Order-Hardening in CuAu

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Single crystals of CuAu were used to examine the changes in hardness, flow stress, and microstructure resulting from heat treatment at 150 to 340° C, which produces the tetragonal superlattice. The crystals, quenched from a high temperature, were in the disordered cubic form to begin with; some were also cold-rolled, to permit comparison of the ageing characteristics of as-quenched and of cold-worked specimens. The as-quenched crystal hardened much more than the cold-rolled ones; a peak hardness was attained and followed by a fall in hardness. At 150° C, no microstructural changes were seen; at 240° C, spontaneous recrystallisation took place at grain boundaries; while at 340° C, there was twinning and spontaneous grain-boundary fracture. The observations are rationalised in terms of the various mechanisms for relief of the large microstrains that accompany ordering in this alloy.

1. Introduction

In most binary metallic solid solutions, the two constituent atomic species are distributed on the lattice sites in a nearly random manner, though there may be some statistical preference for like or unlike nearest neighbours (*short-range order*). In other alloys, the atomic species are entirely segregated to distinct lattice sites, and remain so up to the melting point; such are usually described as *intermetallic compounds*. A third category, much less numerous, are subject to *long-range order*, provided the alloy composition is appropriate. Such alloys are random at high temperatures, but at low temperatures the atomic species are fully segregated on distinct lattice sites. In this condition, the alloy is said to possess perfect long-range order, which is indistinguishable from the structure of an intermetallic compound. At intermediate temperatures, the degree of orderliness in the structure varies continuously, until it disappears at a well-defined *critical temperature*. The degree of order is measured by X-ray diffraction and is defined by an *order parameter*.

An ordered alloy contains distinct domains of order (*antiphase domains*), in which the distribution of atoms is mutually out-of-step; the *antiphase boundaries* between neighbouring domains have important consequences for the properties of the alloy.

The very extensive research effort which has been put into ordered alloys is largely due to the interest which attaches to a material in which the distribution of atoms can be varied while other structural features remain unaltered. In particular, much has been done on the mechanical characteristics of ordered alloys and on how these compare with the same alloys in the disordered condition. Cahn [1] has recently reviewed this work.

The term *order-hardening* denotes the increase in flow stress, or of hardness, when a disordered alloy is heat treated so as to order it. Extensive experimental investigations on both order-hardening and work-hardening of ordered alloys have been carried out and hypotheses have been advanced to describe the mechanisms involved. It is generally agreed that the presence of superdislocations† is in some way responsible

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†Paired ordinary dislocations connected by a strip of antiphase domain boundary, and gliding as a single unit.

for the enhanced hardening of the ordered material [1]. There are, however, differences of opinion as to the exact mechanisms involved. One contends [2] that the production of superjogs during deformation is responsible for increased work-hardening, while another [3] attributes this to pinning down of superdislocations by cross-slip. These investigations have also revealed that the initial state of the disordered material, whether cold-worked or quenched, determines how much increase in strength the alloy acquires during subsequent ordering. The increase in strength on heat treatment has been found to be higher for initially cold-worked alloys than for initially quenched alloys [4].

All these investigations have been carried out on cubic superlattices only, whereas alloys in which order-transformation is accompanied by a change in the originally cubic crystal symmetry have scarcely been examined.

Among the well-known non-cubic superlattices, CuAuI has probably received a maximum of attention in connexion with studies on the kinetics of order-transformation. This superlattice, which exists near 50 at. % Au in the Cu-Au system, forms below 380° C and has a face-centred tetragonal structure (Ll_0 type) with alternate sheets of copper and gold atoms on planes parallel to (001). The degree of tetragonality is well pronounced with a c/a ratio of 0.92 to 0.93. In spite of the popularity of this alloy, few attempts have been made to study its mechanical properties. The only two investigations known to us are due to Nowack [5] and Harker [6] and are concerned with the variation in hardness of quenched and initially disordered CuAu as functions of ordering temperature and time. The hardness isotherms due to Nowack show, for temperatures above 200° C, a marked increase in hardness followed by softening at longer annealing times. The results of Harker are different, however, in that there is no pronounced maximum in his hardness values during ordering. Though macroscopic distortion and fracture of ordering crystals have been reported by various workers [7, 8], no systematic attempts have been made to study these deformation processes as functions of ordering temperature and time.

