

The effect of gravity and temperature gradients on precipitation in immiscible alloys

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The structure of immiscible alloys depends on the temperature gradient and the gravity force during solidification. The temperature gradient causes Marangoni movement of the droplets and the gravity force causes sedimentation or flotation of the droplets. In gradient experiments performed under normal and reduced gravity it is possible to distinguish between these two effects. This paper presents and analyses theoretically the results of experiments on Zn-Bi and Cu-Pb alloys, performed on earth and in the reduced gravity of space.

1. Introduction

It is generally accepted that the field of materials processing in the reduced gravity of space is primarily confined to the preparation of valuable materials which are difficult or impossible to fabricate on earth. Examples are single crystals, eutectic alloys and artificial composites. Much interest has been devoted to the solidification process of alloys containing a liquid-phase miscibility gap. Several experiments have been made in space in order to study the solidification behaviour of this type of alloy [1-5].

During the cooling of immiscible liquid alloys, droplets of one liquid form inside another liquid. On earth these droplets float or settle due to buoyancy forces. This movement favours collision between droplets, causing them to merge into larger ones. Experiments performed under reduced gravity also show the droplets moving, colliding and merging [1-5]. It is suggested that their motion is related to a surface-tension-driven movement as described by Kusnetsov [6] and Young *et al.* [7]. The objective of this investigation was to perform gradient experiments in the Cu-Pb and Zn-Bi systems. The experimental results are theoretically analysed by means of thermodynamic models describing the variation of surface tension with temperature.

2. Experimental procedure

The investigation was performed on one Cu-Pb alloy with 42 wt % Pb and one Zn-Bi alloy with 4% Bi. The Bi-Zn and Cu-Pb phase diagrams are shown in Figs 1 and 2.

The alloys were prepared by a quenching technique. A 23 mm i.d. graphite crucible with a height of 60 mm was used to prepare the alloys. Pure elements were placed in the crucible and heated under an argon atmosphere by a 15 kHz induction coil which directly induced heating currents in the graphite crucible. The temperature was measured and the melt was heated to a temperature above the maximum temperature of the miscibility gap.

The liquid was thoroughly mixed by the magnetic currents and the melt was held for 5 min prior to

sampling. The melts of the Cu-Pb alloys were sucked directly into 6 mm bore quartz tubes and quenched in oil. Alloys of Zn-4% Bi were cast in a copper mould with a diameter of 6 mm.

Directional solidification samples were extracted from the middle part of the quenched or cast samples. The directional solidification samples were turned to the desired dimensions, which were a diameter of 4 mm and a length of 50 mm. In the centre of each sample a hole 1.5 mm in diameter and 35 mm deep was drilled, in which four Thermocoax Type K thermocouples (chromel-alumel) were positioned along the length of the sample. The distances from the bottom of the sample were 15, 23, 31 and 39 mm. The stainless steel Thermocoax shield was protected from dissolving by a thin layer of boron nitride.

The directional solidification space experiments were performed in the gradient furnace assembly in the Swedish module of the TEXUS V and VII rocket flights. The gradient furnaces are described in detail elsewhere [9]. Accordingly, only a schematic view of one of the furnaces is shown here in Fig. 3. Samples were placed in graphite crucibles 65 mm long with 4 mm i.d. and 0.8 mm thick walls and closed at the top with cement. The bottom of the sample was threaded to

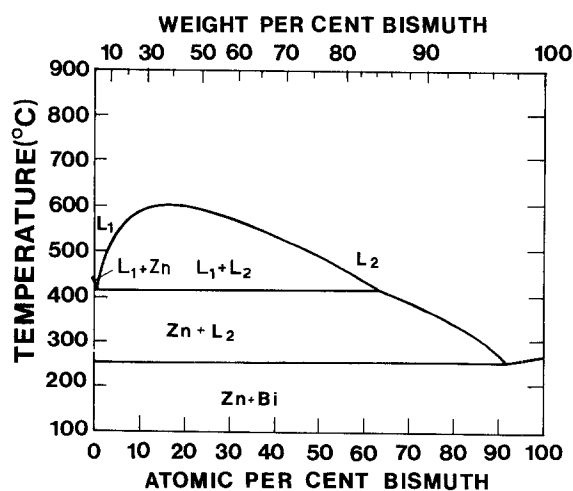


Figure 1 The Bi-Zn phase diagram according to Hansen and Anderko [8].

