

Effect of surface strain on discontinuous precipitation kinetics in a Cu-7.7 at% Ag alloy

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Precipitation of a two-phase aggregate behind a grain boundary advancing into a supersaturated solid solution is called discontinuous precipitation (DP) [1-3]. Usually, a large-angle incoherent boundary, called the reaction front (RF), provides a short-circuit path of solute transport for the precipitate colony growth [2,3]. Recently, it has been demonstrated that recrystallization following prior strain due to scratching or hardness indentation at the external surface may generate grain boundaries capable of initiating DP [4-6]. These exploratory studies, however, did not attempt to quantify the effect of strain on the precipitation kinetics. Earlier quantitative studies on the effect of plastic strain on the overall kinetics of DP employed only bulk deformation like rolling [1, 7-9]. DP is likely to initiate heterogeneously at the deformation bands or sub-structures produced by such bulk deformation [10, 11]. Moreover, the overall effect on transformation kinetics is expected to be determined by the influence of strain on both the nucleation and growth stages. Hence, a study of the interrelationship between the amount of plastic strain or the applied load of deformation and the RF velocity is not practicable with bulk deformation techniques. On the other hand, determination of the velocity of the RF, generated by prior hardness indentation [5, 6], as a function of the applied load may furnish a more direct estimate of the role of plastic strain on the kinetics of DP.

About 300 g of a Cu-7.7 at% Ag alloy was prepared from 99.99 wt% purity Cu and Ag by vacuum induction melting. A large grained ingot of 10 mm diameter was grown from this alloy under Ar atmosphere by a vertical Bridgman technique. Semi-circular disc-shaped specimens of about 5 mm thickness (see Fig. 1a) were cut from the ingot by a slow-speed diamond saw and homogenized at 1033 K for 12 h in a reducing atmosphere prior to quenching in water at room temperature. All flat faces of the specimens were mechanically polished with 0.5 μm diamond followed by electropolishing in concentrated (65%) H_3PO_4 using a stainless steel cathode at a DC potential of 2 V for 20 min to remove all traces of mechanical strain from the specimen surfaces. Surface deformation with a predetermined load (P) was applied on one of the flat semi-circular faces of the specimens by means of the diamond indenter of a Vickers hardness tester (Fig. 1a). A selected set of specimens, after surface deformation, were cleaned with acetone and ethanol and subjected to surface coating of pure Ag (0.3 μm)

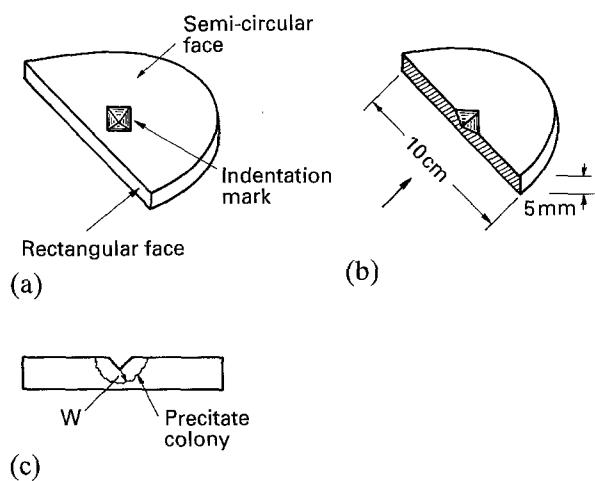


Figure 1 Schematic representation of surface straining by hardness indentation: (a) and (b) isometric view; (c) front view of (b) in the direction of the arrow.

or pure Cu (1.2 μm) separately by vapour deposition. All the specimens with or without surface coating were encapsulated in evacuated pyrex tubes, precipitation annealed at 673 K for varying lengths of time (t) and quenched in water at room temperature. For precise estimation of the effect of surface strain on the precipitation kinetics, microstructural investigations were carried out on the rectangular faces of the specimens after controlled removal of the latter surface up to the centre of the indentation mark (Fig. 1b). This ensures monitoring of the maximum effect of strain on the subsequent precipitation process since the plane of observation now intersects the tip of the indentation perpendicularly (Fig. 1c). It may be noted that the specimens were mounted in bakelite to avoid edge-rounding during mechanical grinding/polishing. Finally, the rectangular faces of all the specimens were polished with 600 grit emery paper and 0.5 μm diamond paste followed by etching with a colour tinting solution containing 200 g CrO_3 , 20 g Na_2SO_4 and 17 ml HCl (35%) in 1000 ml distilled water in order to measure the maximum width of the precipitate colony (W), as shown in Fig. 1c.

