JOURNAL OF MATERIALS SCIENCE 26 (1991) 4888–4892

Initiation sites for discontinuous precipitation in some Cu-base alloys

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A systematic effort has been made to investigate the suitability of various interfaces, natural as well as artificial, to initiate discontinuous precipitation. The interfaces studied in the present investigation include sample surface (external), and grain and interphase boundaries. It has been demonstrated that in addition to grain boundaries, non-conventional initiation sites like coherent faces of a twin or eutectic/eutectoid boundaries under favourable conditions may also nucleate discontinuous precipitation. In general, the ability of an interface to undergo thermally activated migration appears to be the most important criterion for the initiation of discontinuous precipitation.

1. Introduction

The formation of a two-phase aggregate across a moving boundary, advancing into a supersaturated solid solution, is termed as discontinuous precipitation [1–3]. The moving boundary, known as the reaction front, plays a crucial role in providing the primary route of solute transport [1, 3]. It is generally believed that only the large-angle matrix grain boundaries can support the process of heterogeneous precipitation and the concurrent boundary migration required for discontinuous precipitation [4]. Recently it has been demonstrated that the precipitate–matrix-type phase boundaries may also initiate discontinuous precipitation in a Cu–12 at % In alloy [5]. Initiation of discontinuous precipitation has also been reported from small-angle martensite lath boundaries in Zr–Al [6], crystal surfaces with prior deformation in Ni–In, Ni–Sn [7] and Cu–Ag [8], and synthetic grain boundaries in Cu–Ag [8]. However, no systematic effort has been made to date to outline a generalized criterion as to which boundaries are potential agents for the initiation of discontinuous precipitation. The present investigation attempts to explore the relative feasibility of various boundaries, natural as well as synthetic, to initiate discontinuous precipitation in a few Cu-base alloys.

2. Experimental procedure

Four Cu-base alloys containing 7.5 at % In, 12 at % In, 35 at % Ag and 8 at % Mg were prepared by vacuum induction melting and homogenized for 2 weeks at 953, 973, 1043 and 988 K, respectively. The Cu–7.5 at % In alloy ingot was remelted to grow a single-crystal rod of 20 mm diameter by the vertical Bridgman technique, and rehomogenized at 948 K for 2 weeks.

Flat samples with 3 mm thickness and about 5 mm square surfaces were obtained from the Cu–7.5 at % In single-crystal rod by spark erosion cutting, milled with a Reichert–Jung milling machine to polish one of the broad faces with mirror-like finish and annealed at 953 K for 50 h, followed by water quenching. As a final measure to remove all traces of surface strain, the samples were electropolished in a concentrated H_3PO_4 bath at a d.c. potential of 1.5 V for 15 min using a stainless-steel cathode. Cu and In layers of 5 and 10 μm thicknesses, respectively, were deposited on selected sets of samples by vapour deposition. Surface strain with a predetermined load was applied near one of the edges of a different set of samples by a Vickers hardness testing machine (with a diamond pyramid indentor). The In-coated samples were subjected to a pretreatment of isothermal annealing at 423 K for 100 h in an oil bath to develop Cu–In intermetallic phases by interdiffusion of Cu–In and In [9]. All the samples, including In-deposited ones, were precipitation annealed at temperatures between 573 and 723 K for varying lengths of time in evacuated pyrex tubes, followed by water quenching.

Samples of the other polycrystalline alloys containing In, Ag and Mg were also precipitation annealed in vacuum between 573 and 773 K for different time periods and quenched in water in a similar manner.

Following precipitation annealing, all the samples were polished with 4000 grid SiC paper and diamond paste up to 1 μm fineness, and etched with a colour tinting solution containing 200 g of CrO_3, 20 g of Na_2SO_4, and 17 ml of HCl in 1000 ml of distilled water. Detailed metallographic investigations were

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carried out with optical (LM) and scanning electron (SEM) microscopes at appropriate stages of isothermal annealing. It is relevant to mention that the metallographic studies with the Cu–7.5 at % In single crystal samples were always carried out on the surfaces perpendicular to the surfaces of Cu/In deposition or hardness indentation.

