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Undercooling and solidification of droplets of Cu–Ag alloy entrained in the primary phase

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The undercooling behaviour and formation of metastable microstructures have been studied in the melt of Cu–Ag alloy entrained in its primary phase. A maximum undercooling of 180 °C below the liquidus temperature was observed in isolated liquid droplets. The highly undercooled droplets underwent a massive transformation which resulted in the formation of a metastable solid-solution phase containing Ag–28 at% Cu. The metastable phase decomposed on ageing to form the equilibrium phases. The undercooling behaviour and evolution of metastable microstructures in droplets are discussed.

1. Introduction

In the past considerable attention has been focused to achieve an understanding of the origin of metastable microstructures generated in rapidly solidified alloys. Large kinetic undercooling induced in the melt during rapid quenching is considered to change the equilibrium solidification path and favour formation of metastable phases [1, 2]. However, it is difficult to measure the undercooling of a melt in rapid solidification processes. In an alternative approach, large reproducible undercooling is achieved when liquid metals and alloys are fluxed in a suitable glass slag [3–6]. In this process, although the undercooling of the melt is precisely determined, its rapid recalescence during solidification alters the metastable microstructures initially produced.

Any undercooling technique employed to retain the metastable effects must be effective in minimizing the recalescence of the melt. The technique of Mushy-state-quenching possesses this characteristic and has regenerated considerable interest in the study of metastable phase formation in undercooled alloys. In this process, a hypo-eutectic alloy is held in the two-phase liquid–solid region to produce *in situ* droplets entrained in the primary phase. Several investigators [7–10] have shown that such droplets exhibit large undercooling owing to the cleanliness of the matrix and lack of contact of the melt with the atmosphere. It is often convenient to quench droplets from known undercooling. Recently, the potential of this process has been exploited to synthesize metastable phases in a number of alloys [11–15].

In the present investigation, the undercooling behaviour and evolution of metastable structures has been studied in droplets of Cu–Ag alloy entrained in the copper-rich primary phase matrix. This system has been selected due to availability of a reliable phase diagram [16, 17] in the undercooled regime and known metastable effects [18–20] produced by the rapid quenching process.

2. Experimental procedure

2.1. Undercooling procedure

A copper–13 at% silver alloy was prepared from 99.999% purity metals in a graphite crucible. The melting was carried out under an argon atmosphere in a resistance heating furnace. Various samples of 6 mm diameter × 8 mm height were machined from the cast ingot for undercooling experiments. The experimental apparatus employed for the undercooling experiment is shown in Fig. 1. It consisted of a quartz tube evacuated to a pressure of 10^{-3} torr (1.333×10^{-1} Pa), a resistance heating furnace and a water cooling arrangement to quench the sample from the known temperature. The samples were annealed in vacuum at 800 °C in the two-phase solid–liquid region for 2–50 h. The annealing temperature was selected from the phase diagram data so as to produce around 20% liquid in the primary copper-rich matrix. A fine chromel–alumel thermocouple connected to a microvoltmeter was employed to record the temperature of the sample during cooling. The thermocouple was calibrated *in situ* with reference to the melting temperature of the eutectic in order to ensure ± 2 °C accuracy in temperature measurement. The time for every 5 °C drop in temperature of the sample was measured to generate the inverse rate cooling curve. Some samples were subjected to a number of freezing and cooling cycles before final quenching was carried out from the mushy-state.

