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Precipitation hardening in Cu 1.81 wt % Be 0.28 wt % Co

Part 3 *The effect of prior deformation on the ageing sequence*

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The influence of prior cold work (50% reduction) on the ageing sequence of a Cu 1.81 wt % Be 0.28 wt % Co alloy has been investigated with transmission electron microscopy and hardness measurements. At low ageing temperatures (175° C), the effect of deformation is to reduce the vacancy concentration available for the formation of G.P. zones, with the subsequent retardation of the continuous precipitation sequence. In contrast, at higher ageing temperatures (315° C), recovery and recrystallization increased the available vacancy concentration and the continuous precipitation was accelerated in comparison to the undeformed alloy, while no discontinuous precipitation was noted. At ageing temperatures of 425° C, in addition to the continuous precipitation sequence, recrystallized grains of the γ equilibrium precipitate and α matrix were formed.

1. Introduction

The influence of prior deformation upon the ageing process of precipitation hardening alloys has important industrial applications. The deformation may be introduced immediately after the solution treatment and quench or after a prior ageing treatment. The former treatment is often used for commercial copper-beryllium alloys and an acceleration in the ageing process is found for the normal 315°C ageing treatment employed. It cannot be assumed, however, that because an ageing reaction has been accelerated by prior strain that the morphological features developed will be the same as in the directly quenched material.

The work presented in this paper relates to a study on the effect of prior cold work on the precipitation process of a Cu 1.81 wt % Be 0.28 wt % Co alloy. The ageing of the solution treated and quenched material has been described previously [1, 2].

The main objectives of this study were to elucidate the effect of deformation on the precipitation sequence, to study the basic mechanisms involved and to trace the precipitation sequence with transmission electron microscopy.

2. Experimental method

The alloy investigated was a commercial copper-beryllium alloy (Telcon 250) which had a composition of 1.81 wt % Be 0.28 wt % Co. The alloy was examined with and without a 50% cold reduction of the solution treated condition prior to ageing. The material was subsequently aged at temperatures in the range 175 to 425° C, in a horizontal tube furnace under an inert argon atmosphere.

Thin foils were prepared for examination in the electron microscope by electropolishing by the method described earlier [1].

3. Results

3.1. The as-quenched and cold-worked material

The structure of the as-quenched and cold-worked material (50% cold-rolled), as shown in Fig. 1, was similar to that found by Bailey [3] for deformed single crystals of copper. The material was heavily deformed and no cell

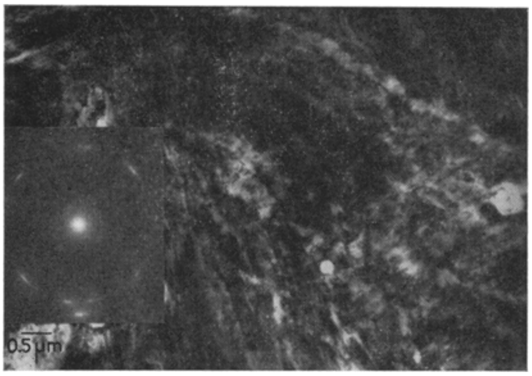


Figure 1 The solution-treated 50% cold-rolled condition in the as-received state.