3. Results and discussion

Fig. 1 reveals the successive stages of growth of the discontinuous precipitate colony at 673 K from the Cu-deposited layer into a Cu–7.5 at % In single crystal. The deposited Cu layer may provide numerous grain boundaries between the crystal surface and the Cu film at the precipitation temperature, T. Apparently these boundaries have initiated discontinuous precipitation growing away from the crystal/coating interface. Similar Cu-coated samples have also been precipitated at $T = 573$, 648, 673 and 723 K for varying lengths of time (t) with careful estimation of the average migration distance of the reaction front (RF), w, from the crystal/coating interface. It is assumed that w, measured on a plane perpendicular to the Cu layer, expresses the maximum width of the precipitate colony. Fig. 2 illustrates the change in w with t at various values of T. The RF migration velocities, v, determined from the slopes of the w–t plots in Fig. 2, have been superimposed on the velocity–temperature spectrum (Fig. 3) reported in the literature [10] for a polycrystalline Cu–7.5 at % In alloy. An excellent agreement between data from the present study and the literature appears to suggest that the synthetic grain boundaries (SGBs) generated at the crystal/coating interface are potential sites for initiation of discontinuous precipitation. It may be noted that similar SGBs generated by a vapour-deposited Cu layer have also been reported to initiate discontinuous precipitation in a Cu–7.7 at % Ag alloy [8].

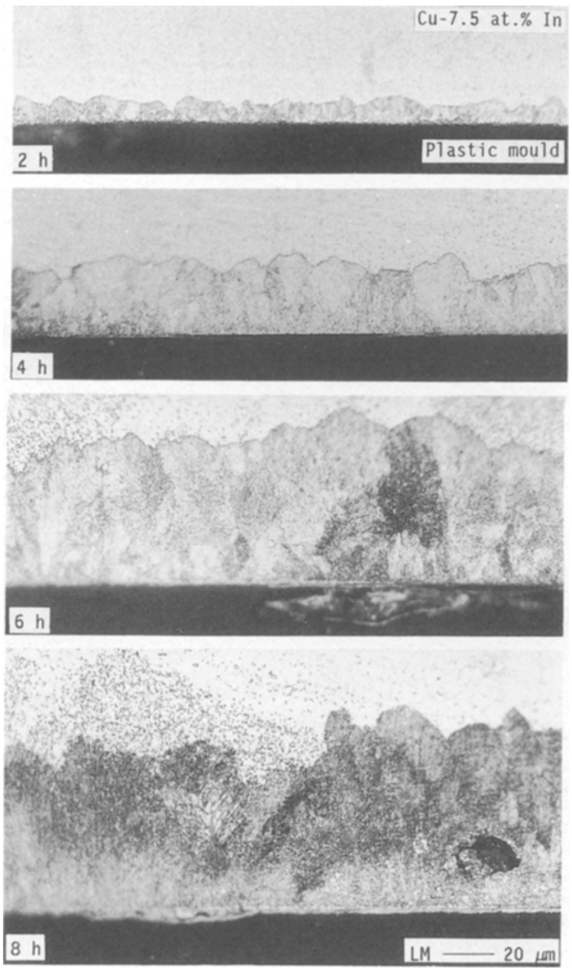

Figure 1 Uniform growth of discontinuous precipitate colony initiated at the vapour-deposited Cu layer (lying perpendicular to the plane of observation) on a Cu–7.5 at % In single-crystal surface at 673 K, at different time intervals.

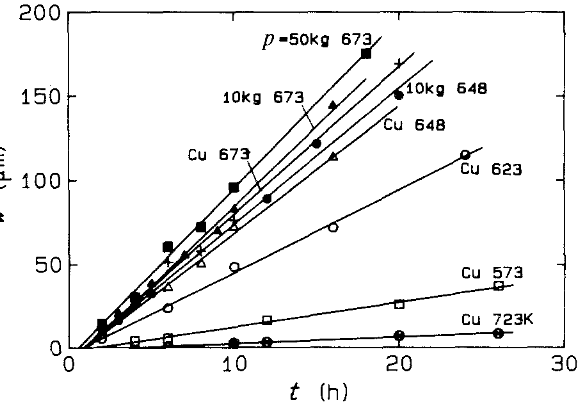

Figure 2 Variation of the migration distance of the discontinuous precipitation RF (w) as a function of the ageing time at different temperatures. The data points with open and filled symbols represent the kinetics of the SGBs and NGBs generated at the single crystal/Cu coating (Cu) and hardness indentation with different loads (P), respectively (see text).

