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On the formation of a microduplex structure in a Cu–15 wt% Ni–37.5 wt% Zn alloy

H. KREYE, U. BRENNER
Institut für Werkstoffe, Ruhr-Universität Bochum, D-4630 Bochum, Germany

Interaction of recrystallization and precipitation during annealing of a cold-worked supersaturated solid solution can lead to the formation of an ultrafine grain size, two-phase microstructure, termed microduplex. In Cu–15 wt % Ni–37.5 wt % Zn this process requires prior cold-work of more than 60% RA. Cell walls and subgrain boundaries introduced by the deformation act as preferred nucleation sites for second phase particles. A high density of small particles is formed before recrystallization can start. Recrystallization then becomes controlled by the coarsening of the particles. A microstructure with grains and particles of less than 1 μm diameter results.

1. Introduction

Tensile and fatigue strength properties of two phase alloys can be improved by the formation of an ultrafine grain size, two phase microstructure. Such a microstructure has been successfully produced in a variety of alloys, by thermomechanical processing, e.g. stainless steel [1], copper–beryllium [2], copper-zinc [3], and copper–nickel–zinc [4, 5]. The processing generally involves either cold working of solid solution, followed by annealing in the two phase region or hot-working through the solvus temperature. Recent experiments on Cu–Ni–Zn alloys [4, 5], have demonstrated how the composition of the alloy, the degree of cold work, annealing time and temperature have to be balanced in order to obtain the microduplex structure. The authors stated that recrystallization and precipitation must occur simultaneously and that a microduplex structure will not result, when either of these processes occurs before the other.

The present work was initiated to study the interaction of recrystallization and precipitation during annealing of a cold-worked supersaturated Cu–15 wt % Ni–37.5 wt % Zn alloy. Precipitation in this alloy resembles that of the binary Cu–Zn system. A bcc β phase (A2) precipitates from the fcc α solid solution (Fig. 1). No metastable phases have been observed during the earlier stages of this process. The formation of β should be favoured by defects introduced by prior cold-work. Also, if precipitation precedes recrystallization, the size and distribution of β particles may affect the mechanism and kinetics of recrystallization. Thus, the microstructure should depend on the degree of deformation, annealing time and temperature. The purpose of this investigation was to determine the combination of recrystallization and precipitation conditions that result in the formation of a microduplex structure.

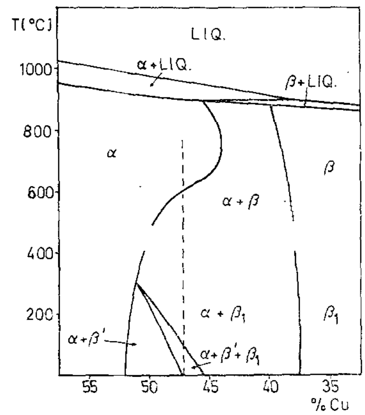

Figure 1 Section through the Cu–Ni–Zn phase diagram at 15% nickel, after Schramm [6]. The dashed line indicates the composition of the alloy used in this investigation.

2. Experimental procedure

The material, supplied by The International Nickel Co Inc, was melted as described earlier [5]. The chemical analysis was Zn 37.5, Ni 15.1, Mn 0.01, Mg 0.022, Cu balance (in wt %). Samples of this material were homogenised at 700° C and rolled at room temperature. The amount of rolling was varied between 10 and 95 % reduction in area. The rolled samples were annealed at various temperatures between 150 and 600° C. Their microstructure was then examined by light and transmission electron microscopy. Tensile testing was done on standard strip specimens, 0.5 mm thick, with a 20 mm gauge length. The specimens were cut, parallel to the rolling direction from the 90% deformed material and annealed at various temperatures.