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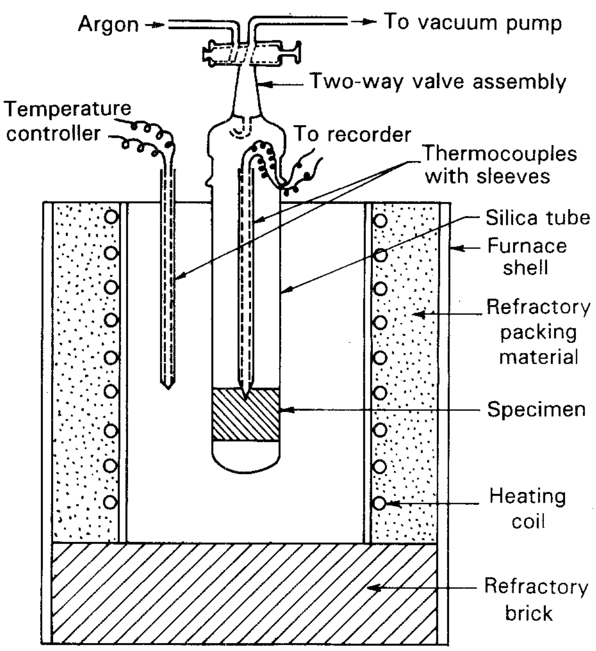

Figure 1 Schematic diagram of the experimental apparatus.

2.2. Microstructural examination

The specimens for metallography and microhardness testing were prepared using a standard polishing technique and were etched with $FeCl_3$ solution. The microstructure of the sample was examined in a Leitz Metallux-3 optical metallograph whereas the microhardness measurements were made using a Tucon micro-hardness tester at a load of 50 g. The X-ray diffractograms from the sample were obtained in a Rigaku diffractometer using CuK_{α} radiation. Because several droplets on solidification exhibited featureless regions, their compositional variation was studied in a Jeol JC XA 733 Electron Probe Micro-Analyser (EPMA) operating at 25 kV.

3. Results

3.1. Thermal analysis

The inverse rate cooling curve exhibited lower undercooling for solidification of grain-boundary liquid. The exothermic peak appeared at 10 °C below the eutectic temperature. When the sample was annealed for a long time and subjected to several melting and freezing cycles, the grain-boundary liquid migrated to form isolated droplets of liquid in the matrix. Subsequent cooling of the sample showed considerably large undercooling of droplets. Fig. 2 shows a typical inverse rate cooling curve of the sample annealed for 20 h and subjected to five consecutive thermal cycles. The exothermic peak is centred around 710 °C and has a spread of 12 °C. The peak in the freezing curve indicates the temperature at which solid nucleates in the liquid droplets within the primary copper matrix. Further, the droplets have a wide size distribution. Therefore, this peak can be considered as an average nucleation temperature for the whole system of droplets and amounts to an undercooling of 70 °C below the eutectic. The results of thermal analysis thus indicate different undercooling behaviour of grain-boundary liquid and droplets. It also emphasizes the importance of generation of isolated droplets in the primary copper-phase matrix to achieve large undercooling of the melt.

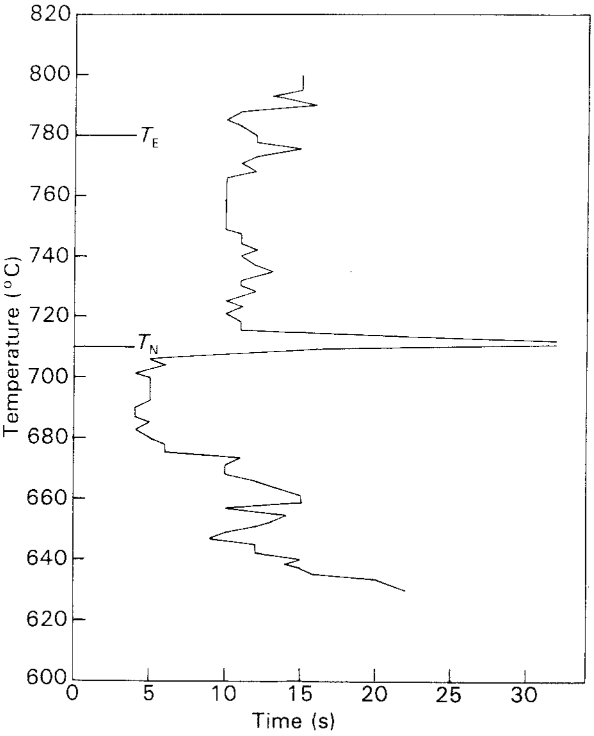

Figure 2 Inverse rate cooling curve exhibiting exothermic peak during freezing of droplets.