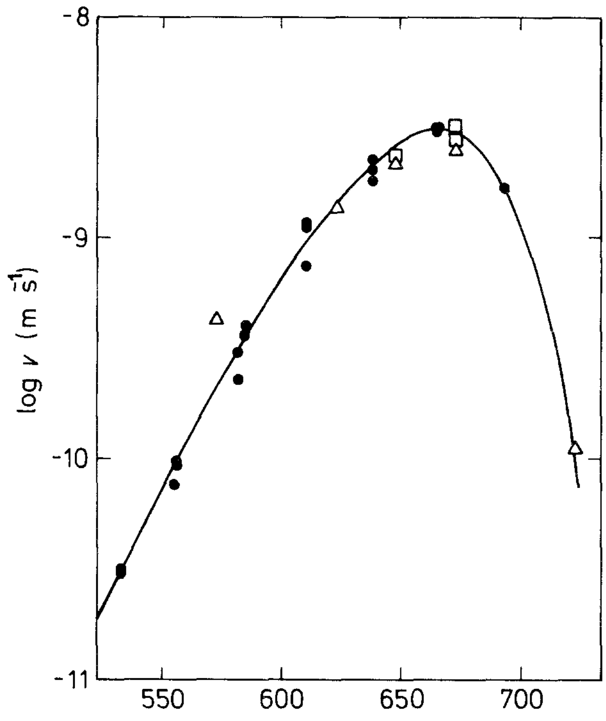

Figure 3 Comparison of the RF migration velocity (v) values in the present study with the v–T spectrum for a Cu–7.5 at % In polycrystalline alloy reported by Predel–Gust [10], ●. SGB (△) and NGB (□) represent the data points due to synthetic and natural (by recrystallization) grain boundaries, respectively.

Fig. 4 reveals that a predetermined degree of surface strain induced by hardness indentation may also initiate discontinuous precipitation at 673 K in the Cu–7.5 at % In single crystal. It is interesting to note that the precipitation is confined only around the indentation mark while the adjoining strain-free crystal surface totally refrains from initiating discontinuous precipitation. While recrystallization due to surface strain induced by hardness indentation creates natural grain boundaries (NGBs) which may undergo the so-called strain-induced boundary migration [11], the totally strain-free crystal surface is unable to undertake thermally activated migration and support discontinuous precipitation. Similar qualitative observations on the role of free surfaces in initiating discontinuous precipitation, with or without surface strain, have also been reported in Ni–Sn [7] and Cu–Ag [8].

The changes in w with t for $P = 10$ kg at $T = 673$ and 648 K, measured on a plane perpendicular to the surface of indentation and intersecting the indentation mark, have been incorporated into Fig. 2. An additional measurement for $P = 50$ kg is carried out at $T = 673$ K to explore whether the magnitude of P may influence the resultant precipitation kinetics significantly. Superimposition of the corresponding v values in Fig. 3 shows that the growth rates of the precipitated colonies originating from the NGBs closely follow the kinetics of discontinuous precipitation determined by Predel and Gust [10] for a Cu–7.5 at % In polycrystalline alloy. It is also interesting to note that the growth kinetics are nearly independent of the applied load of hardness indentation (P) at 673 K. Perhaps the growth rate of discontinuous precipitation, once the reaction has been initiated, is independent of the precise origin of the nucleation site.

Fig. 5 illustrates that the phase boundaries, under favourable circumstances, may also initiate discontinuous precipitation in a Cu–12 at % In alloy. Detailed microstructural studies have established that the eutectoid or peritectic phase boundaries necessitate a prior transformation of the boundaries concerned into essentially precipitate–matrix-type boundaries to be eligible for discontinuous precipitation initiation [5]. It has also been demonstrated that the genesis and kinetics of discontinuous precipitation from such precipitate–matrix phase boundaries are in close agreement with those established for grain boundary-initiated discontinuous precipitation [5].

Since SGBs are capable of initiating discontinuous precipitation (Fig. 1), as are NGBs, an attempt has been made to investigate whether the analogy may also be extended to the synthetic phase boundaries. Isothermal annealing of an In-deposited Cu–7.5 at % In single crystal at 423 K up to 100 h is supposed to generate a number of In-rich intermetallic phases and replace the crystal surface with the respective phase boundaries [9]. Precipitation annealing at 673 K up to 100 h following the pretreatment at 423 K, however, indicates that the synthetic phase boundaries may not be potential sites for discontinuous precipitation (Fig. 6). A detailed study of the kinetics and constitution of the interdiffusion products at 423 K has concluded that the alloyed zone consists of a mixture of intermetallic phases in which $Cu_{11}In_9$ is the major constituent [9]. Careful X-ray diffraction analysis has further indicated that the δ phase, if at all

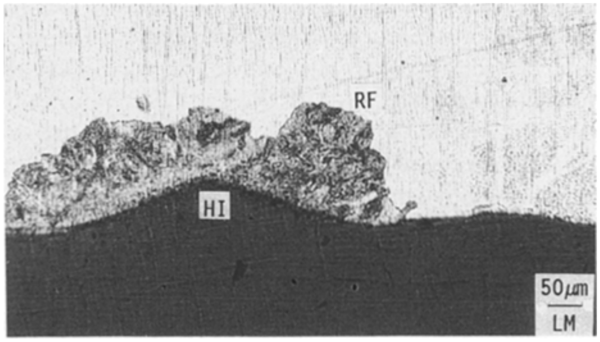

Figure 4 Role of free surface to initiate discontinuous precipitation in a Cu–7.5 at % In single crystal at 673 K. While surface strain due to prior hardness indentation (HI) with $P = 10$ kg results in uniform growth of the discontinuous precipitate colony into the sample interior, adjoining strain-free surface areas refrain from initiating discontinuous precipitation.