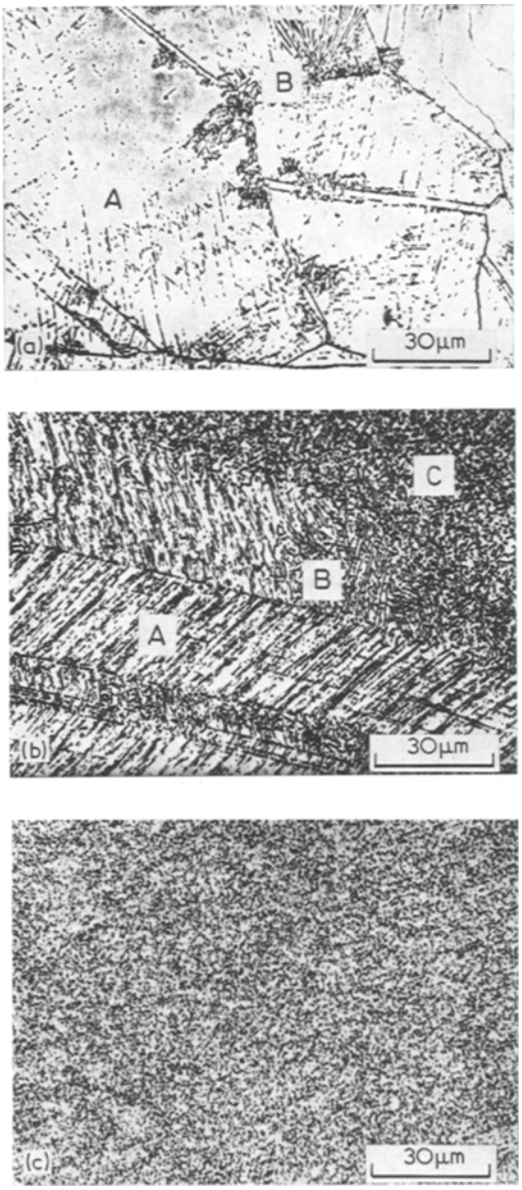

Figure 2 Microstructure after different amounts of cold-work and 1 h anneal at 500° C. (a) 30 % RA, reactions A and B; (b) 70 % RA, reactions A, B and C; (c) 95 % RA, reaction C only.

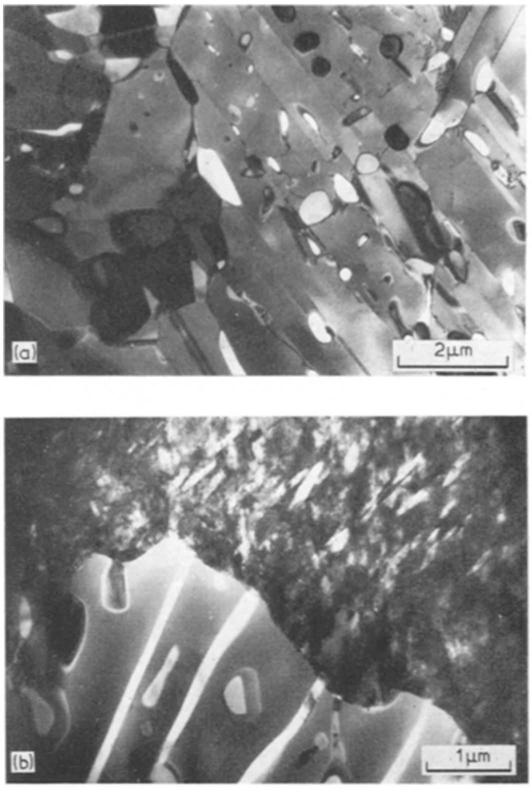

Figure 3 TEM-micrographs showing the different micro-structures resulting from reactions A and B. (a) 30 % RA, 1 h 500° C (A); (b) 60 % RA, 1 h 500° C (B).

3. Experimental results

During the annealing of undeformed samples, a heterogeneous nucleation of β starts at grain and twin boundaries. The precipitates grow preferentially along these defects until they form a continuous film. After longer annealing times, the β phase also nucleates within grains and twins giving a Widmanstätten type structure. There was no evidence for the formation of metastable phases. These precipitation phenomena are also observed in previously deformed and annealed samples, up to about 70% RA (Figs. 2a, b and 3a) (type A). In addition, discontinuous precipitation takes place during annealing of samples deformed by 30 to 80 % RA (Fig. 2a and b). Grain boundaries move into the supersaturated and deformed solid solution. Discontinuous precipitation and annihilation of dislocations at grain boundaries occur simultaneously. A lamellar arrangement of β and recrystallized α results (type B). This reaction can start at portions of the original grain boundaries not yet covered by a continuous β film and at newly formed grain boundaries. Precipitation of β in front of a moving grain boundary can impede or stop the discontinuous reaction (Fig. 3b). A third precipitation mode (type C) leading to a uniform distribution of β particles and small α grains can be found during annealing of the highly deformed samples (> 60% RA). TEM micrographs taken after different annealing times, indicate that *in situ* recrystallization and coarsening of β particles occurs simultaneously (Fig. 4a, b and c). The β particles are identified by the extra spots in the electron diffraction pattern, along rings labelled β in Fig. 4d. Weaker spots in these positions are already found in the diffraction patterns corresponding to Fig. 4a and b and to 90% deformed samples annealed for 1 h at 300° C.