3.2. Microstructural features

The microstructure of the as-cast Cu–13 at % Ag alloy is shown in Fig. 3a. A continuous network of eutectic is noticed in the interdendritic region. This eutectic region melts and forms isolated droplets during annealing and thermal cycling of the alloy. The microstructure of such samples quenched from the mushy-state is shown in Fig. 3b. There are two noteworthy features in the above micrograph. Firstly, isolated pockets of silver-rich phase are revealed in contrast to a continuous network of eutectic observed in the as-cast alloy. Secondly these regions show fine dendritic morphology co-existing with a featureless region. The dendrites are observed to be arranged in a specific geometrical fashion and their volume fraction decreases with decrease in the droplet size. On further increase in thermal cycling, completely featureless regions are observed in the isolated droplets (Fig. 3c). The featureless regions reveal a microhardness value of 100 kg mm^{-2} compared with a hardness of 65 kg mm^{-2} of the eutectic in the as-cast alloy.

The X-ray diffractograms from the mushy-quenched alloy showed strong reflections from the equilibrium β phase with a lattice parameter of 0.364 nm. In addition, the diffractogram also exhibited weak reflections which could be indexed as arising from metastable solid-solution phase containing Ag–13 at %Cu with a lattice parameter of 0.4035 nm. This phase was earlier designated α′ by other investigators [9, 20]. A secondary electron image obtained by electron probe micro-analysis with corresponding compositional