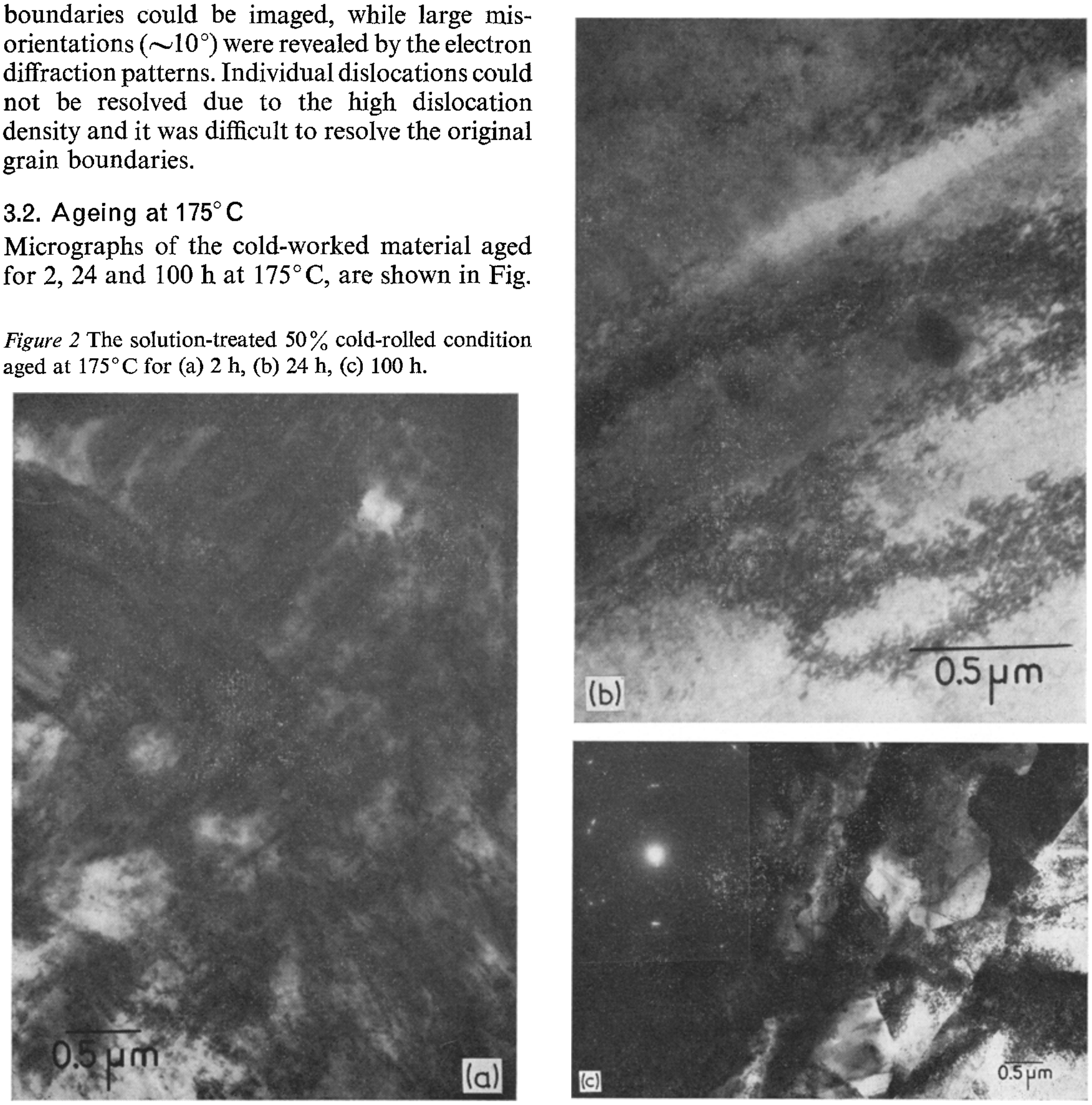
boundaries could be imaged, while large misorientations (~10°) were revealed by the electron diffraction patterns. Individual dislocations could not be resolved due to the high dislocation density and it was difficult to resolve the original grain boundaries.

3.2. Ageing at 175° C

Micrographs of the cold-worked material aged for 2, 24 and 100 h at 175° C, are shown in Fig. 2a, b and c respectively. The 2 h condition exhibited a structure similar to that of the as-received cold-worked material but on ageing for 24 h recovery was observed in some areas, as shown in Fig. 2b. After ageing for 100 h at 175° C a recrystallization reaction was noted in some regions, with heavily deformed areas also present, as shown in Fig. 2c.

No evidence of any precipitation of G.P. zones or the intermediate precipitate γ' was found for ageing times up to 100 h. These observations can be correlated with the hardness measurements shown in Fig. 3. The cold-worked material exhibited a slow increase in hardness to

Figure 2 The solution-treated 50% cold-rolled condition aged at 175° C for (a) 2 h, (b) 24 h, (c) 100 h.