The volume fraction of the samples covered by each of the three precipitation mechanisms A, B and C has been determined from a series of micrographs after a 10 h anneal at 500° C using the point-count analysis described elsewhere [7]. This volume fraction is plotted versus the amount of prior cold work in Fig. 5. Similar measurements at deformed samples annealed at 400, 450 540° C, respectively, show no significant difference. The resulting microstructure, therefore, is determined mainly by the amount of prior cold work. A microduplex structure throughout the whole material can only be attained in the 90 and 95% deformed and annealed samples (Fig. 2c). The reaction is completed after approximately 0.1 h at 540° C, or 1 h at 500° C, 10 h at 450° C and 100 h at 400° C. The extent of the continuous reaction C in the 60 to 80% deformed samples can be increased at the expense of the discontinuous reaction B, when the samples are

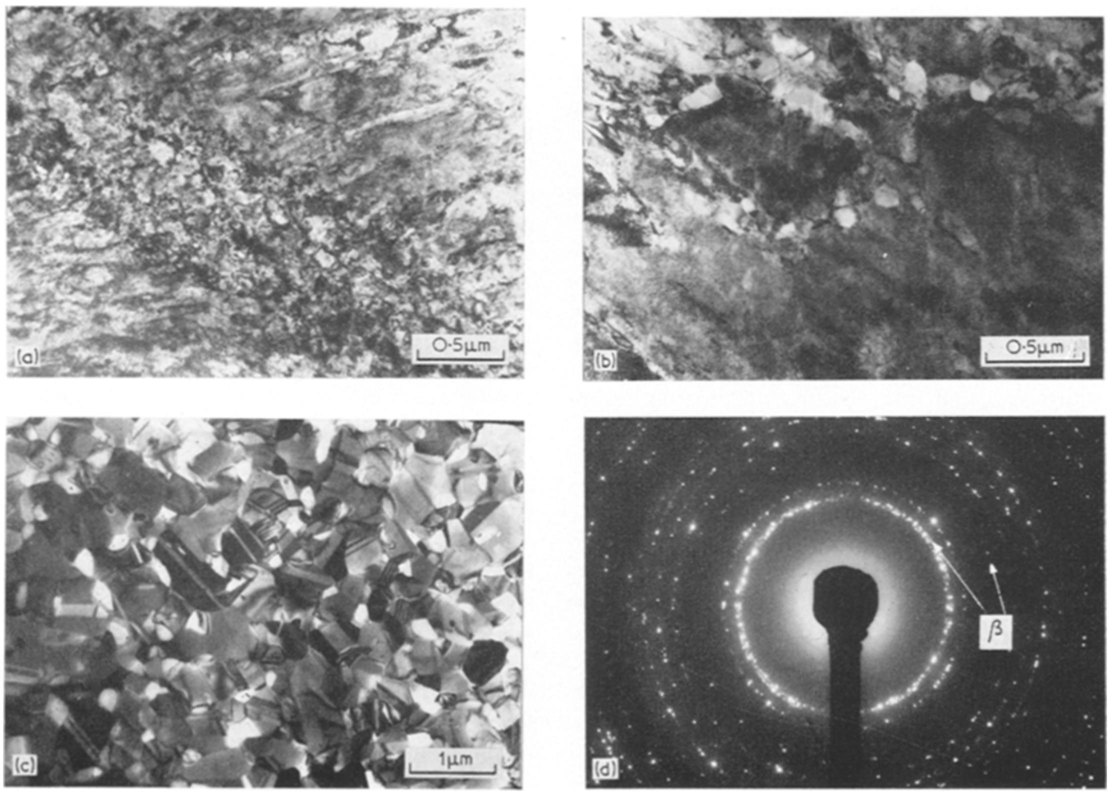

Figure 4 TEM-micrographs of different stages of the formation of a microduplex structure, 90% RA and (a) 1 min 500° C, (b) 2 min 500° C, (c) 6 min 500° C, (d) Selected-area diffraction pattern, 6 min 500° C.

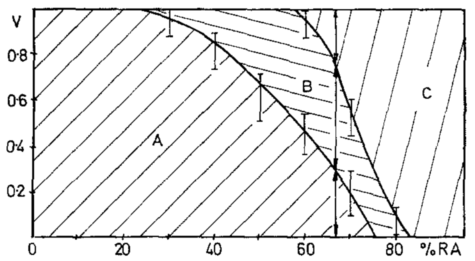

Figure 5 Volume fraction, V, covered by the different reaction, after annealing of deformed samples for 10 h at 500°C versus amount of prior cold-work. A, large α grains containing β particles; B, lamellae of α and β formed by discontinuous precipitation; C, microduplex structure.

pre-annealed at low temperatures (e.g. 1 h 200°C), after deformation.

