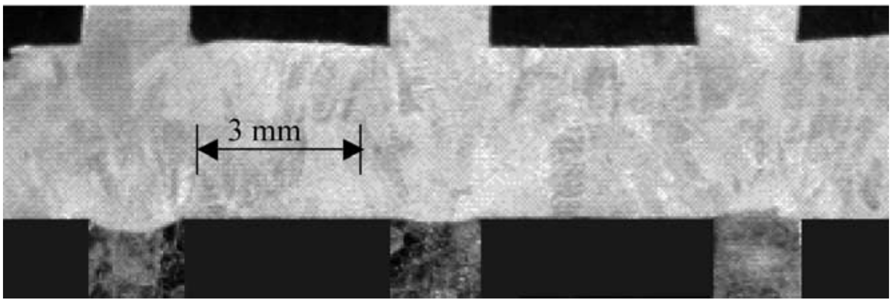

*Figure 3* The interfaces in the Sn/Sn-1 wt% Au diffusion couple.

properties. Hence, it was possible to adjust the cooling effect of the mould on the molten metal in order to control the position of the interface created between the two halves of the diffusion couple.

After evacuation of the system seen in Fig. 2a, the alloy charge was melted inductively in its graphite crucible. The molten alloy of approximately 3.0 ml was transferred from its crucible to the mould by tilting the induction furnace. This allowed the molten alloy to flow across and melt the top ends of the three solvent rods which projected up to 1.0 mm above the runner surface, the actual projection height depending on their location from the sprue end as seen in Fig. 2b for 2.0 mm diameter solvent rods. These solvent rods were positioned earlier in the mould before pouring of the melt. The cast alloy/solvent rods gallery given in Fig. 2c was removed from the mould upon solidification. The covalent samples, e.g., Sb and its compounds and to a lesser extend Bi and its compounds, were very brittle and required very gentle handling since they often fractured on removal from the mould. In view of this, each of the three diffusion couple candidates were cut off from the cast alloy/solvent rods gallery by electro-discharge-machining (EDM).

A metallographic section of a diffusion couple formed between Sn-1wt% Au alloy and pure tin solvent rods of 2.0 mm diameter in which the pouring and graphite mould temperatures were 630°C and 25°C, respectively is given in Fig. 3. In this particular example, the mold shown in Fig. 1a had rod cavity extensions on the cast alloy gallery; these filled with the alloy on pouring allowing interdiffusion specimens to be prepared by electro-die machining the gallery away from the alloy halk of the interdiffusion sample.

## 3. Results and discussion

### 3.1. Interface position of the diffusion couple

The diffusion couple interface formed between the first tin solvent rod in the graphite mould from the sprue (from left) and the Sn-1 wt% Au alloy, as seen in Fig. 3, was displaced approximately 200 $\mu$m in to the tin solvent rod, although its top end was deliberately left about 1.0 mm above the runner surface prior to pouring of the alloy as given in Fig. 2b. It is evident that this projection was melted during pouring of the alloy and there was some excess superheat left to extend melting slightly into the tin solvent rod kept in the graphite mould. The displacement of the diffusion couple interface was reduced to less than 50 $\mu$m into the second (middle) tin solvent rod and the interface appears to be free of any oxide films or discontinuities. The location of the third interface, i.e., seen as the shortest rod in Fig. 3, on the contrary, was moved about 45 $\mu$m into the Sn-1 %wt Au casting which indicates that the molten alloy had lost much of its superheat before reacting with the third tin solvent rod. Hence, the quality of a diffusion couple prepared with this method can be characterized readily under an optical microscope. The ideal position of the interface, i.e., when the diffusion interface forms exactly at the tin solvent rod/alloy casting junction, as a function of pouring temperature can be estimated from an experimental plot given in Fig. 4. The ideal interface would be located at 0 mm in Fig. 4, i.e., when it is not displaced into either the tin solvent rod or into the alloy casting. The lines 1, 2 and 3 correspond to the first, second (middle) and third Sn/Sn-1 wt% Au casting interfaces, respectively under various pouring temperatures when the graphite mould was kept at room temperature. It can be estimated from the plot that the zero interface displacements can be achieved with pouring temperatures 630°C, 640°C and 655°C respectively, for the first, second and third diffusion couple interfaces.

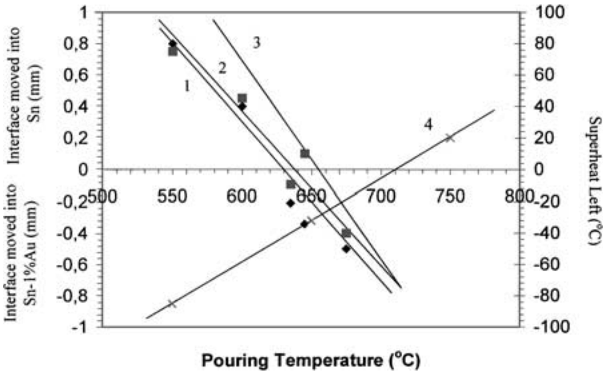

*Figure 4* Effects of pouring temperature on interface position the Sn/Sn-1 wt% Au diffusion couple and also on the superheat left in the alloy melt estimated from Equation 1.