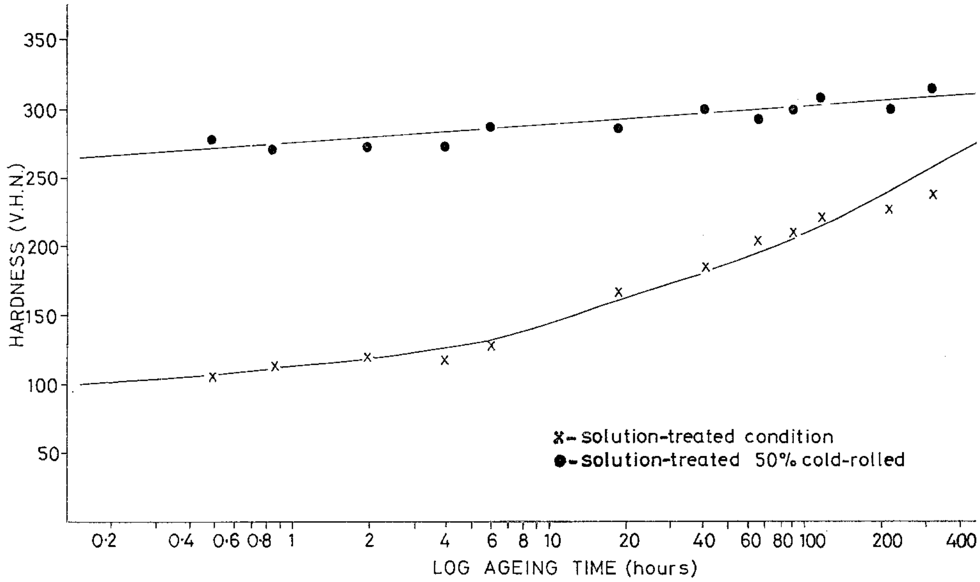


Figure 3 Hardness versus log ageing time for ageing at 175°C. (At zero time, hardness of solution-treated condition = 94 V.H.N.; hardness of solution-treated 50% cold-rolled condition = 252 V.H.N.)

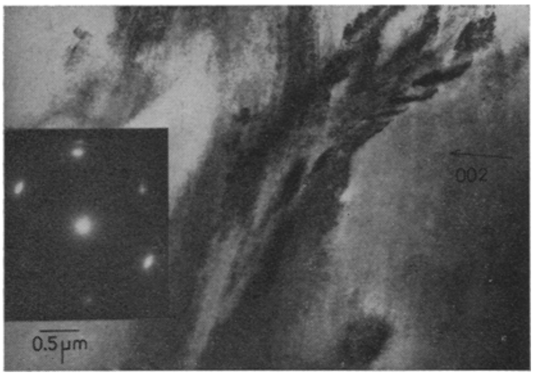


Figure 4 The solution-treated 50% cold-rolled condition aged for 15 min at 315°C.

325 V.H.N. after 1040 h ageing. In contrast, the solution-treated condition without any cold work aged at 175°C, exhibited an initial linear relationship between hardness and log ageing time up to ~10 h ageing corresponding to the formation of G.P. zones. This was followed by a curve of increased slope, a hardness of 375 V.H.N. being obtained after ageing for 1040 h which corresponded to the G.P. zones →γ' transformation [1].

3.3. Ageing at 315°C

The recovery process was found to occur more rapidly during ageing at 315°C, as shown in Fig. 4 (15 min at 315°C). Accompanying the recovery was the formation of G.P. zones which, on further ageing transformed to the intermediate precipitate γ'. This transformation was identical to that found on ageing the solution-treated material without any cold work [1]. A typical example of the "tweed" structure and the "arrowhead" in the electron diffraction pattern produced by the G.P. zones →γ' transformation is shown in Fig. 5.