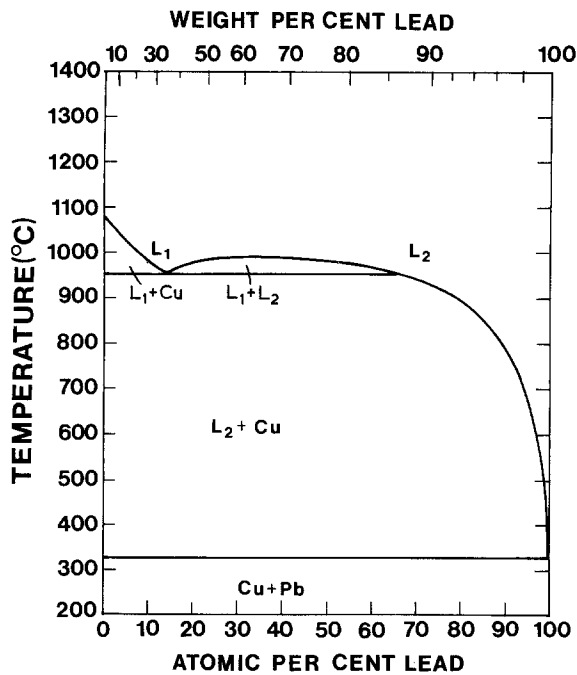


Figure 2 The Cu-Pb phase diagram according to Hansen and Anderko [8].

a 6 mm diameter copper rod which was attached to a phase-change heat sink. The heat sink consisted of a container filled with solid paraffin with a melting range of 69 to 73°C. When the power is turned off, the heat balance of the sample is determined mainly by the extraction of heat from the sample to the phase-change heat sink. The unidirectional extraction of heat from the sample will result in directional solidification of the sample.

Reference samples were processed under normal gravity conditions on earth in the same way and in the same furnace assembly as the space samples. Samples were examined on sections parallel and perpendicular to the growth axis after having been cut into suitable pieces with a low-speed single-blade circular saw. Micrographs were taken of the as-polished surfaces.

3. Results

3.1. The space samples

3.1.1. Cu-42% Pb

This sample was remelted to a distance of 25 mm from

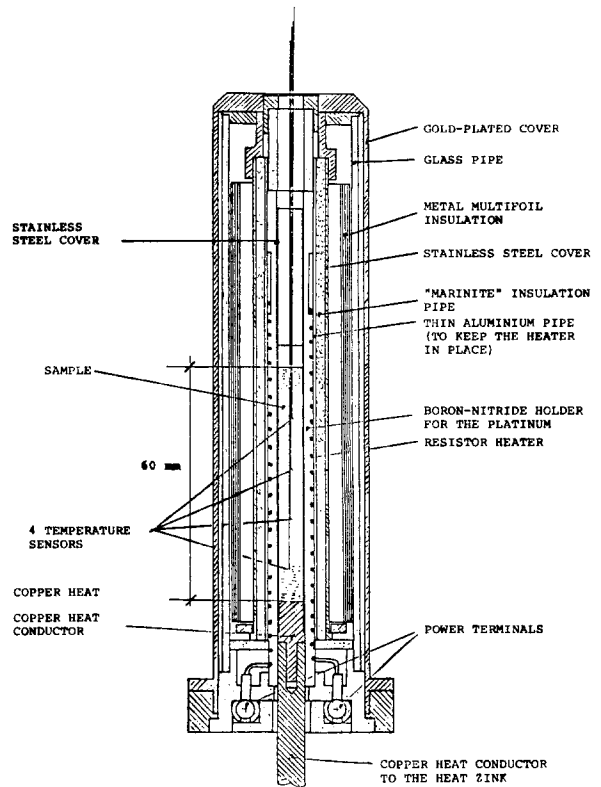


Figure 3 Gradient furnace [9].

the bottom and the temperature-time curves are displayed in Fig. 4, from which the velocity of the moving interface (the growth rate) is evaluated at around 0.7 mm sec⁻¹. The velocity was roughly constant during the experiment. The temperature gradient was 50 K cm⁻¹ at the solidification front at the beginning of the experiment and 10 K cm⁻¹ at the end of the solidification process. The structure just above the limit of the quenched base material is shown in Fig. 5. Isolated areas of aligned composite structure can be seen in this picture. The frequency of aligned areas decreases with increasing distance from the bottom of the sample, and at the top of the sample a large lead-rich area has formed due to segregation of lead (Fig. 6).