The casting of Pb/Pb-1 wt% Au diffusion couple was more problematic. All the three interfaces were displaced into the alloy casting half of the diffusion couple when the identical casting conditions used above were employed. That is, a diffusion couple could not be made due to the premature freezing of the molten alloy, preventing its reaction with the lead solvent rods. It was found that in order to get the desired interface position, i.e., the zero displacement in Fig. 4, the graphite mould and the Pb-1 wt% Au melt were needed to be heated to

300°C and 1100°C, respectively. High temperatures induced also extensive oxidation of the molten lead alloy in air. Consequently, the effects of the thermal properties of both molten alloys and the mould materials on undercooling and freezing time were investigated in order to adjust the mould design and casting parameters accordingly.

## 3.2. Estimation of the temperature loss during mould filling

The temperature loss experienced by a molten alloy in a gating system during mould filling ($\Delta T$) can be predicted using the Equation 1 below proposed by Henzel [16], which allows for a given pouring time ($t$) to examine independently the effects of:

(i) Mould material, i.e., $k$, $\rho$ and $C_{md}$ and also mould temperature, $T_{md}$.
(ii) Melt, i.e., $C_l$, $W_c$ and $T_p$.
(iii) Mould design, i.e., $D_r$ and $L_r$.

$$\Delta T = \frac{\pi D_r L_r (T_p - T_{md}) t^{1/2}}{W_c C_l} \left( \frac{k_{md} \rho_{md} C_{md}}{\pi} \right)^{1/2} \qquad (1)$$

Assuming that the melt being poured is almost pure lead and also the heat lost in heating/melting of the lead rods in the graphite mould is negligible; then the $\Delta T$ in the Equation 1 and hence, the final melt temperature ($T_f$), can be estimated with respect to various mould materials and mould temperatures ($T_{md}$) for the Pb-1 wt% Au melt. It was observed that all the moulds were filled approximately in 2 seconds. The calculated values of undercoolings and the final temperatures of melts ($T_f$) are given in Table I. It can be seen that a melt faces considerable chilling in the graphite mould. For a pouring temperature of 1023 K (750°C), the molten alloy was cooled already below its melting point whether the graphite mould was kept at room temperature (298 K) or preheated to 523 K (250°C) during mould filling. Although it is estimated to be smaller than the one for the graphite mould, a large chilling of the melt still cannot be avoided in the porous graphite mould. These calculations suggest that under identical casting parameters, the lead alloy melt would remain above its melting point after mould filling only in the machinable ceramic mould, which had the smallest thermal diffusivity among the three mould materials.

On the other hand, the calculations reveal that the Sn-1 wt% Au melt would not suffer the same extensive chilling as the lead alloy during pouring into the same graphite mould which posseses a runner cross sectional area of 18 mm$^2$. In fact, the molten tin alloy would not be expected to be chilled to below its melting point even the graphite mould is not preheated. From Equation 1 it is evident that the specific heat of the metal is an important property in determining $\Delta T$. These calculations are in agreement with the metallographic observations mentioned in the previous section.

The fourth curve in Fig. 4 is a plot of estimated superheat ($T_f$-$T_m$) left in front of the third tin solvent rod in Fig. 3 vs. the pouring temperature of molten tin alloy. The curve predicts that the remaining superheat of the melt approaches zero as it arrives at the third tin solvent rod, for a pouring temperature of about 710°C. On the other side, the zero displacement of the diffusion couple interface for the same tin solvent rod, i.e., curve 3, is determined to be around 655°C from metallographic examination (Fig. 3). The difference in the two temperatures may arise from the simplifying assumptions made above in calculating the $\Delta T$. Nevertheless, Equation 1 can be used to make an educated guess for a suitable pouring temperature prior to casting an actual diffusion couple, thus reducing much of the experimental iterations.

## 3.3. Estimation of the freezing time in the mould

Assuming no temperature drop has occurred during mould filling, i.e., $\Delta T$ is zero, the freezing time ($t_f$) of the same molten lead alloy in the previous moulds mentioned above can be estimated and compared briefly using the more familiar Chvorinov's equation [17] below:

$$t_f = B \left\{ \frac{V}{S_A} \right\}^2 \qquad (2)$$

where $$B = \left\{ \frac{\rho \sqrt{\pi \alpha_{md}} [L_f + C_l (T_p - T_l)]}{2 k_{md} (T_l - T_{md})} \right\}^2$$

The change in the freezing time of molten lead alloy at 750°C with respect to the mould material, mould temperature and runner cross-sectional area are given in Table II. In parallel with those calculations for $\Delta T$ in Table I, the $t_f$ is indirectly proportional to the thermal diffusivity of the mould material hence, the molten lead alloy cools most slowly in the machinable ceramic mould. The preheating of the moulds to 523 K, i.e., below the melting point of the lead solvent rods, also increases the freezing time of the lead melt as expected.