Typical features observed after ageing for 24 h at 315°C, Fig. 6a and b, were γ' precipitates, ~50 nm in diameter, some regions of high dislocation density and small nuclei, ~40 nm

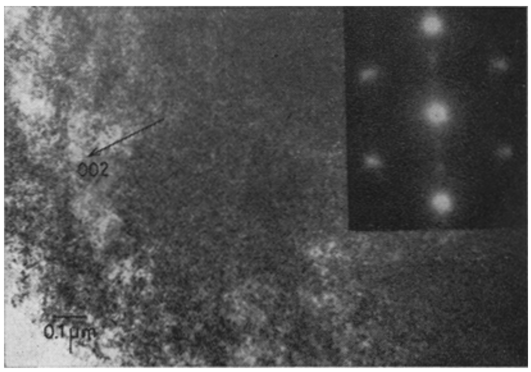


Figure 5 The solution-treated 50% cold-rolled condition aged for 1 h at 315°C.

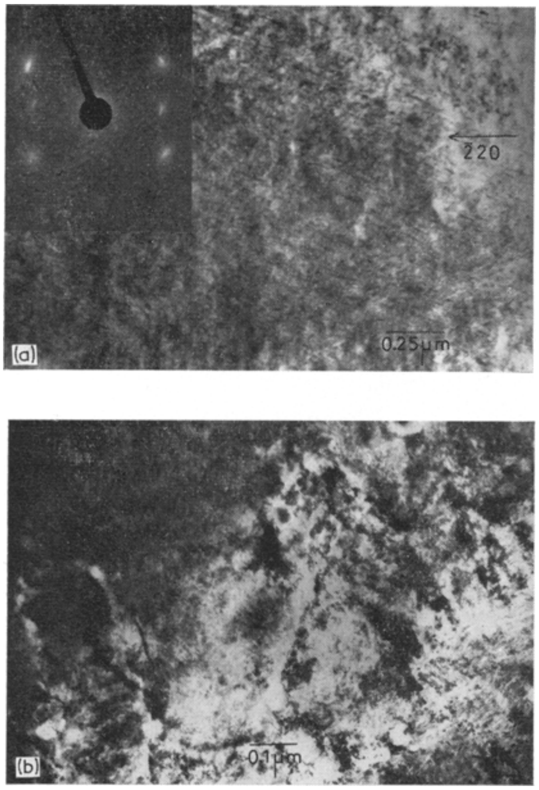


Figure 6 (a) and (b) The solution-treated 50% cold-rolled condition aged for 24 h at 315°C.

in size, at grain boundaries or in highly deformed regions. The cellular reaction was not observed in the cold-worked material and it is tentatively suggested that the nuclei represent the initial formation of recrystallized grains of the α matrix and the γ equilibrium precipitate.

The hardness—log ageing time curves obtained at 315° C for the solution-treated condition, with and without cold work, are shown in Fig. 7. For both conditions, the hardness initially increased to a maximum value, corresponding to the G.P. zone to γ' transformation ("arrowhead" structure present in electron diffraction patterns), followed by a slow decrease in hardness with further ageing time due to the coarsening of γ'. A maximum hardness was obtained after ageing the solution-treated and cold-rolled material for 2 h (~450 V.H.N.) and after ageing the solution-treated material for 24 h (~420.. V.H.N.). The hardness measurements made for the solution-treated material which had been directly quenched to 315°C and subsequently aged are also shown. For short ageing times, the hardness was greater than that for the water quenched material whereas after 2 h a similar curve was obtained. It is interesting to note that the maximum hardness values, for both the solution-treated and cold-rolled conditions, are higher than those reported by Nutting [4] for