3.1.2. Zn-4% Bi

The temperature-time profile of the processed sample is shown in Fig. 7. The sample was melted to a

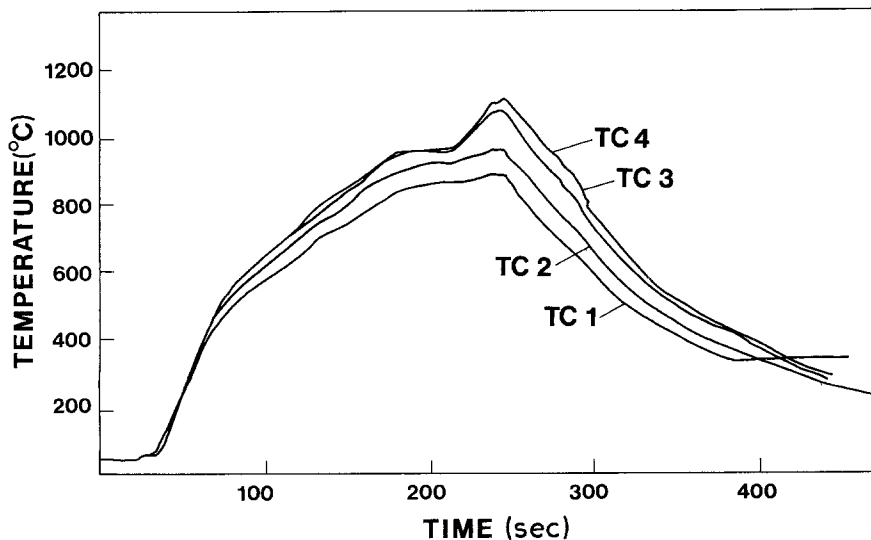


Figure 4 Temperature-time curve for Cu-42% Pb space sample.

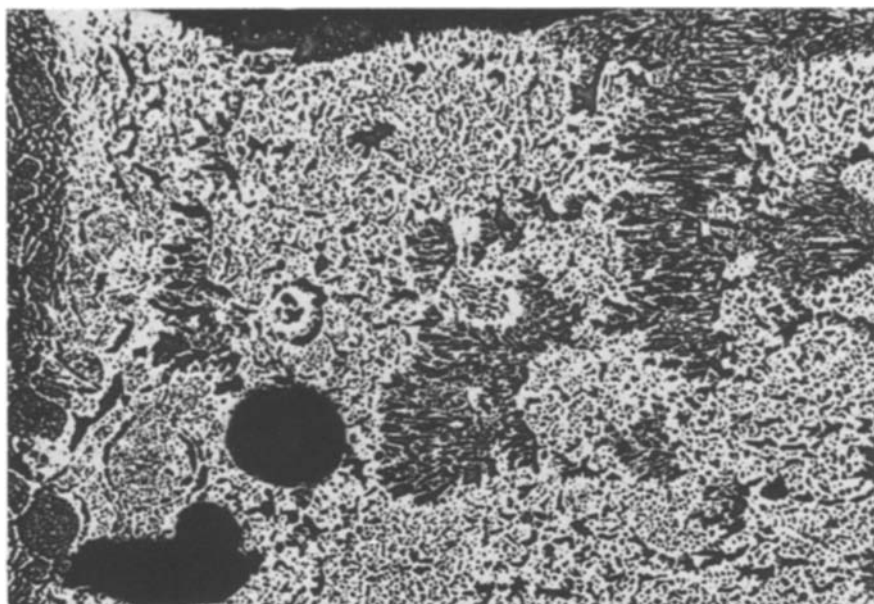


Figure 5 Cu-42% Pb space sample. Longitudinal section. Areas of aligned composite structure in a copper-rich matrix. Solidified from left to right. $\times 30$

distance of 17 mm from the bottom. The solidification rate was determined at 0.8 mm sec^{-1} and the initial gradient at 50 K cm^{-1} , at the solidification front. The gradient at the end of the solidification process was determined to less than 10 K cm^{-1} . The sample was divided and analysed metallographically. Small droplets of bismuth in a zinc matrix were observed. The maximum size and the number of droplets were determined as functions of the distance from the limit of melting. The result is presented in Fig. 8, where it is shown that there is a precipitation-free zone close to

the melted border. Next to it there is a region with a few very large droplets and at the end of the sample the number and size of the droplets decreases again. The same type of droplet distribution was found in a second run, not reported here.

3.2. The reference samples

3.2.1. Cu-42% Pb

This reference sample was remelted to a distance of 10 mm from the bottom. The temperature change with time for this sample is shown in Fig. 9 and the growth rate was found to be around 0.4 mm sec^{-1} . A copper-rich structure was observed at the bottom of the resolidified part of the sample. Just above this area a band of lead was formed across the sample (Fig. 10). An aligned structure was formed above this band. At a distance of 34 mm from the bottom of the sample an area consisting of copper dendrites was found, and the uppermost part of the sample consisted entirely a dendrite copper-rich structure. This structure is the contrary to that observed in the space sample, where the lead-rich area was found at the very top of the sample.