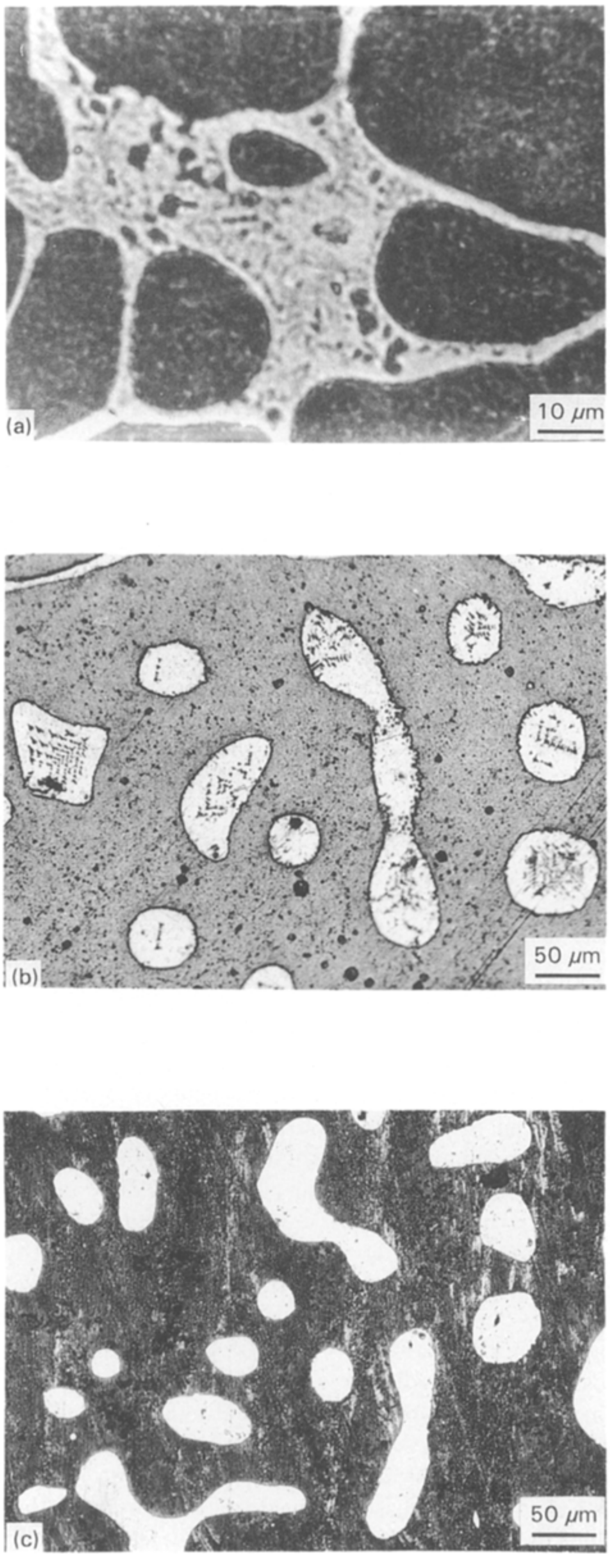

Figure 3 Microstructure of the Cu–13 at %Ag alloy showing (a) eutectic phase in an interdendrite region, (b) isolated pockets in mushy-quenched alloy showing co-existing fine dendrites with the lightly etched phase, and (c) isolated pockets showing the completely featureless region.

profiles for copper and silver along the section of mushy-quenched sample, are shown in Fig. 4a and b. The X-ray images due to CuK_α and AgK_α radiations are presented in Fig. 4c and d, which indicate that featureless regions are enriched in silver. The electron probe, focused for quantitative compositional analysis on several points in featureless regions, consistently provided a composition of Ag–28 at % Cu. It is worthwhile to mention that the electron probe micro-analysis indicates the overall composition of the phase due to its limited spatial resolution, whereas X-ray diffraction analyses the constituent phases. The present result points towards the possibility of massive solidification of a Ag–28 at % Cu phase which subsequently decomposes to form α′ phase with a composition of Ag–13 at % Cu.

3.3. Decomposition of metastable phase

Fig. 5 shows the change in hardness of the metastable solid-solution phase with time at room temperature (40 °C). The ageing curve shows a peak hardness of 130 $\mathrm{kg\,mm^{-2}}$ which decreases to 70 $\mathrm{kg\,mm^{-2}}$ after 200 h. The decomposition of this phase is rapid at higher temperature. The microstructures of the sample aged at 200 and 500 °C for 1 h are shown in Fig. 6a and b. Although the featureless region decomposes at 200 °C, considerable precipitation is noticed in the regions corresponding to solidification structure of isolated droplets aged at 500 °C. The X-ray diffraction pattern from a specimen aged at 500 °C revealed only reflections due to equilibrium α and β phases.

4. Discussion

4.1. Undercooling behaviour

The phase diagram of a Cu–Ag system with extrapolated lines in the metastable phase field is shown in Fig. 7. As indicated in the above diagram, when an alloy of Cu–13 at % Ag is annealed at 800 °C, it generates a liquid containing Cu–45 at % Ag in the intergranular region of the β phase. This liquid forms isolated droplets with prolonged annealing of the alloy.

As mentioned earlier, the composition of the liquid droplets follows the liquidus during slow cooling of the sample, with local equilibrium being maintained. This equilibrium is disturbed and solidification occurs at an undercooling of 70 °C below the eutectic. However, during mushy-state quenching, one obtains a massively solidified silver-rich phase with 28 at % Cu. The calculated liquidus temperature found by extending the copper-rich part of the liquidus is 700 °C. This is 10 °C below the observed exothermic peak temperature during slow cooling. This shows that a small departure from local equilibrium conditions occurs during solidification on quenching. Further, the overall undercooling for a liquid of Ag–28 at % Cu is thus 190 °C below the liquidus temperature for this composition.

The maximum undercooling of liquid observed in the present investigation is less than that reported earlier [8]. At this stage, it is difficult to determine the reasons for this discrepancy. However, the difference in undercooling behaviour of grain-boundary liquid and droplets are related to several inter-related effects such as the spatial distribution of liquid in the primary phase, isolation of nucleants in droplets and potency of nucleants. Because the grain-boundary liquid forms a continuous network, a single nucleation event is sufficient for its crystallization. In contrast, nucleation events and subsequent crystallization are independent