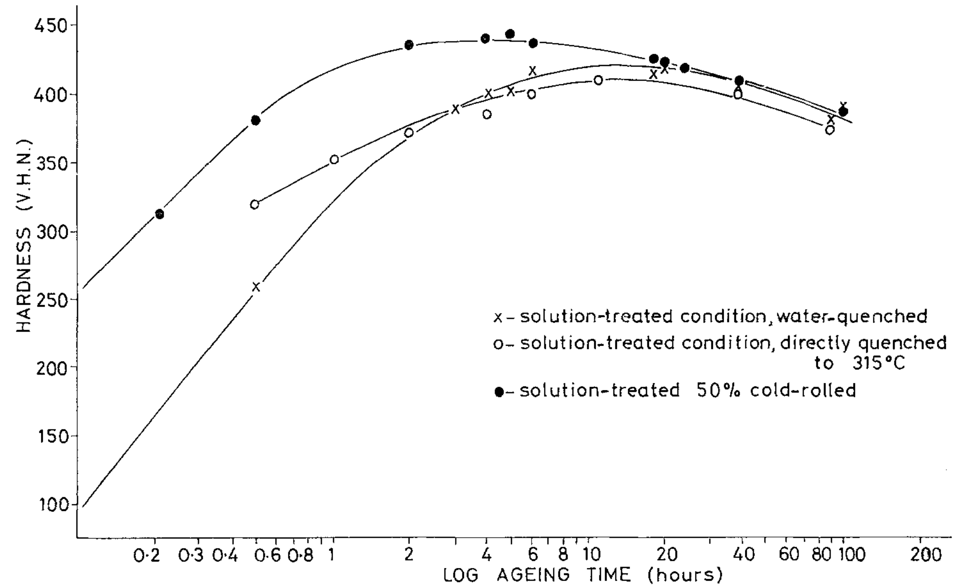


Figure 7 Hardness versus log ageing time at 315°C. (At zero time, hardness of solution-treated condition = 94 V.H.N.; hardness of solution-treated 50% cold-rolled condition = 252 V.H.N.)

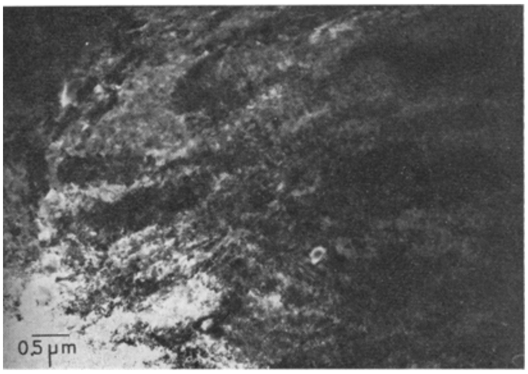


Figure 8 The solution-treated 50% cold-rolled condition aged for 30 min at 425° C.

equivalent conditions in a binary Cu 2.0 wt % Be alloy (370 and 405 V.H.N., respectively).

3.4. Ageing at 425° C

The ageing of the cold-rolled material at 425° C proceeded at a faster rate than at lower temperatures, with enhanced recovery and recrystallization. Fig. 8 (30 min at 425° C) shows the original deformed material together with γ' precipitates and the nuclei of recrystallized grains. After ageing for 2 h at 425° C (Fig. 9), two competing mechanisms were noted, namely the formation of the γ' intermediate precipitate and the nucleation of recrystallized grains, and areas of highly deformed material were also present.

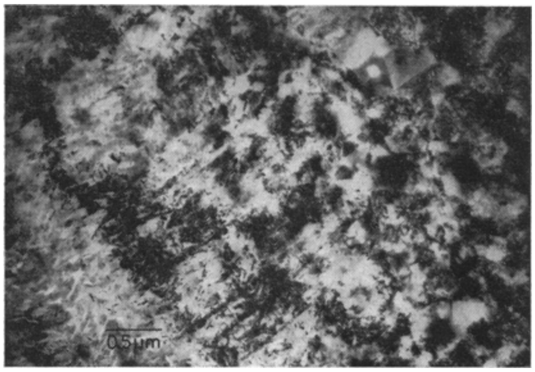


Figure 9 The solution-treated 50% cold-rolled condition aged for 2 h at 425° C.