3.2.2. Zn-4% Bi

The sample was melted to a distance of 16 mm from the bottom. Fig. 11 shows the number and size of the droplets as functions of distance from the limit of remelting. At the bottom of the sample a few large droplets were found and at the top a large number of small droplets. This is also contrary to the observation in the space sample, in which no droplets were found in the lowest part of the sample. The number of droplets then increases, to decrease again at the top of the sample. Fig. 12 shows the temperature-time profile during the experiments.

4. Discussion

In order to study the movement and growth of the droplets in the miscibility gap due to buoyancy forces and temperature gradients, the following calculations were made.

Fig. 13 shows a schematic picture of the solidification process. It is assumed that the crucible moves



Figure 6 Cu-42% Pb space sample. Longitudinal section. Large lead accumulation in the topmost part of the sample. $\times 100$

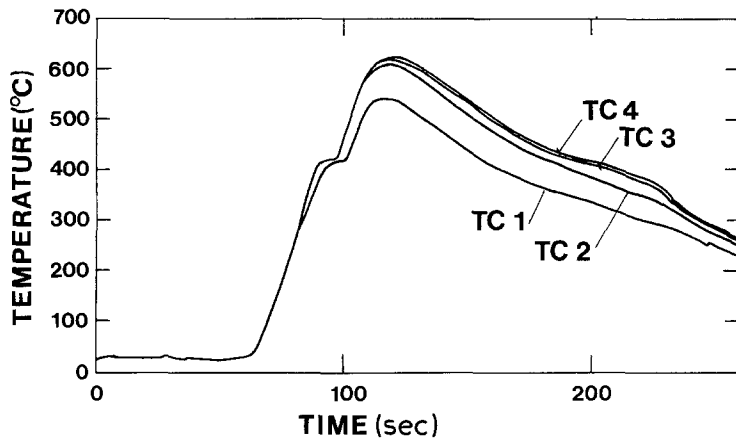


Figure 7 Temperature-time curve for Zn-4% Bi space sample.

downwards at a constant velocity in a constant temperature gradient. The droplets are moving due to the surface-tension-driven convection and due to the gravity. Gravity acts against the direction of growth. In the calculations it is assumed that a certain number of droplets, N , are formed when the temperature of the liquid reaches the temperature of the miscibility gap. The size of the droplets increases with decreasing temperature. In our case we have assumed that this increase is described by the lever rule, written as follows:

$$\frac{N(4/3)\pi R^3 V_m^{L(Bi)}}{[1 - N(4/3)\pi R^3]V_m^{L(Zn)}} = \frac{X_0^L - X_{Bi}^{L(Zn)}}{X_{Bi}^{L(Bi)} - X_{Bi}^{L(Zn)}} \quad (1)$$

where N = number of particles per cm^3 , R = particle radius, $V_m^{L(Bi)}$ = molar volume of bismuth-rich liquid, $V_m^{L(Zn)}$ = molar volume of zinc-rich liquid, X_0^L = mole fraction of original liquid and $X_{Bi}^{L(N)}$ = mole fraction of liquid (N) in equilibrium with liquid (M) where N and M correspond to Zn and Bi or vice versa.

$X_{Bi}^{L(Zn)}$ and $X_{Bi}^{L(Bi)}$ are functions of temperature given by the phase diagram, and the size of the droplets as a function of the temperature for a given number of droplets can thus be calculated.

The movement of the droplets due to gravity is described by Stokes's law and the movement due to

surface tension gradients is described by an expression derived by Kusnetsov [6] and Young *et al.* [7]. Combining expressions for the two effects one obtains

$$V_{\text{droplet}} = \frac{2}{9} \frac{\rho_{Zn} - \rho_{Bi}}{\eta_{Zn}} R^2 + \frac{2}{3} \frac{R}{2\eta_{Zn} + 3\eta_{Bi}} \left(\frac{d\sigma}{dT} \right) \left(\frac{dT}{dy} \right) \quad (2)$$

where η = viscosity, ρ = density, σ = surface tension and T = temperature.

By combining Equations 1 and 2 the movement of the droplets as a function of their number can be calculated. This has been done. Kusnetsov's equation includes the surface tension gradient which is generally not known. However, as a first attempt it can be derived as follows.