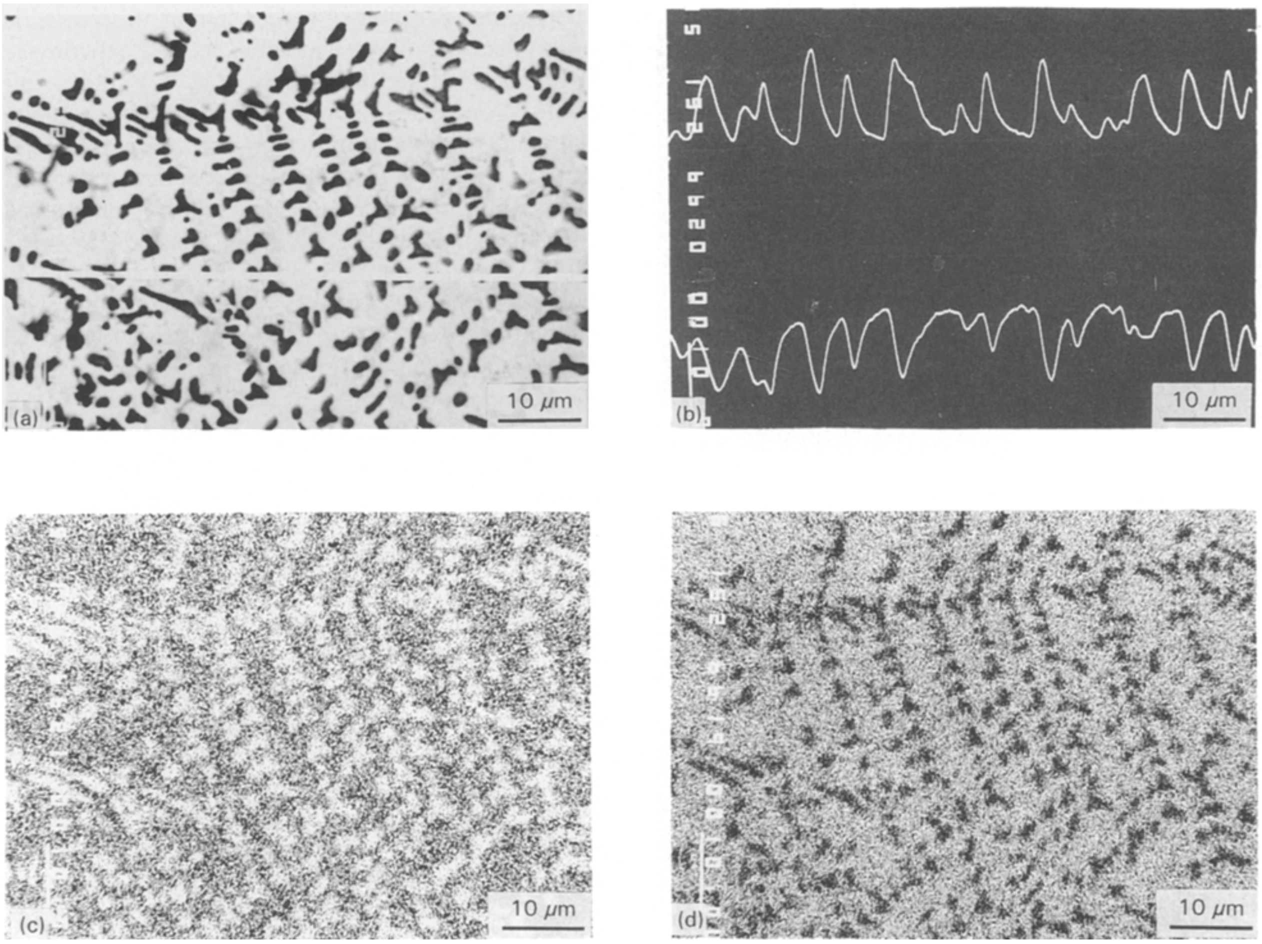

Figure 4 Micrographs of a mushy-quenched sample showing (a) secondary electron image, (b) compositional profiles of copper (top) and silver (bottom), (c) CuK_α image, and (d) AgK_α image.