## 3.4. Mould design

The castings in Figs 3 and 4 and also those calculations in Table I utilized moulds with a runner cross-sectional area of 18 mm$^2$ and length of 120 mm, i.e., Design 1 in Table II. It is evident now that, this is not a suitable design in making diffusion couples for lead alloys due to the premature freezing of its melts when

TABLE I Estimate of approximate values of undercoolings and final melt temperatures as a function of mould material, pouring and mould temperatures for Sn-1 wt% Au and Pb-1 wt% Au melts

| Melt | Mould | $T_p$ (K) | $T_{md}$ (K) | $\Delta T$ (K) | $T_f$ (K) |
|---|---|---|---|---|---|
| Sn-1 wt% Au | Graphite | 1023 | 298 | 473 | 525 |
| | | 923 | 298 | 450 | 473 |
| Pb-1 wt% Au | Graphite | 1023 | 298 | 845 | 178 |
| | | 1023 | 523 | 766 | 257 |
| | Porous graphite | 1023 | 298 | 556 | 437 |
| | Machinable ceramic | 1023 | 298 | 150 | 873 |

TABLE II Estimate of approximate freezing times ($t_f$) for the Pb-1 wt% Au melts in various moulds

| Mould material | $T_p$ (K) | Freezing time, $t_f$ (sec) | |
|---|---|---|---|
| | | Design 1 | Design 2 |
| Graphite | 298 | 0.03 | 0.08 |
| | 523 | 0.3 | 1.1 |
| Porous graphite | 298 | 0.2 | 0.7 |
| | 523 | 1.8 | 6.1 |
| Machinable ceramic | 298 | 0.7 | 1.6 |
| | 523 | 6.8 | 24.3 |

pouring temperatures are below 1100°C. Nevertheless, even in a graphite mould the $(\frac{V}{SA})^2$ ratio of the casting can be designed so that the freezing time of the molten lead alloy in the runner can be increased to permit it to react and to form diffusion couples with the lead solvent rods. In order to increase the $t_f$, the runner cross-sectional area is increased to 36 mm$^2$ and the length is reduced to 70 mm in Design 2 as given in Table II.

Interface positions for the first, second (middle) and third rods in the Pb/Pb-1 wt% Au diffusion couple in this case was measured as 200 $\mu$m into the lead solvent rod, 95 $\mu$m into the lead solvent rod and 80 $\mu$m into the alloy casting, respectively when the pouring and mould temperatures 825°C and 250°C, respectively were used. This corresponds to a 275°C reduction in the pouring temperature as compared to Design 1.

The preparation of diffusion couples involving antimony was more challenging. In addition to its brittleness during removal from the mould, the thermal properties of antimony made it difficult to obtain diffusion couples with the desired interface locations. Nevertheless, the high tendency for the premature freezing of Sb-1 wt% In alloy in making antimony diffusion couples containing indium could be avoided by replacing this alloy with one of higher indium content and hence lower freezing point.

### 3.5. Thermal recovery of diffusion couples

The diffusion couple manufacturing technique described here has been developed in order to provide solid samples for subsequent use in the determination of diffusion coefficients ($D$) in the liquid state. In these experiments, the solid diffusion couples would be first placed in an inert crucible of graphite or boron nitride with one end in contact with a spring-loaded plug to accommodate any volume changes on melting. This crucible is then sealed in a two further metal shrouds to prevent oxidation of and contain all chemical constituents of the diffusion couple. These samples would then be processed with the specimens in the liquid state in an isothermal environment at a series of temperatures ($T$) before being radially quenched to solidify the sample. These experiments would be conducted in a terrestrial laboratory (with the possibility of buoyancy flows contributing to the solute transport) and also in a low-earth orbiting laboratory where special measures would be taken to avoid transient gravitational changes ("g-jitter"). These experiments are designed to measure the variation of $D$ with $T$. To date we have shown that in all the system examined $D \propto T$.

It is recognized that the diffusion couples produced with the cast-coating technology described here may not be directly suitable for the determination of diffusion coefficients due to the possible interference in the measurements of morphology changes in the end materials during the diffusion anneal. However, such problems can be mitigated by using a coarse-grained or single crystal solvent rod and taking note of the fact the cast-coated end is usually coarse grained, the grain size being dependent on the actual thermal conditions used in the couple's manufactory.

## 4. Conclusions

The "cast coating" method of long capillary diffusion couple preparation developed by us is here refined. The method involves the casting of a molten alloy, which contains the impurity element to be diffused, on to the tops of solvent rods placed in a mould under a controlled atmosphere. Since it occupies a small volume (~3.0 ml), the molten alloy is subjected to significant chilling and may become prone to premature freezing before reacting with the solvent rods. It is shown that the problem can be avoided, by the informed selection of the mould material, mould design and the pouring and mould temperatures.

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