The distortion is due to the substantial change of shape of the unit cell on ordering. One unit-cell edge of the cubic disordered alloy contracts by 5.3% to become the ordered c axis; the other two edges expand by 2.3% to become the ordered a axes. These large strains should be compared with a change in cubic cell parameter of about one part in a thousand, when, for instance, Cu_3Au acquires its *cubic* superlattice. The large strains in an ordered CuAu crystal are partially relieved because individual ordered domains are extremely small, and adjacent domains have mutually perpendicular c axes, so that the c contractions and a expansions partially compensate [6].

An investigation on order-hardening in CuAu thus seems of great interest for an evaluation of the hardening mechanisms operating in non-cubic superlattices as well as studying the formation of long-range order itself at different temperatures. This paper reports results on investigations carried out with the aim of determining the hardening of both quenched and cold-worked CuAu as functions of ordering temperatures (within the CuAuI range) and time. Optical and transmission electron microscopy observations in addition to microhardness measurements have been employed in this study. The investigation was not extended to cover the properties of the orthorhombic CuAuII superlattice produced in a narrow temperature range above 380° C.

2. Experimental

Alloys were prepared by melting together 99.999% copper and 99.999% gold in a graphite crucible to form equiatomic CuAu (exact chemical composition: 49·8 at. % Cu). They were then hammered, well homogenised, and disordered by quenching from 450° C. Cold-worked specimens in the form of strips were produced from this alloy by cold rolling to 90% reduction in thickness. Some specimens cut from these rolled samples were annealed at 700° C for about 5 h to produce recrystallised samples. These recrystallised samples were also quenched from 450° C to retain the disordered state.

Some single crystals of CuAu, which had been produced in connexion with a different investigation on the "stress-ordering" effect in CuAu [9], were also used in this investigation. The technique for the preparation of strain-free single crystals of CuAu is described elsewhere [10].

The rate of ordering of CuAu was the main determining factor in the choice of ordering temperatures for both quenched and cold-worked CuAu. Earlier investigations (e.g. reference 7) have shown that, at low temperatures (~200° C), the rate of ordering is sluggish and so the persistence of coherency between ordered nuclei and disordered matrix is long compared with specimens annealed at higher ordering temperatures. At higher ordering temperatures (~300° C), the rate of ordering has been found to be so fast that rapid stress-relief mechanisms, particularly twinning, accompany the formation of order (e.g. reference 16). To allow all these processes to be examined, order-annealing was carried out at 150, 240, and 300° C.

All specimens were sealed in evacuated pyrex capsules and were annealed at the required temperatures (maximum fluctuation ±5° C) for periods ranging from 15 min to about 15 h.

Microhardness measurements were made on cold-mounted and suitably polished specimens. Microhardness values were obtained as an average of 15 to 20 widely spaced indentations made on each sample using a 100 g load.

Optical examinations were made after electropolishing and etching, using the electrolyte recommended by Smith and Bowles [11]. Electron microscope investigations were carried out on thin foils which were prepared from heat-treated bulk samples by electrolytic thinning. The electrolyte used for this thinning was a mixture of chromic acid and glacial acetic acid, as recommended by Fisher and Marcinkowski [12]. Observations were made with a Siemens Elmiskop I operating at 100 kV. Both bright- and dark-field observations were made and combined with selected-area diffraction patterns. Observations on fractured specimens were carried out using the novel "Stereoscan" scanning electron microscope made by the Cambridge Instrument Co. This provides a much greater depth of focus than does a replica examined in a conventional electron microscope.

3. Results

3.1. Microhardness Measurements

The results of the microhardness measurements carried out at different temperatures are shown in figs. 1, 2, and 3. Apart from the cold-rolled alloy ordered at 150° C, all other measurements show an increase in hardness after order-annealing, and the rapidity of this increase rises with temperature. For quenched specimens annealed at 240 and 350° C, this increase is closely followed by softening. However, for the quenched alloy ordered at 150° C, the hardness

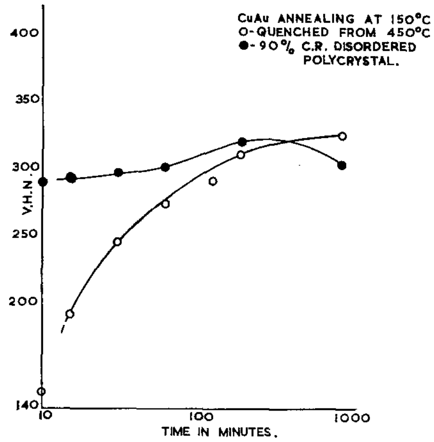


Figure 1 Isothermal hardness curves of disordered CuAu, ordered at 150° C; both quenched and cold-worked specimens.