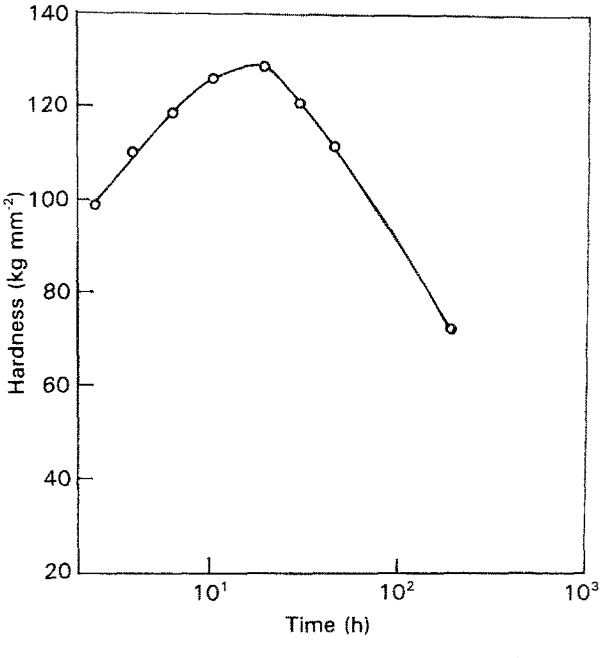

Figure 5 Variation in microhardness of metastable solid-solution phase with time at room temperature.

in isolated droplets. At the same time, heterogeneous nucleants may also be statistically distributed into few droplets, whereas others devoid of nucleants may crystallize at large undercooling. The present work also shows that thermal cycling of the melt helps in increasing the undercooling. This effect is consistent with the undercooling behaviour of liquid fluxed several times in a glass slag [5]. Repeated melting and freezing of the liquid is considered to alter the potency of a nucleant present in the melt. These effects greatly contribute to large undercooling of droplets compared to the grain-boundary liquid.

4.2. Evolution of metastable microstructure

One of the important observations of the present investigation is the formation of lightly etched massive phase in the samples quenched from the mushy-state. Although the X-ray diffraction could resolve a metastable solid solution phase with a Ag–13 at % Cu, the EPMA study clearly established the composition of these regions as Ag–28 at % Cu. This result obviously points towards massive transformation of droplets undercooled 57 °C below T_0 temperature for liquid of this composition (the free energy of liquid and solid of a given composition is equal at T_0). Such transformation has already been observed in the splat-quenched Ag–Cu alloys [20].

In a recent work [9] on mushy-quenched Ag–Cu alloy it has been argued that once the liquid establishes local equilibrium with the primary phase, it may not undergo a massive transformation, even though the liquid is undercooled below T_0 temperature. This observation was mainly based on optical microscopy and X-ray diffraction techniques employed by these