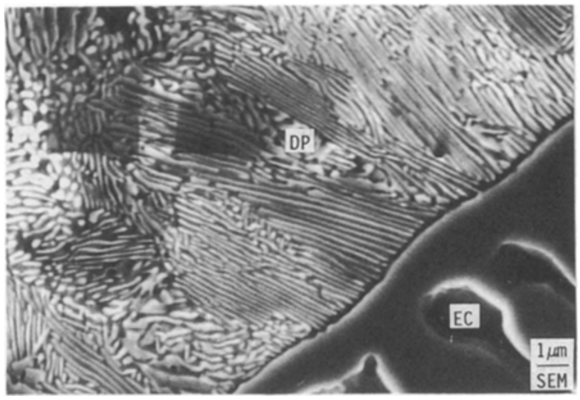

Figure 5 Initiation of discontinuous precipitation (DP) from the precipitate (δ)/matrix (α_0) phase boundary bordering a eutectoid colony (EC) in a Cu–12.0 at % In alloy at 648 K after 4 h. The sample was homogenized at 973 K for 14 days, directly transferred to 798 K for isothermal annealing of 14 h, and water quenched prior to isothermal precipitation.

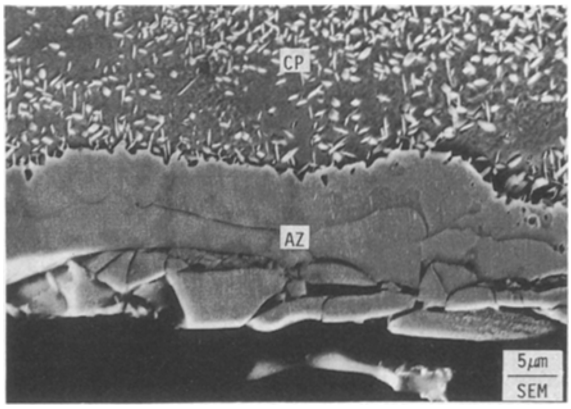

Figure 6 Synthetic interphase boundaries (created by interdiffusion between vapour-deposited In layer and a Cu–7.5 at % In single crystal at 423 K for 100 h) at the alloyed zone (AZ)/matrix interface, totally refraining from initiating discontinuous precipitation at 673 K even after 100 h. Only Widmannstätten-type continuous δ precipitates (CP) are seen in the matrix. Discontinuities in the AZ arise due to brittleness of the constituent intermetallic phases and removal of residual traces of pure In by etching.

present, constitutes only a negligible volume fraction of the phase mixture [9].

Since the precipitate phase resulting from the discontinuous precipitation of Cu–7.5 at % In is the δ phase [10, 12], prior interdiffusion annealing at 423 K may not provide the aimed precipitate–matrix-type phase boundaries during precipitation annealing at 573–673 K in the present investigation. It may be noted that similar attempts to investigate the feasibility of discontinuous precipitation initiation from the precipitate/matrix-type interfaces synthesized by vapour-deposited Ag layer on a Cu–7.7 at % Ag alloy has also indicated that the synthetic phase boundaries may not be quite effective to initiate discontinuous precipitation [8]. It is known that the boundary structure and characteristics have a profound influence on the nucleation and growth kinetics of discontinuous precipitation [1, 2, 13]. Perhaps the synthetic boundaries do not always possess identical structure and mobility as the natural counterparts of discontinuous precipitation. Further, the absence of discontinuous precipitation even after 100 h in Fig. 6 appears to suggest that decomposition of a supersaturated matrix by the discontinuous mode may be completely suppressed in a single crystal by proper surface coating to deactivate or eliminate all possible boundaries which may undergo thermally activated migration.