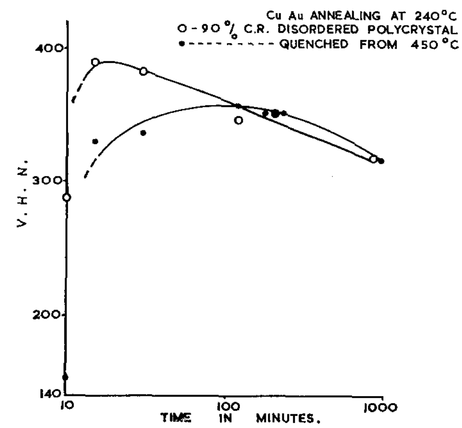


Figure 2 Isothermal hardness curves of disordered CuAu, ordered at 240° C.

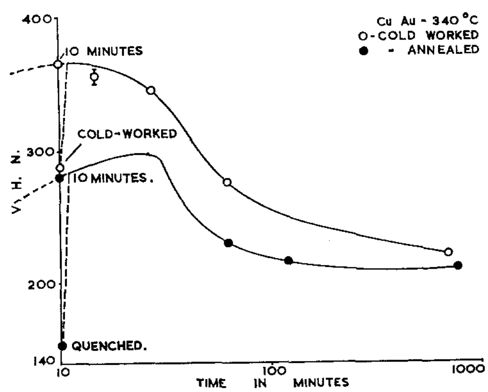


Figure 3 Isothermal hardness curves of disordered CuAu, ordered at 340° C.

was found to be still increasing after 1000 min, when annealing was discontinued.

A significant difference in behaviour between cubic superlattices and non-cubic superlattices is seen in these hardness measurements: the increase in hardness in CuAu was *greater* for quenched specimens than for cold-worked specimens; where the superlattice has cubic symmetry, the order-hardening is greatest for the cold-rolled alloy [4]. For cold-worked specimens of CuAu order-annealed at 150°C, this increase was so small as to be negligible. However, with increasing ordering temperature, the difference decreased and, at 340° C, the increase in hardness for the cold-worked specimens was nearly half as great as that of the quenched samples.

Because of the inherent ambiguity of hardness tests which cannot distinguish between changes of yield stress and changes in work-hardening [4], some tensile samples were also prepared from the quenched specimens annealed at 150° C. These were tested in an Instron tensile-testing machine at room temperature. The results of the yield-stress measurements are shown in fig. 4. There is a rapid increase in

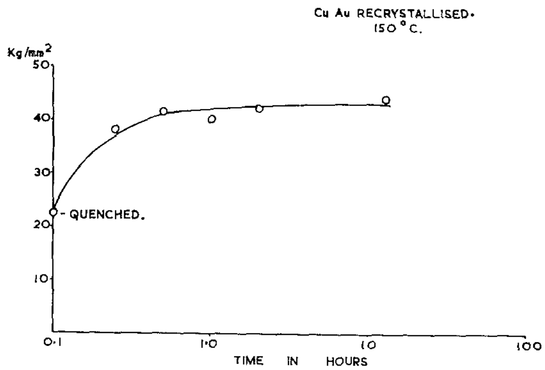


Figure 4 Yield-stress measurements on quenched and disordered CuAu, ordered at 150° C.

yield stress after only 15 min of annealing. Further increases on prolonged annealing were negligible compared with the initial rise. The total increase in yield stress of the quenched samples was about 92% compared with the corresponding increase in hardness of about 130%.

3.2. Optical Microscopy

In this section, we shall concern ourselves only with observations carried out with specimens annealed at 240 and 340° C as there were no significant changes in microstructure at 150° C.