Plastic strain induced by hardness indentation on an otherwise strain-free specimen surface develops a discontinuous precipitate colony during precipitation at 673 K for loads $P = 1, 5, 10, 20$ or 40 kg. Fig. 2 reveals a typical colony growth ahead of the indentation tip for $P = 10$ kg in an uncoated specimen. DP, initiated from the external surface, proceeds towards the specimen interior. The dark

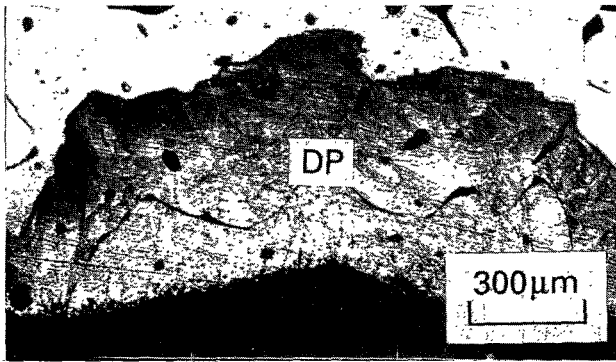


Figure 2 An optical micrograph showing a typical DP colony growth during isothermal ageing at 673 K for 2.5 h from the tip of a prior hardness indentation with $P = 10$ kg.

eutectic nodules embedded in the matrix did not act as the nucleation site in this alloy either in a strained or unstrained condition [6]. Fig. 3a reveals the variation of W (measured as shown in Fig. 1c) as a function of t in uncoated specimens for $P = 1, 5, 10, 20$ and 40 kg. The data for any given P are fitted to the equation of a straight line as follows:

$$W = W_0 + vt \quad (1)$$

where $W_0 = W$ at $t = 0$ and v is the velocity of the reaction front, obtained from the slope of the $W-t$ plot. It is interesting to note that none of the straight lines in Fig. 3a passes through the origin and the intercepts (W_0) at $t = 0$ are quite large ($>350 \mu\text{m}$) compared with the maximum value of W at $t = 6$ h. The computed values of W_0 and v for different P , within an error limit of about $\pm 15\%$, are reported in Table I.

In order to study the role of artificial interfaces generated by the surface coatings [5, 6], similar experiments have been repeated with two separate sets of specimens coated with Ag and Cu on the external surface after hardness indentation. The precipitation characteristics or growth kinetics ahead of the indentation mark does not seem to be influenced by the surface coating. Figure 3b and 3c presents the W versus t plots for Ag and Cu coated specimens with similar straight lines fitted to the data for the respective P as in Fig. 3a. The corresponding computed values of W_0 and v are summarized in Table I. It may be noted that no systematic change in W_0 or v is apparent as a function of P .

Surface strain induced by hardness indentation with $P = 1$ to 40 kg appears sufficient to initiate DP from the specimen surface at 673 K (Fig. 2). This corroborates earlier reports [4–6] postulating that the prior mechanical strain may develop a recrystallized layer below the specimen surface at the precipitation temperature and provide migrating boundaries to initiate DP. However, the velocity of migration of such boundaries in the course of DP does not seem to be proportional to the applied load (P) of prior strain. For instance, v values for coated/uncoated specimens appear to be independent of P for $P < 5$ kg, though for higher values of P ,

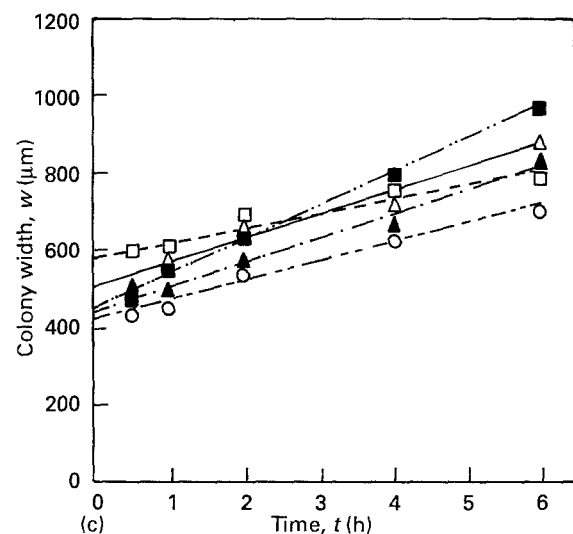
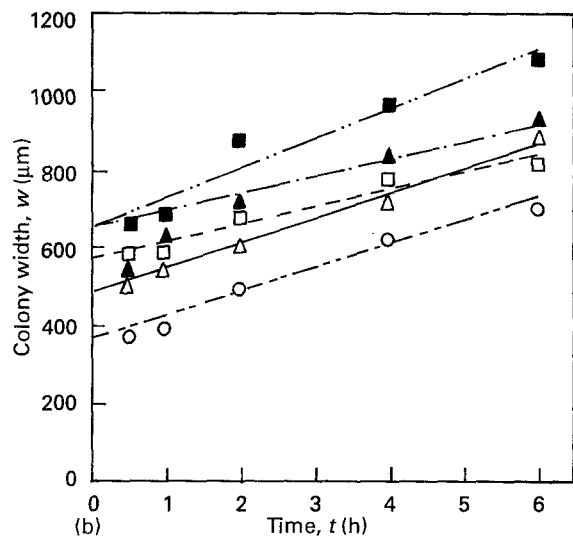
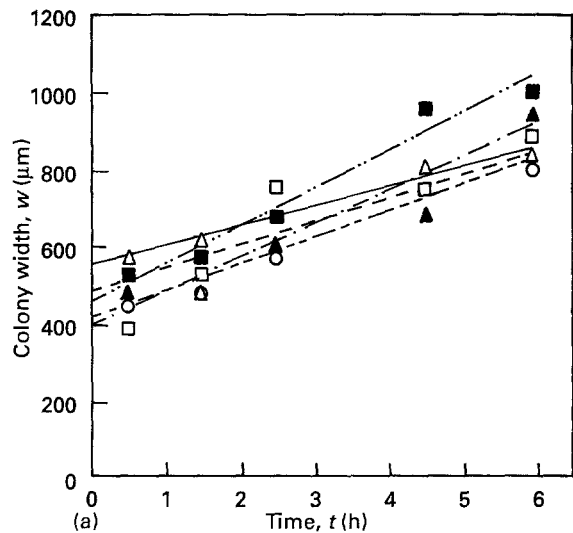