According to Becker [10] the surface tension can be related to the bonding energy between the atoms. From the same principle the following expression for surface tension can be derived:

$$\sigma = \frac{n}{2} \left[-2X_{Zn}^{L(Zn)} X_{Bi}^{L(Zn)} v^{Zn} - 2X_{Zn}^{L(Bi)} X_{Bi}^{L(Bi)} v^{Bi} + (v^{Zn} + v^{Bi})(X_{Zn}^{L(Zn)} X_{Bi}^{L(Bi)} + X_{Zn}^{L(Bi)} X_{Bi}^{L(Zn)}) \right] \quad (3)$$

where n = number of bonds per unit area, v^{Zn} = excess Gibbs energy per Zn-Bi bond in the zinc-rich liquid and v^{Bi} = excess Gibbs energy per Zn-Bi bond in the bismuth-rich liquid.

The excess Gibbs energy per bond can be evaluated from the excess Gibbs energy of the solution ${}^E G_m$ by the following relation

$$v = \frac{{}^E G_m}{ZN} \quad (4)$$

where Z = coordinating number and N = Avogadro's number.

The excess Gibbs energy for a regular solution is often written

$${}^E G_m = X_1 X_2 \Omega \quad (5)$$

where Ω is a constant for the regular model independent of the temperature and concentration. In most cases Ω is dependent on both temperature and concentration and therefore a more complex expression is

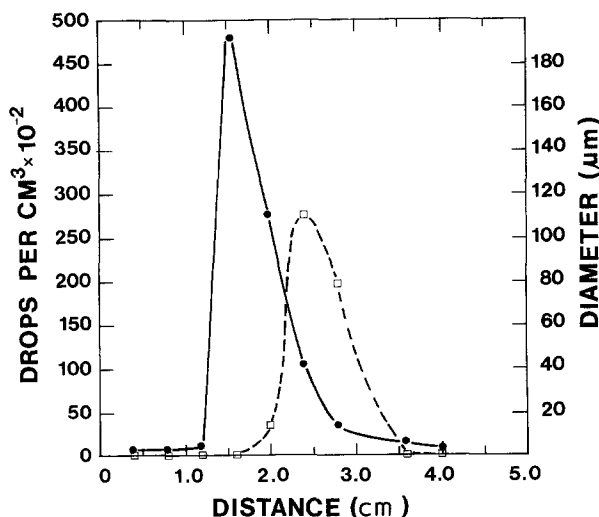


Figure 8 (●) Size and (□) number of incorporated particles at various distances in the space sample of the Zn-4% Bi alloy.

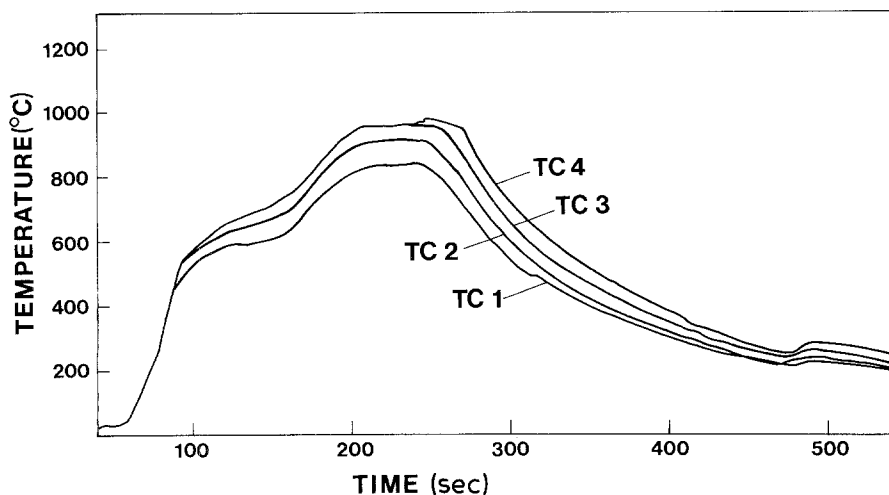


Figure 9 Temperature-time curve for Cu-4% Pb reference sample.

used. For the Zn-Bi alloy the following expression for excess Gibbs energy was derived from the phase diagram:

$$\begin{aligned}
 {}^E G_m = & X_{Zn} X_{Bi} [17893 - 8.727T] \\
 & + (9.1588T - 12707)(X_{Zn} - X_{Bi}) \\
 & + 2887(X_{Zn} - X_{Bi})^2 - 2727(X_{Zn} - X_{Bi})^3] \quad (6)
 \end{aligned}$$

The excess free energy for the Cu-Pb system has been derived by Chakrabarti and Laughlin [11]. These authors give the following expression:

$$\begin{aligned}
 {}^E G_m = & X_{Cu} X_{Pb} [(36450 - 41700X_{Pb} + 57250X_{Pb}^2 \\
 & - 25000X_{Pb}^3 - T(5.04 - 9.20X_{Pb} + 12.63X_{Pb}^2)] \quad (7)
 \end{aligned}$$

By combining Equations 6 or 7 with Equations 3 and 4 the surface tension σ was calculated. The result is shown in Figs 14 and 15 for Bi-Zn and Cu-Pb alloys, respectively.