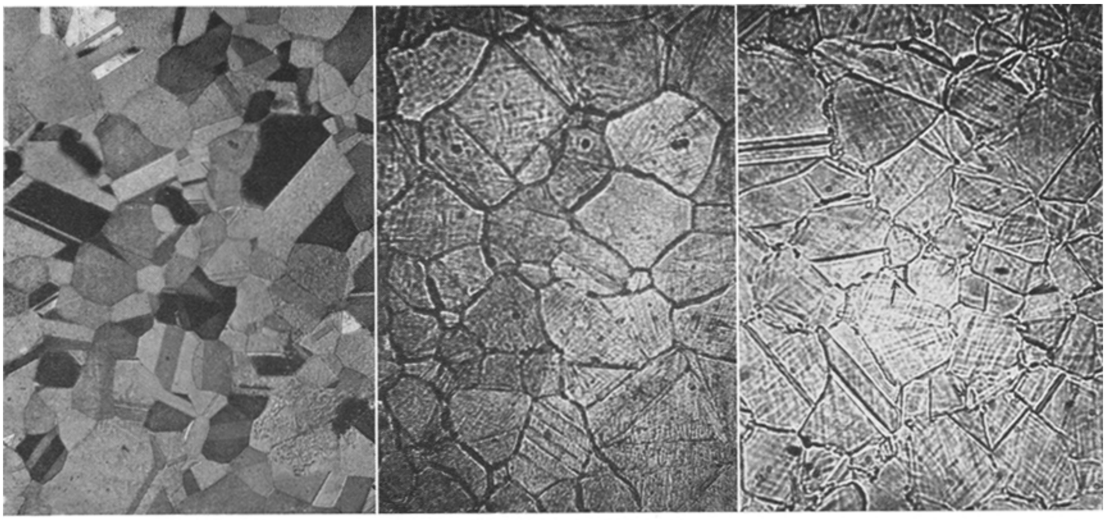
Microstructures of quenched samples order-annealed at 240° C for varying periods are shown in figs. 5a, b, and c. Grain boundaries were found to become "thick" after about 3 h at 240° C, and pronounced twin markings within grains were visible. This structure is similar in appearance to the observations of Harker [6] who found a "rippled" microstructure. Though a detailed analysis was not carried out, careful examination of the micrographs shows that a certain amount of sliding has taken place along the boundaries. The micrographic "thickness" of these boundaries may very well be due to this. With further increases in annealing time a fair number of small new grains were visible along most of the grain boundaries. An enlarged micrograph of some of these new grains is shown in fig. 6. This kind of spontaneous recrystallisation phenomenon has not been reported in CuAu hitherto, although it has been found in the somewhat similar alloy CoPt. The growth rate of these new grains appeared to be low; as is evident from their small size even after long anneals.

Annealing at 340° C produced no new grains along the boundaries. Instead, the structure was completely littered with coarse twin markings after only a few minutes of annealing. In addition, signs of fracture were observed along some of the boundaries. With annealing, these cracks appeared to propagate rapidly along the boundaries, and a typical micrograph depicting such a spontaneous fracture is shown in fig. 7.

Scanning electron micrographs of the quenched alloy ordered at 340° C for about 1 h are shown in figs. 8a and b*. Because of the large depth of focusing available with this instrument, it is possible to study both the depth and the morphology of these fractured surfaces. In these pictures, deeper parts of the cracks appear with dark contrast while shallower parts appear lightly shaded.

Both types of intergranular fracture [13], viz. wedge-shaped fracture where three grains meet, and cavitation fracture, have been observed. The incidence of wedge-shaped fracture was higher, and only a few instances of cavitation fracture were observed. Both wedge-shaped fracture and some small cavities characterising the other type of fracture can be seen in fig. 8a. A striking manifestation of a

*We are grateful to Dr P. R. Thornton for taking these micrographs.



(a) (b) (c)

Figure 5 Photomicrographs of quenched CuAu ordered at 240° C for varying periods: (a) disordered and quenched; (b) and (c) ordered at 240° C for 3 h and 6 h respectively (×90).

wedge-type fracture is shown in fig. 8b. Some slip (or twin) markings can also be seen in this figure.

It is worthwhile pointing out here that no *cold-worked* samples were found to fracture on order-annealing. In fact, annealing at 340° C resulted in the cold-worked structure giving way progressively to a recrystallised microstructure. By contrast, the internal stresses induced in *quenched* samples on order-annealing are not sufficiently large to permit any extensive recrystallisation, and spontaneous fracture supervenes to relieve the stresses.