After ageing for 110 h at 425° C, large precipitates, ~0.5 μm, were observed, with deformed areas present between the precipitates, as shown in Fig. 10a. An analysis of the habit plane and the selected-area diffraction patterns, showed that the precipitates had the same structure and orientation as the intermediate precipitate γ' and it is reasonable to assume that they were formed by the continuous growth of γ'. Fig. 10b is a dark-field micrograph of the $(010)_{\gamma}'$ reflection which images the γ' precipitates. Also present after this ageing time were small recrystallized grains, ~1.0 μm, of the α matrix and the γ equilibrium precipitate as shown in Figs. 11a and 12a. The growth of the recrystallized grains into the deformed α matrix is shown in Fig. 12a. Recrystallized grains of the α matrix and γ phase are shown in dark-field contrast in Figs. 11b and 12b respectively.

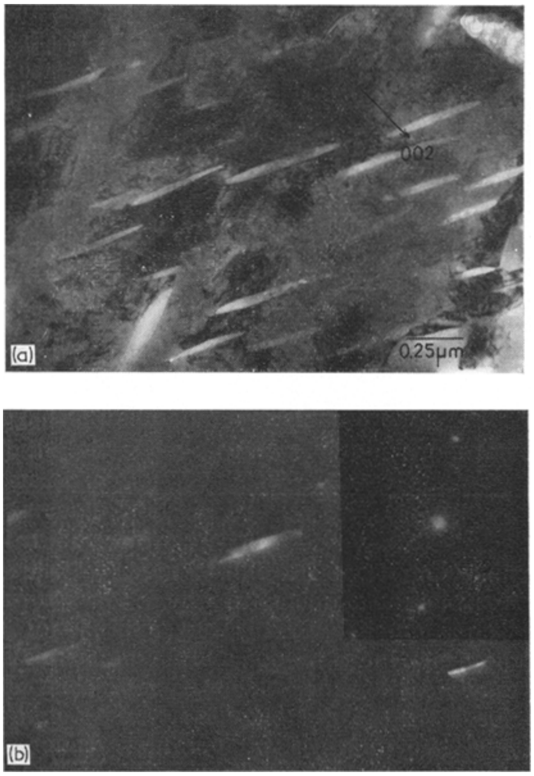


Figure 10 (a) γ' precipitates present in the solution-treated 50% cold-rolled material aged for 110 h at 425° C. (1 1 0) foil plane. (b) Dark-field micrograph of the $(100)_{\gamma}'$ reflection.

From an analysis of the selected-area diffraction patterns, the γ equilibrium precipitate was determined as a B2 superlattice structure, with $a = 0.270$ nm. The angle between the $[002]_{\alpha}$ and $[010]_{\gamma}$ directions was 10.0°, as shown in Fig. 11b. The orientation relationship determined was

$$(\bar{1}11)_{\alpha} // (110)_{\gamma} : [110]_{\alpha} // [001]_{\gamma} \ .$$

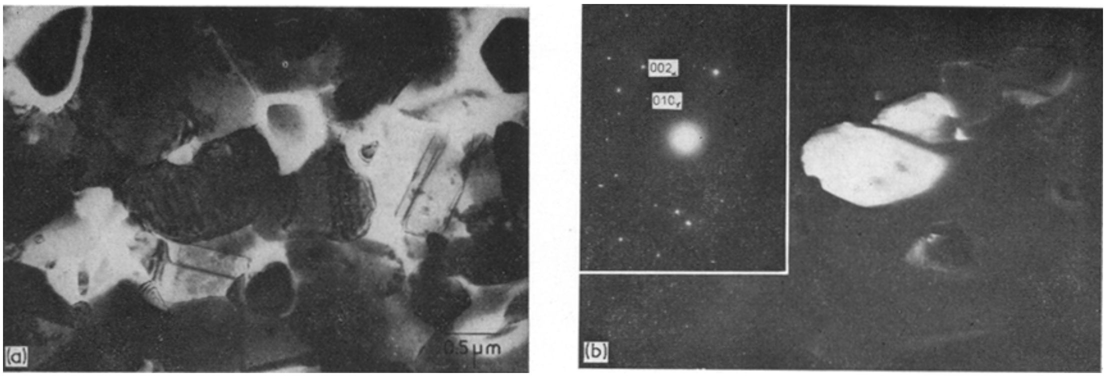


Figure 11 (a) Recrystallized grains of α and γ observed after ageing the solution-treated 50% cold-rolled condition for 110 h at 425°C. (b) The dark-field micrograph of the $(1\,1\,1)_\alpha$ reflection.