The results of the room temperature tensile tests are shown in Fig. 6a and b. Samples deformed to 90% RA and annealed at different temperatures exhibit a maximum in the strength versus annealing temperature curve at about 300°C. Such a maximum is also obtained during isothermal annealing at 500°C after 1 min.

4. Discussion

Three types of microstructure have been found in the deformed and annealed samples, depending mainly on the amount of prior cold-work. (A) Large α grains containing β particles (0 to 70% RA). (B) Lamellar structure of α and β (30 to 80% RA). (C) Microduplex structure (> 60% RA). The observed phenomena can be interpreted as a result of the combined effect of recrystallization and precipitation. The microstructure depends on which of the two processes occurs first and how the motion of grain boundaries is affected by precipitated particles [8].

In undeformed samples, formation of β starts at grain boundaries and twin boundaries due to a low activation energy for nucleation at these defects. Nucleation within the grains and twins requires a higher activation energy and, therefore, a low nucleation rate leads to a coarse distribution of β particles. Dislocations produced by small and medium amounts of cold work do not alter the precipitation mechanism or the morphology of the β phase. The distance of the β particles is large compared to the diameter of recrystallization nuclei. Therefore, during annealing the dislocations can rearrange between the particles to form new grain boundaries. The driving force, P_N, for migration arising from the difference of dislocation densities on either side of the grain boundary, exceeds the pinning force, P_P, which the β particles exert at the grain boundaries ($P_N + P_P > 0$). Therefore, large scale motion of grain boundaries can lead to large α grains containing β particles (Fig. 3a). P_N is approximately given by $P_N = \alpha\mu \boldsymbol{b}^2 (N_2 - N_1)$ where α is a constant factor, μ is shear modulus, $\boldsymbol{b}$ is Burgers vector and N_2, N_1 are the dislocation densities in front of and behind the moving grain boundaries. If the particles are stable with respect to the grain boundary, P_P is given by the Zener relation, $P_P = -(3f/2r)\gamma_{Gb}$, with f the precipitated volume fraction, r the radius of the particles, and γ_{Gb} the grain-boundary energy [9].

The discontinuous precipitation (B) does not occur during annealing of samples deformed by less than 30% RA. Before the reaction can start, the grain boundaries are blocked by a continuous β film. After 30 to 80% RA the discontinuous reaction starts before the grain boundaries are totally covered by the β film. The driving force at the reaction front can be assumed as a superposition of different terms $P = P_N + P_C + P_P$. The chemical term P_C is given by $P_C \approx \nu_m RT \ln (C_1/C_0)$ where ν_m is the mole number, R is the gas constant, T is the absolute temperature, and C_1, C_0 referring to the concentration of the supersaturated solid solution and the equilibrium concentration, respectively. The velocity of the reaction is increased by increasing amounts of cold-work (increasing P_N). It is slowed down, when particles precipitated in front of the grain boundaries exert a pinning force and also the chemical force P_C is reduced (Fig. 3b). After high amounts of cold-work the acceleration of precipitation in front of the grain boundaries in the deformed areas reduces the chemical term P_C to zero. Simultaneously, the pinning force exceeds the driving force P_N. A similar behaviour, with the extent of discontinuous precipitation exhibiting a maximum after 50 to 60% RA and becoming completely suppressed by prior cold-work of 90% RA, has been reported in a Cu–2Be alloy [2].

In the highly deformed samples (C) the well-defined cell walls and subgrain boundaries produced by the deformation and/or developed during the earlier annealing stages, also act as preferred nucleation sites. This leads to a much finer distribution of β particles as compared to the precipitation of type A. The small particles