Figure 6 An enlarged micrograph of fig. 5c. Recrystallised grains at grain boundaries can be seen (×500).

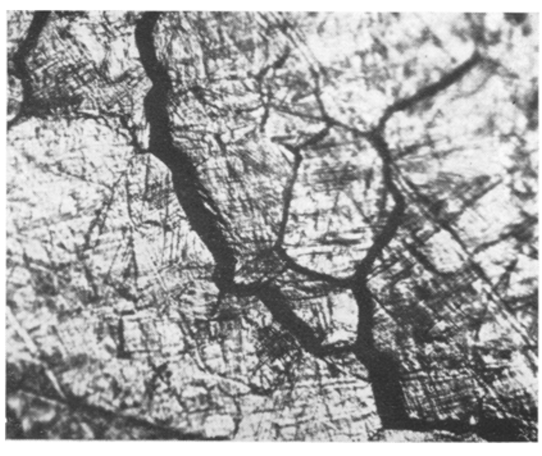
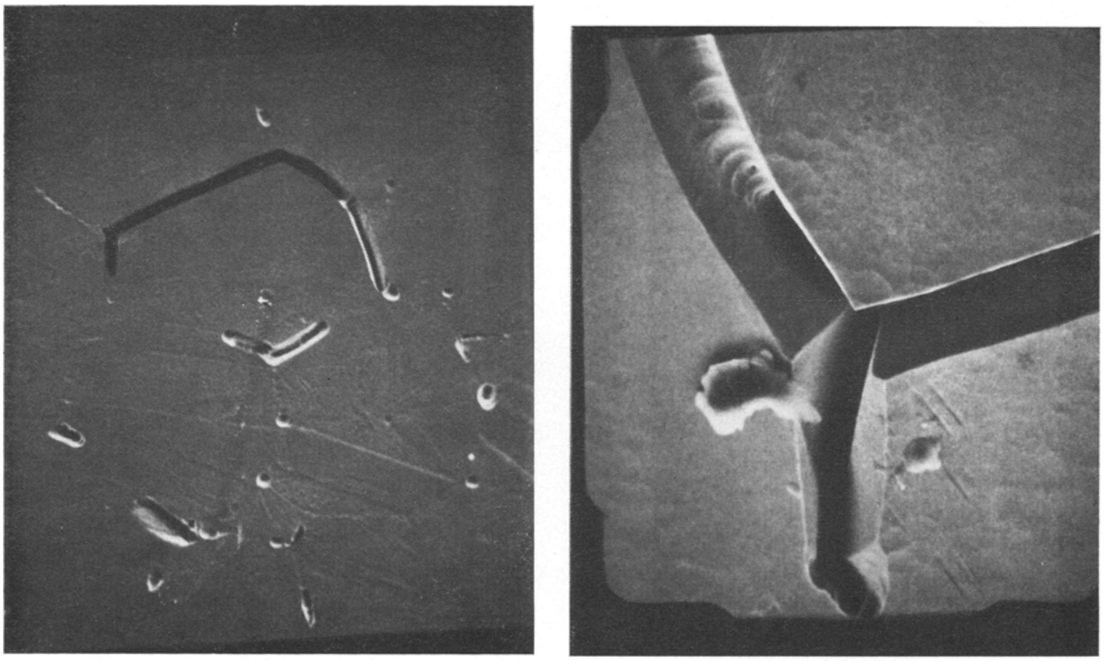


Figure 7 Grain boundary fracture in quenched CuAu, ordered at 340° C for 1 h (×200).