Fig. 7 evidences initiation of discontinuous precipitation from the boundary between a eutectic colony and a supersaturated matrix phase (α_0) at 673 K in a Cu–35 at % Ag alloy. Eutectic transformation itself being a discontinuous mode of reaction, the boundary between the eutectic colony and α_0 may be assumed to be a large-angle boundary capable of supporting discontinuous reactions. Therefore, initiation of discontinuous precipitation from eutectic boundaries is comparable to the growth of a separate precipitate colony from the discontinuous precipitation RF. In accordance with the Fournelle–Clark mechanism [14], the eutectic boundaries with predominantly concave–forward curvature towards the matrix phase appear to be more favourable sites for nucleation of discontinuous precipitation (Fig. 7).

Discontinuous precipitation from similar eutectic/matrix interfaces has been observed also in a Cu–8.0 at % Mg alloy. However, isolated islands of eutectic area embedded in the matrix grains refrain from initiating discontinuous precipitation (Fig. 8). Earlier, similar inaction of individual eutectic nodules in a Cu–7.7 at % Ag alloy has also been noted [8]. Perhaps, the unfavourable curvature (i.e. convex–forward) of the boundaries concerned [14] precludes possibilities of discontinuous precipitation initiation from the eutectic nodules/islands. In addition, a few discontinuous precipitate colonies have been observed to initiate from the coherent faces of the twins (Fig. 8). Considering the prerequisite of a large-angle incoherent boundary to support boundary diffusion, concurrent for a discontinuous reaction, Fig. 8 appears to suggest that apparently improbable nucleation sites may also undergo suitable modification and initiate discontinuous precipitation. A possible mechanism could be the repeated dissociation of large-angle boundaries (i.e. faceting) into coherent and incoherent components, enabling one of the products [15] to assume the role of a discontinuous precipitation RF. However, apart from demonstrating the feasibility, the present study does not suggest any specific route of transforming a coherent boundary into an incoherent discontinuous precipitation RF.

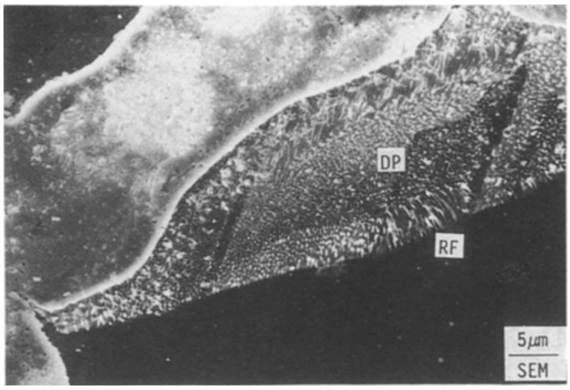

Figure 7 Initiation of discontinuous precipitation from a eutectic–matrix boundary at 673 K after 4 h in a Cu–35 at % Ag alloy.

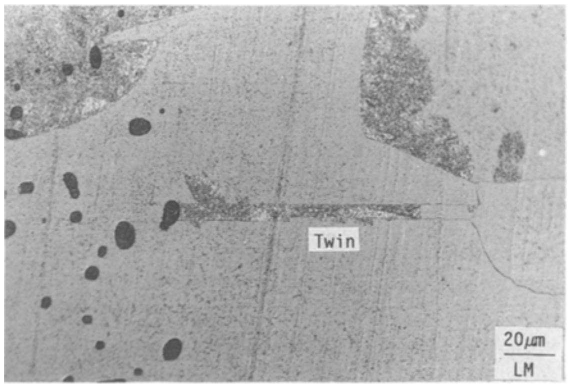

Figure 8 Initiation of discontinuous precipitation from broad (coherent) faces of a twin at 648 K after 25 h in a Cu–8 at % Mg alloy. Dark nodules of eutectic areas embedded in the matrix refrain from initiating discontinuous precipitation.

4. Conclusions

The occurrence of discontinuous precipitation depends primarily on the availability of a short-circuit route of solute transport. While matrix grain boundaries (both natural and synthetic) are the most suitable candidates, non-conventional nucleation sites like precipitate/matrix phase boundaries, or coherent faces of a twin, may also initiate discontinuous precipitation provided the boundaries concerned may undergo thermally activated migration. Perhaps the ability to undertake such thermally activated migration is more crucial than the nucleation of boundary precipitates to initiate discontinuous precipitation. Finally, discontinuous precipitation may be completely suppressed by eliminating or deactivating any boundary otherwise able to migrate at the precipitation temperature.

Acknowledgements
One of the authors (I.M.) expresses his gratitude to Deutscher Akademischer Austauschdienst (DAAD) for financial support during this work. Thanks are also due to Mrs G. Speck and S. Kühnemann for their respective help in preparing the manuscript and carrying out the SEM investigations.

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Received 10 April 1990
and accepted 15 January 1991