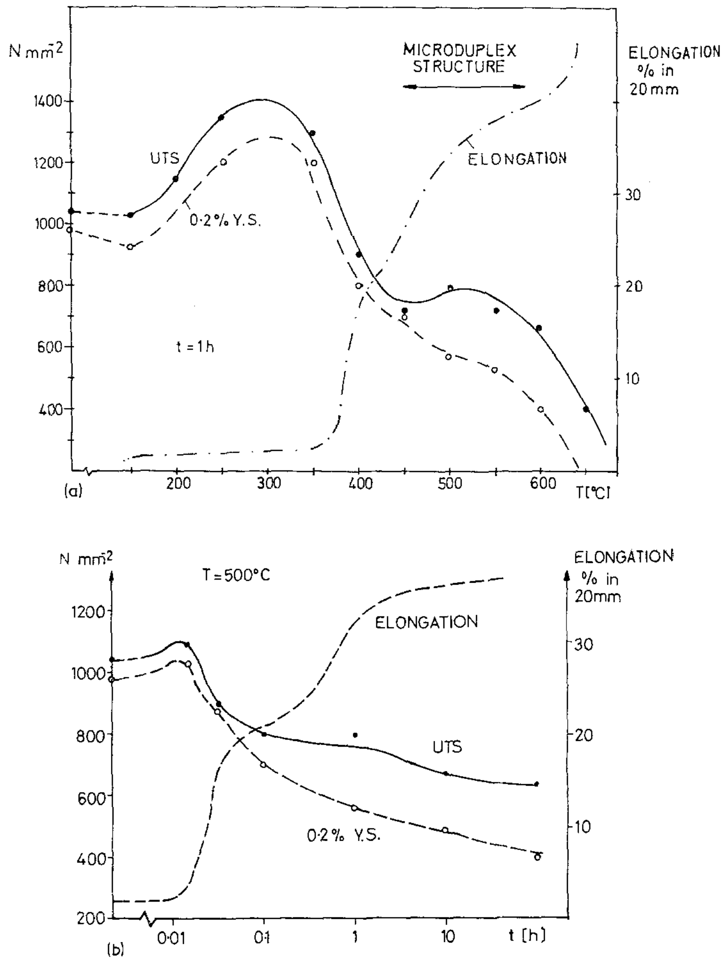

Figure 6 Tensile properties of 90% deformed samples after different annealing treatments.

pin the dislocation and subgrain boundaries. Rearrangement of dislocation, necessary for the formation of new grain boundaries, becomes controlled by the coarsening of the particles [10]. The pinning force, due to the particles exceeds the driving force, $P_N + P_P < 0$. Therefore, no large scale motion of grain boundaries can occur. The different stages of this *in situ* type recrystallization leading to the microduplex structure are shown in Figs. 4 and 7. The β-particles in the deformed areas have been identified by electron diffraction. In addition, the increase in strength during isothermal and isochronal annealing of 90% deformed samples can be interpreted only as a superposition of work-hardening and precipitation hardening [11]. The extent of the discontinuous reaction B can be reduced in the 60 to 80% deformed samples by pre-annealing at low temperatures. However, a 100% microduplex structure is only obtained after deformation of more than 80% RA.

5. Conclusions

Annealing of a supersaturated and deformed Cu-15 wt% Ni-37.5 wt% Zn alloy leads to a variation in microstructure depending mainly on the amount of prior cold-work. For $\epsilon < 70\%$ RA, large α grains containing β particles; for $30\% < \epsilon < 80\%$ RA, lamellar distribution of α and β formed by a discontinuous reaction; for $\epsilon > 60\%$ RA fine distribution of α and β grains (microduplex).

A high amount of prior cold-work is required to obtain the desired microduplex structure. The defects introduced during deformation favour the precipitation of β. A fine distribution of

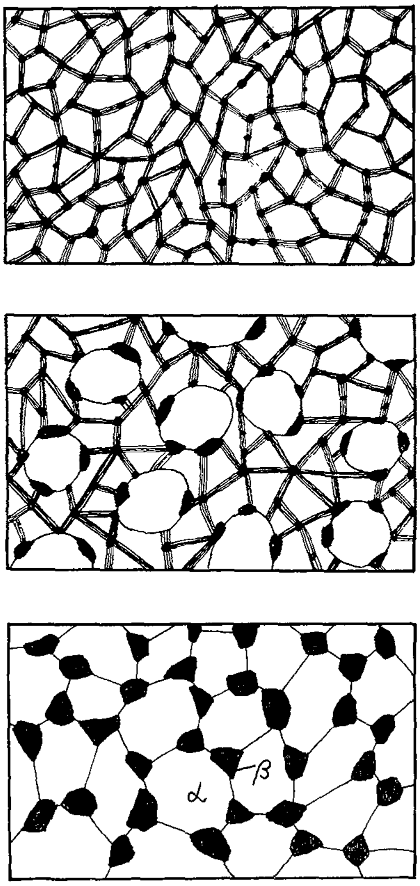

Figure 7 Proposed mechanism for the formation of a microduplex structure (schematic): precipitation of β at dislocation networks and subgrain boundaries, *in situ* recrystallization controlled by the coarsening of β.

particles is formed before recrystallization can start. Rearrangement of dislocations necessary for the formation of recrystallized grains becomes controlled by the coarsening of the particles. No large scale motion of grain boundaries can occur.

Deformation of more than 80% RA is required to suppress the discontinuous reaction completely and to obtain a 100% microduplex structure.

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