3.3. Electron Microscopy

The electron microscope observations were limited to quenched alloys annealed at 240° C. The appearance of a pattern of thin, black lines over fine-textured background was the first visible sign of ordering and was observed after about 10 min of annealing at 240° C (fig. 9a). The contrast in this instance is possibly due to a particular distribution of c axes among the nuclei. It can be seen easily that, during ordering, each new ordered nucleus must choose one of the three cube axes of the disordered structure to become the tetragonal c axis of the ordered nucleus. This results in ordered nuclei having different sub-lattices. Unlike normal, cubic, antiphase sub-lattices, which are related to each other only by a displacement vector of the type $\frac{1}{2}$ <101>, these sub-lattices are also related to each other by a rotation of 90°. Dark-field observations on the same area shown in fig. 9a have confirmed that the black lines were from nuclei having a particular c orientation. With increasing annealing time, the fine lamellar structure which appeared faint at first became well pronounced, giving a clear, cross-textured appearance (fig. 9b). The normal antiphase domains (i.e. those related by a $\frac{1}{2}$ <101> displacement only, with *parallel* c axes) can be observed in dark areas of this micrograph. These characteristic striae have been observed previously by Hirabayashi and Weissmann [14], though only after somewhat longer anneals at 150° C. These authors have attributed this cross-texture to microtwinning on {101} planes created as a result of tetragonality strain. Possible implications of this interpretation will be discussed in a later section. Appearance of unmistakable twin lamellae became pronounced after annealing at 240° C for about 4 h (fig. 9c). Normal antiphase-boundary contrasts also can be seen in this micrograph. Recrystallisation induced by the stress-induced boundary migration was also observed in the electron microscope, confirming the findings of optical microscopy. Fig. 10 shows one such boundary migration. Some fine twins can also be seen on areas just swept over by the moving grain boundary.



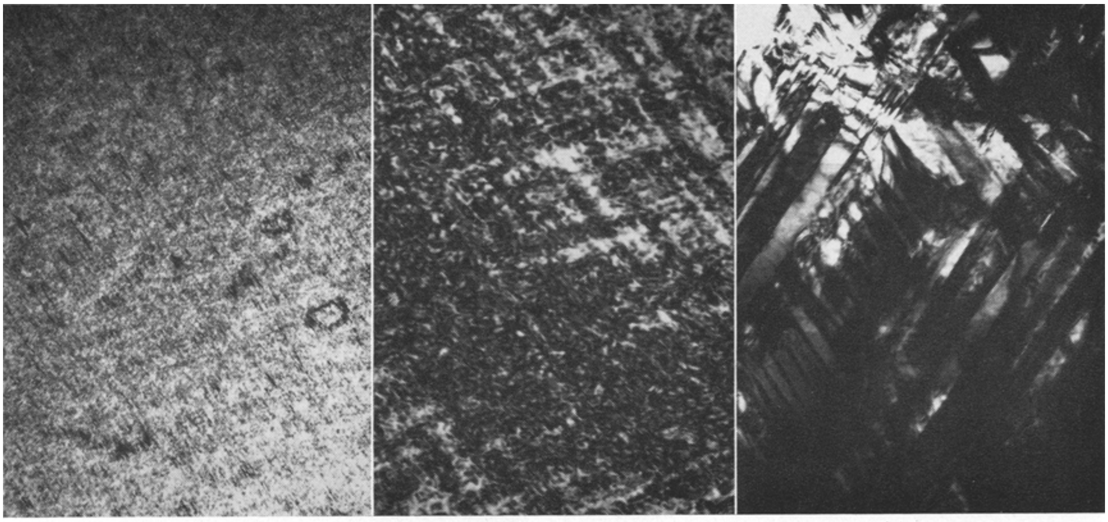
(a) (b)

Figure 8 Scanning electron micrographs of quenched CuAu ordered at 340° C for 1 h: (a) ×300; (b) ×1000.

4. Discussion

4.1. Formation of Order in CuAu

We shall now consider the formation of long-range order in CuAu. The most revealing early work on the kinetics of ordering in CuAu was published by Borelius [15]. He found both homogeneous and nucleation modes of ordering



(a) (b) (c)

Figure 9 Electron micrographs of quenched CuAu ordered at 240° C for varying periods. (a) Fine-scale <001> axis distribution produced by the onset of order on CuAu ordered for 10 min (×36 000). (b) Characteristic striations in CuAu ordered for 15 min {110} planes (×144 000). (c) Twins in ordered CuAu, 4 h. Normal antiphase domain contrast also can be seen (×36 000).