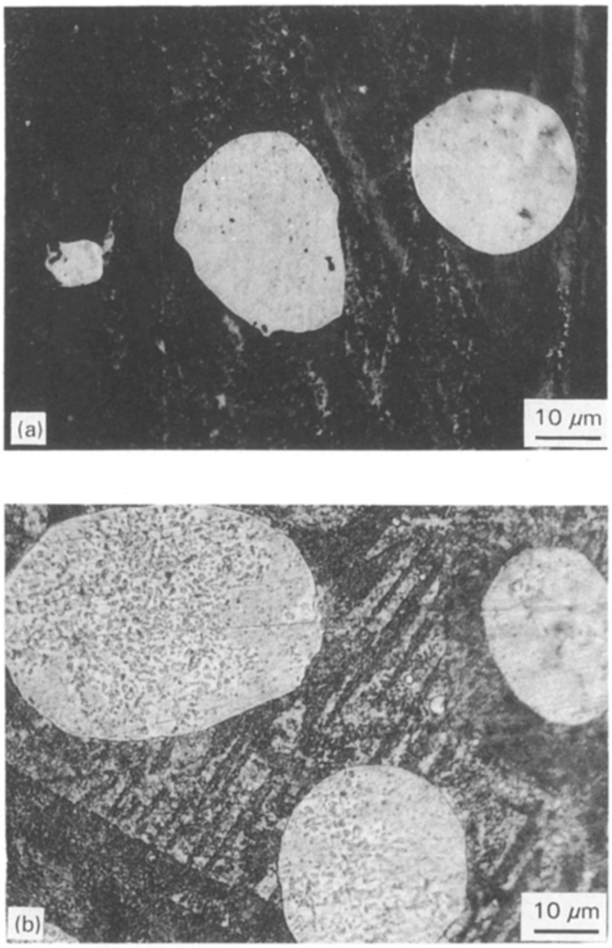

Figure 6 Micrographs showing fine precipitates in the sample aged at (a) 200 °C and (b) 500 °C for 1 h.

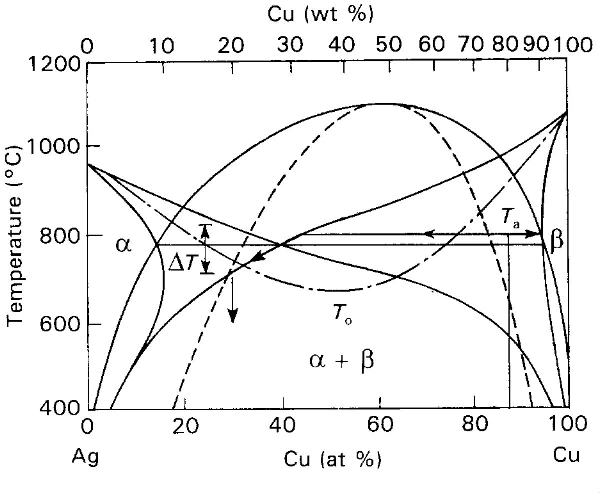

Figure 7 Phase diagram of the Cu–Ag system with extrapolated lines [16, 17].

investigators to characterize the phase in the mushy-quenched sample. In a subsequent thermodynamic study [21], the formation of metastable microstructure in mushy-quenched Ag–Cu alloy was explained on the basis of classical homogeneous nucleation theory. It was considered that homogeneous nucleation conditions exist in the droplets prior to crystallization. However, the compositional analysis by EPMA techniques employed in the present work establishes the occurrence of massive transformation in undercooled droplets in a way similar to that in the splat-quenched alloys. The undercooling experiments have demonstrated the ability of such liquid to nucleate below T_0 temperature. In the mushy-quenching experiments, rapid heat extraction by the surrounding matrix further enhances the undercooling of the melt. On further cooling of the bulk alloy after massive transformation, it is difficult to retain the supersaturated solid-solution phase owing to the slow cooling rate of the sample in the solid state. Consequently, it decomposes to α′ phase with 13 at % Cu and a copper-rich phase. Our X-ray results show that the observation of the α′ phase is an outcome of this transformation path. On ageing of such structures, equilibrium phases are formed by diffusional processes.

5. Conclusions

1. The grain-boundary liquid and isolated droplets of Cu–Ag alloy entrained in the primary phase matrix exhibit different undercooling behaviour. A maximum undercooling of 70 °C below the eutectic temperature is observed for droplets, which amounts to an undercooling of 180 °C below the liquidus. The maximum undercooling of the melt is observed to depend on annealing time in the liquid–solid region and the number of melting–freezing cycles of the phase entrained in the matrix. The large undercooling of droplets is explained on the basis of the nature of their spatial distribution in the matrix, isolation of nucleants and change in their potency due to thermal cycling.

2. Quenching the alloy from the mushy-state leads to complete absence of eutectic reaction. Optical microscopy shows lightly etched features in the transformed region with a microhardness of 100 kg mm^{-2}. Although the X-ray diffraction study indicates a metastable α′ phase with a lattice parameter of 0.4035 nm, the compositional analysis of the lightly etched region reveals a metastable solidification phase with Ag–28 at % Cu. These results indicate that liquid highly undercooled below T_0 undergoes a massive transformation. The metastable solid-solution phase decomposes even at room temperature with time but the decomposition is rapid at high temperature with a large amount of fine precipitates.

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