$d\sigma/dT$ can be evaluated from the slopes of the curves in Figs 14 and 15 and the movement of the droplets can be calculated with the help of Equation 2. The result is shown in Figs 16 to 18. The figures have

been calculated in order to show whether or not the droplets are incorporated in the solidification front for a given solidification rate. The figures show the relation between the number or size of the droplets as a function of the temperature gradients. Figs 16 and 17 show the calculated values for Bi-Zn. Fig. 16 refers to a gravity force of $10^{-4}g$ and Fig. 17 to a gravity force of $1g$. The curves show a minimum point because the Stokes flotation is opposed to the surface-tension-driven movement.

Fig. 16 shows that the reduced gravity of space still has an influence on the movement of droplets when they are very large. The calculations show that the temperature gradient movements override the gravity sedimentation on earth for small droplets (Fig. 17). In our experiments the growth rate was around 0.7 mm sec^{-1} and the gradient at the start of the solidification process was around $50^\circ \text{C cm}^{-1}$. From the diagram (Fig. 16) we can see that all droplets larger than $150 \mu\text{m}$ will be floated in space and not incorporated at the solidification front. During the experiments the growth rate decreases and so does the gradient. In the experiment the gradient decreases to less than $10^\circ \text{C cm}^{-1}$. The figure now shows that all particles smaller than $300 \mu\text{m}$ will be incorporated at

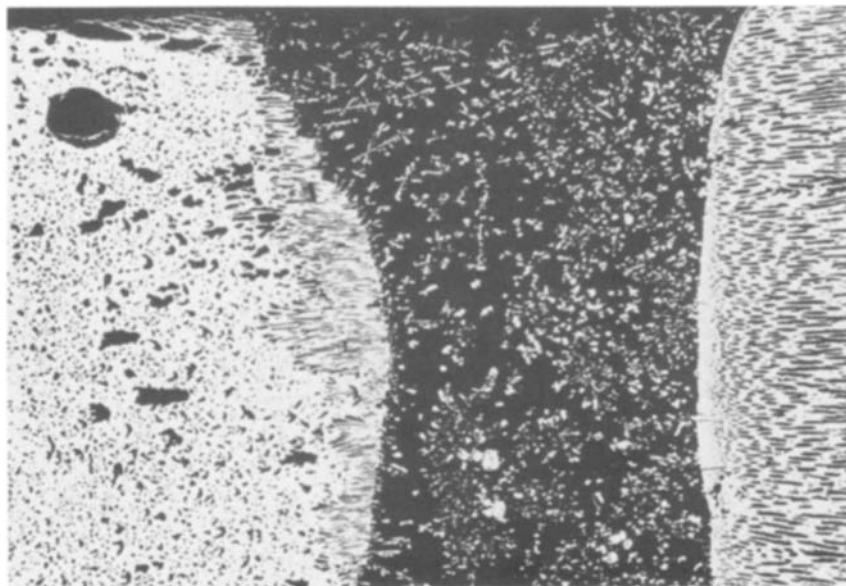


Figure 10 Cu-42% Pb reference sample. Longitudinal section. A lead-rich band across the sample and aligned composite structure close to growth direction to the right. $\times 50$

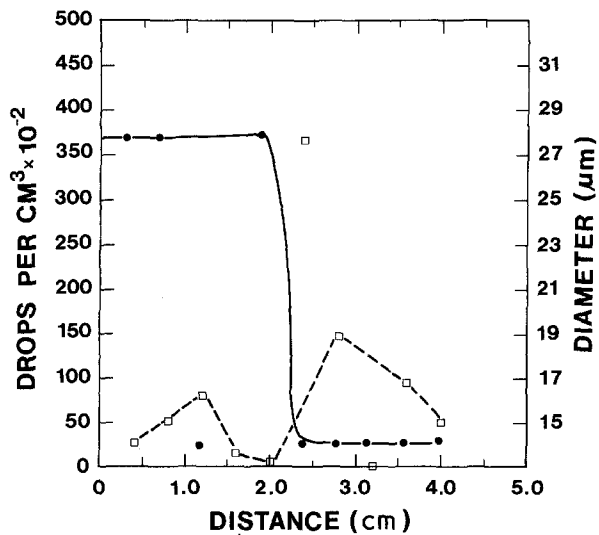


Figure 11 (●) Size and (□) number of incorporated particles at various distances in the reference sample of the Zn-4% Bi alloy.