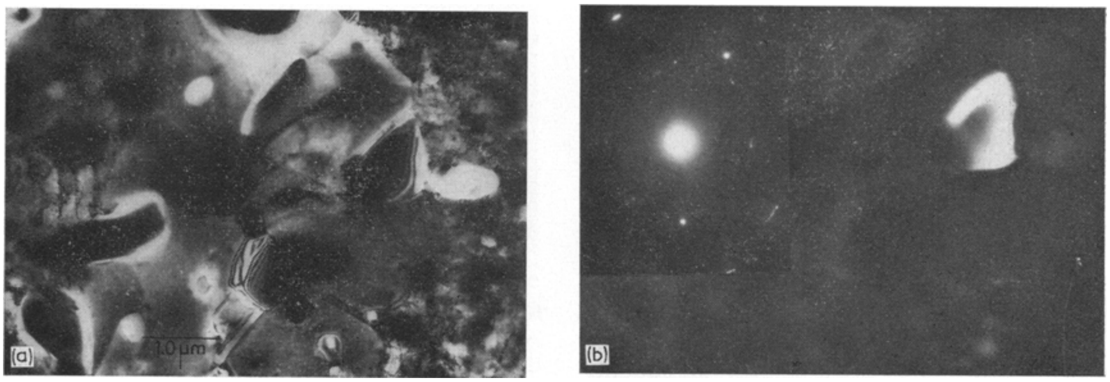


Figure 12 (a) Recrystallized grains of α and γ observed after ageing the solution-treated 50% cold-rolled condition for 110 h at 425°C. (b) The dark-field micrograph of the $(1\,1\,1)_\gamma$ reflection which images the γ phase.

The hardness—log ageing time curves for ageing at 425°C are shown in Fig. 13. for the solution-treated condition with and without cold work. The solution-treated material exhibited an initial increase in hardness to 300 V.H.N. after 2 h of ageing, corresponding to the formation of γ'. This was followed by a decrease of hardness with log ageing time, which was attributed to discontinuous precipitation. The hardness of the solution-treated and cold-rolled material initially increased rapidly to a plateau, from ~0.2 to ~2 h at 425°C, after which it decreased in a similar manner to that found for the solution-treated condition, although no discontinuous precipitation was observed.

4. Discussion

The ageing of the solution-treated and cold-rolled material presents a more complicated problem than that of the solution-treated condition without any cold work. Four distinct processes need to be considered, namely, continuous precipitation, discontinuous precipitation, recovery and recrystallization. The problem is compounded further by these four processes having different characteristics at different ageing (annealing) temperatures. Furthermore, the presence of a precipitate once formed may have a marked effect on the subsequent recovery and recrystallization reactions. Recovery and recrystallization occur by the release of stored energy produced by the cold work and in the present discussion, recovery will be defined as the annealing phenomena which occurs before the appearance of new strain-free recrystallized grains. Recrystallization is defined as the nucleation and growth of strain-free grains and the gradual consumption of the remaining cold-worked material by the movement of high-angle boundaries.

The continuous precipitation process observed in the solution-treated and aged material [1]