Figure 3 Variation of the maximum width of the DP colony (w) as a function of time (t) in: (a) uncoated; (b) Ag-coated; and (c) Cu-coated specimens. Load $P = 1$ kg (\circ), 5 kg (\triangle), 10 kg (\square), 20 kg (\blacktriangle) and 40 kg (\blacksquare).

they undergo marginal increase (within the same order of magnitude) as P increases. Comparison of the results in Fig. 3 further indicates that the surface coatings with Ag or Cu also do not have any

TABLE I Values of W_0 and v as a function of P for uncoated, Ag coated and Cu coated samples

Load P (kg)	Uncoated		Ag coated		Cu coated	
	W_0 (10^{-6} m)	v (10^{-8} m s $^{-1}$)	W_0 (10^{-6} m)	v (10^{-8} m s $^{-1}$)	W_0 (10^{-6} m)	v (10^{-8} m s $^{-1}$)
1	418	1.89	372	1.61	424	1.36
5	549	1.42	484	1.78	510	1.67
10	482	1.68	566	1.31	581	1.03
20	402	2.33	559	1.67	453	1.67
40	459	2.69	646	2.11	475	2.28

significant effect on v at any level of P , though similar coating with Cu is reported to be effective in initiating DP from a strain-free specimen surface [6]. Perhaps, prior strain by surface deformation may provide sufficient nucleation sites through recrystallization [12] and strain-induced boundary migration [13] so that generation of additional nucleation sites by surface coating does not manifest any noticeable influence.

It is quite interesting to note that v in the deformed region of the present alloy has the same order of magnitude as that reported for a strain-free Cu–3.8 at% Ag bicrystal at 673 K [14]. However, an important distinction between the growth kinetics in the unstrained condition [14] and the present study is that the W against t plots in the former investigation usually pass through the origin (i.e. $W_0 = 0$ in Equation 1) while W_0 has a large positive values in the present investigation for all measures of P (Table I). This appears to suggest that the initial growth rates (v_0) in the strained region is unusually fast at the early stage ($t < 0.5$ h) of precipitation. However, v_0 seems to be insensitive to P . Assuming a linear relationship of $W_0 = v_0 t$ for $t < 0.5$ h where $W_0 = 492 \mu\text{m}$ (i.e. the average of the W_0 values from Table I), $v_0 = W_0/t = 2.7 \times 10^{-7} \text{ m s}^{-1}$, which is one order of magnitude higher than v at $t > 0.5$ h (Table I) or the existing data for the unstrained Cu–Ag alloy [14]. The overall Gibbs free energy change estimated by Gust *et al.* [14] for a strain-free Cu–Ag alloy is 0.3 kJ mol^{-1} at 673 K. Assuming the unusually large magnitude of v_0 is directly related to the induced strain energy at the surface, the magnitude of the stored strain energy should be of the order of 3 kJ mol^{-1} . Comparison with strain energy values of heavily cold deformed Cu [15] indicates that the above estimate is quite unrealistic. Therefore, v_0 may not be linearly related to the stored strain energy. Perhaps, the detailed structural changes associated with strain induced boundary migration warrants particular attention for a precise explanation of the large magnitude of v_0 , which is beyond the scope of this investigation.

The matrix strain due to bulk deformation may enhance the continuous precipitation and thereby, decrease the DP kinetics in systems where both types of precipitation are feasible [1]. Though Cu–Ag alloys may undergo both continuous [16] and discontinuous [6, 14] modes of precipitation, microstructures in the present study do not evidence the former. Moreover, the kinetic data also do not

show any reduction in growth kinetics of DP due to surface strain. Apparently, the localized nature of surface strain employed in the present study does not provoke concurrent continuous precipitation and related complexities.

In summary, surface strain induced by hardness indentation with load varying between 1 and 40 kg is capable of nucleating DP from the surface. Growth kinetics, however, do not register any appreciable change due to the strain, except for an unusually rapid reaction rate confined to an early stage (< 0.5 h) of the transformation which cannot be attributed to the driving force due to the strain energy of surface deformation. Perhaps, the limited depth of deformed region induced by the surface indentation is responsible for the accelerated growth kinetics in the early stage.

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