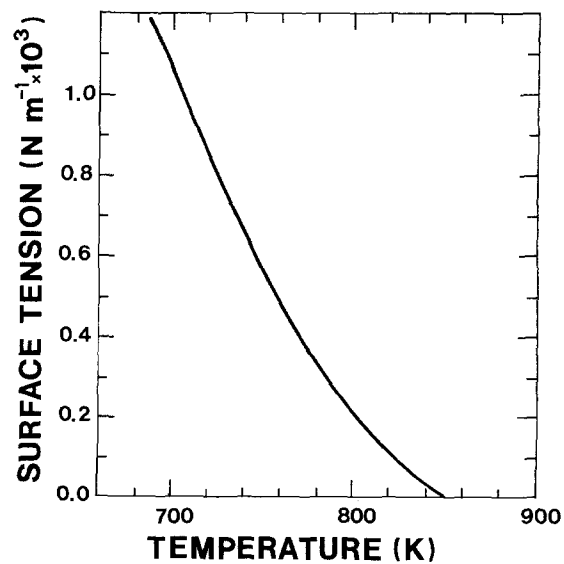


Figure 14 Surface tension of the Bi-Zn alloys.

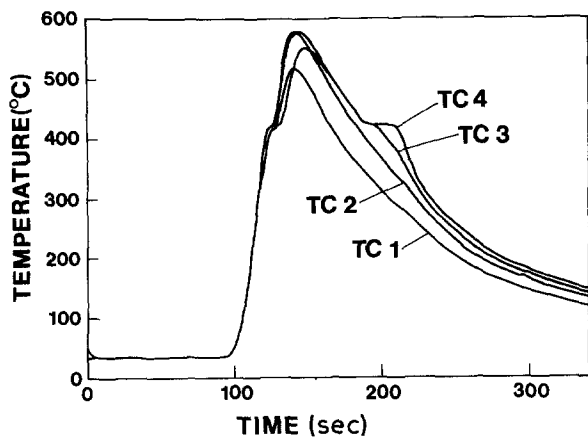


Figure 12 Temperature-time curve for Zn-4% Bi reference sample.

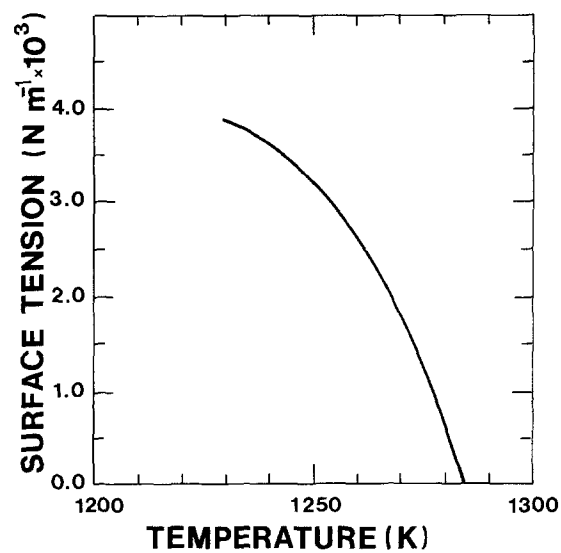


Figure 15 Surface tension of the Cu-Pb alloys.

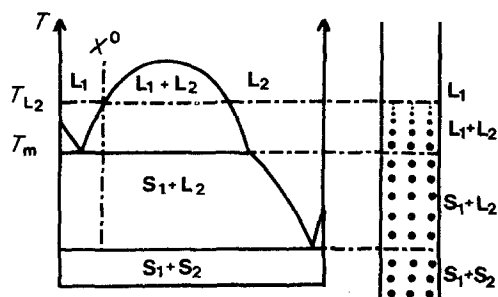


Figure 13 Precipitation of droplets in a gradient-solidified monotectic alloy. x^0 = original composition.