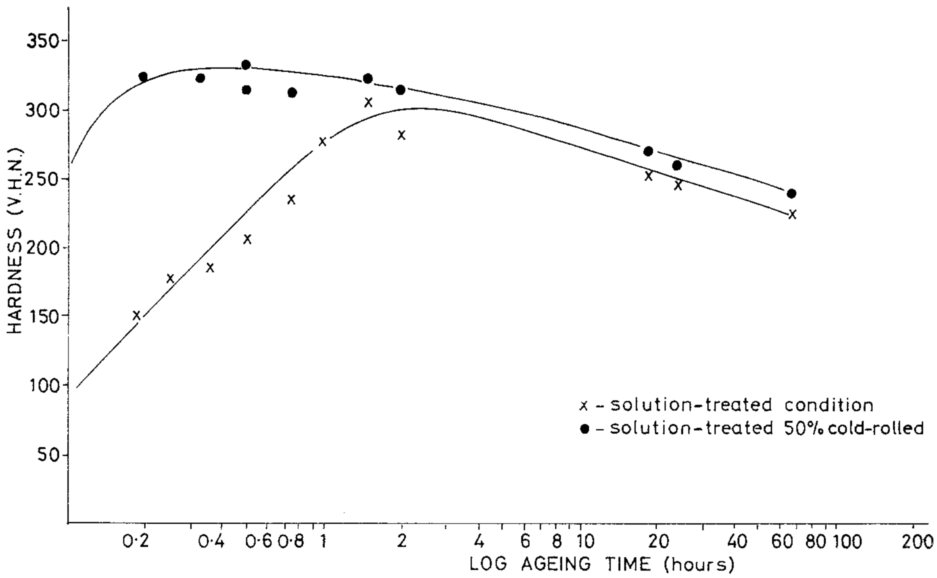


Figure 13 Hardness versus log ageing time for ageing at 425°C. (At zero time, hardness of solution-treated condition = 94 V.H.N., hardness of solution-treated 50% cold-rolled condition = 252 V.H.N.)

proceeds by the formation of G.P. zones, which is aided by the presence of a supersaturation of vacancies produced during the quench. This distribution is modified by the presence of cobalt [2]. The vacancy concentration introduced by quenching is 10^{-4} and the room temperature equilibrium concentration is 10^{-7} [5]. The effect of plastic deformation introduces a vacancy concentration of 10^{-6}, but the quenched-in vacancy concentration is reduced by glissile and sessile dislocations. The removal of vacancies by plastic strain may be expected to suppress the formation of zones and slow down the overall hardening rate.

Observations in agreement with the above concept were found for ageing at 175°C, at which temperature the formation of G.P. zones was greatly retarded. For long ageing times (100 h), small recrystallized grains in a highly deformed matrix were observed, which suggests that polygonization had occurred.

In contrast, ageing at 315°C produced an acceleration in the precipitation sequence for the cold-worked material compared to that of the solution-treated material. This observation can be explained by the presence of an increased vacancy concentration for the formation of G.P. zones due to recovery. On ageing, the G.P. zones transformed to the γ' intermediate precipitate, by the mechanism described earlier [1]. In addition to the continuous precipitation sequence, small recrystallized grains were observed, but no discontinuous precipitation reaction was noted.

Recovery and recrystallization also occurred rapidly on ageing at 425°C. Two competing processes were in operation, namely, the continuous precipitation sequence and the recrystallization reaction which formed grains of the α matrix and the γ equilibrium precipitate. The structure and orientation determined for γ was in good agreement with the results obtained for the discontinuous precipitation sequence [2] and those reported by Geisler *et al* [6].

5. Conclusions

1. 50% cold-rolling of a solution-treated Cu 1.81 wt% Be 0.28 wt% Co alloy suppressed G.P. zones formation on subsequent ageing at 175°C. This effect was related to the annihilation of vacancies by dislocations introduced by the deformation. Recovery and recrystallization occurred on a limited scale.

2. Ageing the solution-treated and cold-worked alloy at 315°C initially produced recovery and recrystallization, with a subsequent increase in the vacancy concentration available for the formation of zones. On further ageing the G.P. zones transformed to the γ' intermediate precipitate by the same mechanism found in the solution-treated material for continuous precipitation. No discontinuous precipitation was observed.

3. Ageing the solution-treated and cold-worked alloy at 425°C produced faster rates of recovery, recrystallization and continuous precipitation, together with the formation of recrystallized grains of the α matrix and γ equilibrium precipitate. γ had a B2 superlattice structure with $a = 0.270$ nm and an orientation relationship

$$(\bar{1}\,1\,1)_\alpha \,//\, (1\,1\,0)_\gamma : [1\,1\,0]_\alpha \,//\, [0\,0\,1]_\gamma \ .$$

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