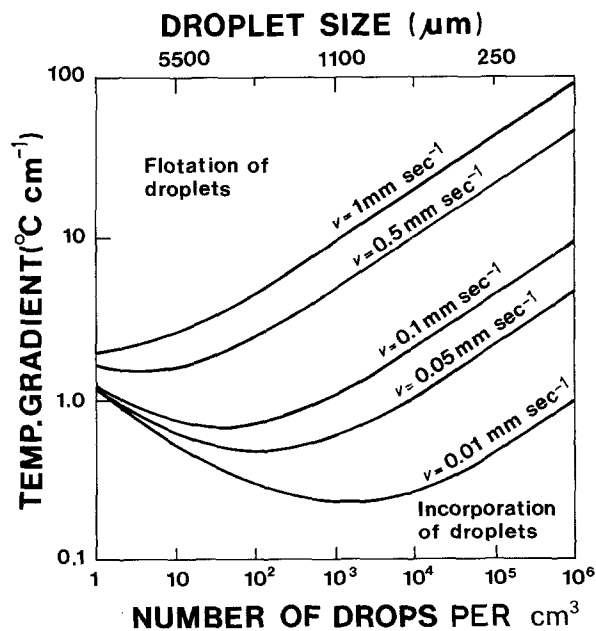


Figure 16 The movement of Zn-Bi droplets as a function of the size and temperature gradient at a gravity of $10^{-4}g$.

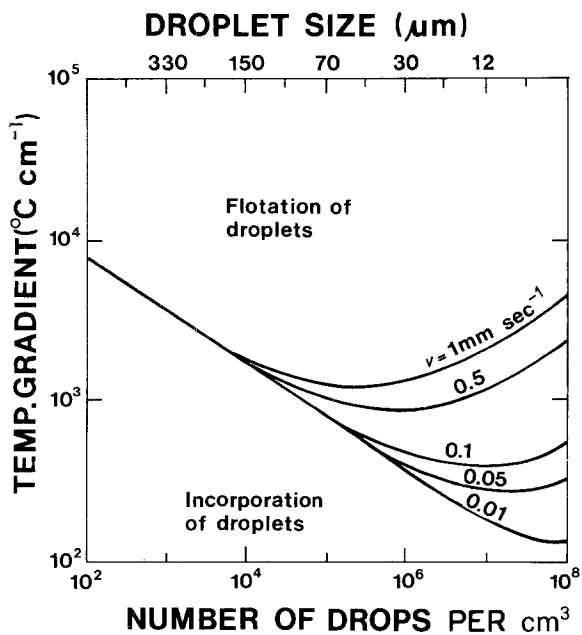


Figure 17 The movement of Zn-Bi droplet as a function of the size and temperature gradient at a gravity of 1 g.

the front. The experiment showed (Fig. 8) that droplets of a size of 200 μm and smaller are incorporated after a certain distance. The experiments also show that no particle was incorporated at the beginning of the experiments due to the very high temperature gradient at this moment.

Fig. 18 shows the same calculation for the Cu-Pb alloy as Fig. 16 shows for the Zn-Bi alloy. A comparison between Figs 16 and 18 shows that lead droplets in copper float more strongly than bismuth droplets in zinc. This is also in accordance with the experimental observations in the Cu-Pb alloy processed in space, where no lead droplets were incorporated. All the hypermonotectic precipitated lead was found at the very top of the sample (Fig. 3).

5. Concluding remarks

The precipitation of droplets in gradient-solidified Zn-Bi and Cu-Pb alloys has been investigated. The droplet distribution was theoretically analysed and the experimental results were explained. The movement was due to a surface-tension-driven convection.

Acknowledgements

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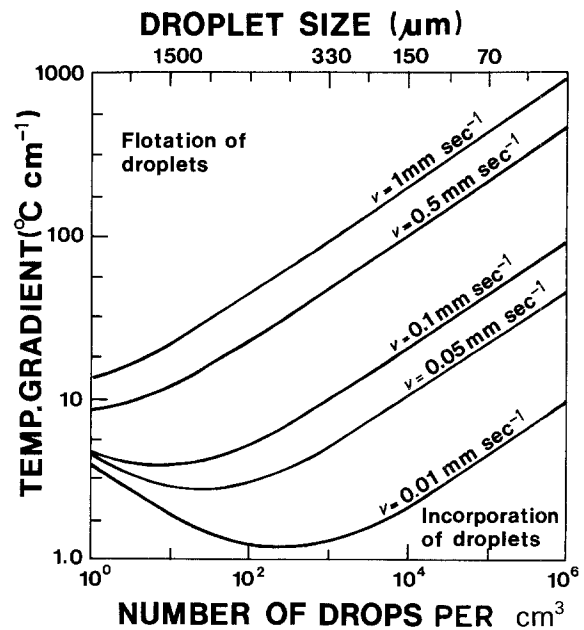


Figure 18 The movement of Pb-Cu droplets as a function of the size and temperature gradient at a gravity of $10^{-4}g$.

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