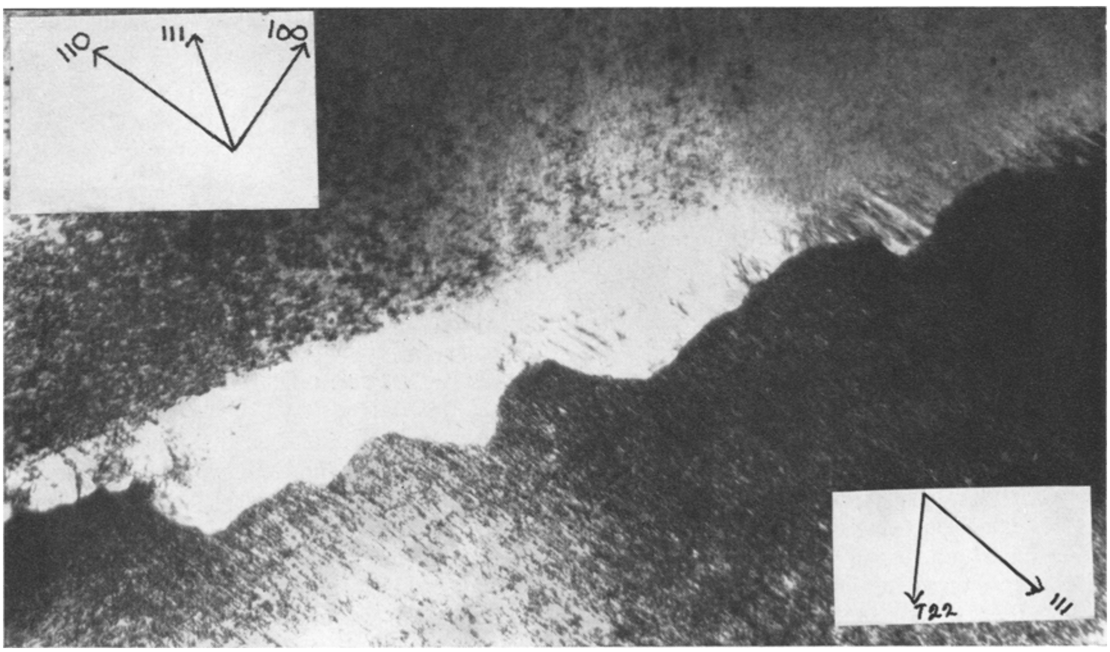


Figure 10 Stress-induced boundary migration due to ordering, 240° C, $6\frac{1}{2}$ h (×32 000).

to be operative in CuAu, largely on kinetic evidence. At low ordering temperatures, order was established by homogeneous ordering, and at higher ordering temperatures the transformation was of the nucleation and growth type. This difference in behaviour was attributed to the existence of a potential barrier between ordered and disordered state, forcing the nucleation type of transformation at high ordering temperatures.

Kuczynski and his coworkers [16, 17] have re-investigated these kinetics in detail and found the transformation to be of nucleation and growth type even at low ordering temperatures.

Gradual shifting of X-ray fundamental lines during transformation (which was interpreted by Borelius as due to homogeneous ordering) was explained by O'Brien and Kuczynski [17] as due to the broadening of reflections which would mask the separation of the distinct ordered peak from the disordered peak. By analysing the superlattice reflections, they showed conclusively that no homogeneous ordering process was involved during the formation of order in CuAu.

Some interesting experiments on this ordering have been carried out by Hirabayashi and Ogawa [7], and Hirabayashi and Weissman [14], using single-crystal X-ray analysis, and transmission electron microscopy, respectively. The X-ray experiments were carried out on single crystals of CuAu ordered at low temperatures and their Laue patterns were analysed for diffuse intensity distribution. They found a rod-like distribution of diffuse intensity in reciprocal space along $<101>$ direction through relpoints belonging to the matrix plane. From these analyses, the ordering process was visualised by these workers as a coherent formation of $\{101\}$ ordered platelets in the disordered matrix. These platelets grow in size with time, and, as the average atomic volume of an atom in the disordered matrix would be different from that in the ordered matrix, elastic strains would be produced. With longer order-anneals, the accumulated strain energy would be released by self-deformation such as twinning.

Electron microscope investigations by Hirabayashi and Weissmann have generally confirmed this model. The twinning was observed first by Pashley and Presland [18] and more recently by Hansson and Barnes [19].

Experiments on the kinetics of ordering in CuAu single crystals using a sensitive transducer-coupled dilatometer have been carried out by us. The results of these investigations show that ordering takes place in two distinct stages. The identification of these two processes is to be discussed in a separate paper [9]. Suffice it to state here that a reasonable explanation of the ordering of CuAu can be provided by postulating at first a coherent growth which breaks down (in the sense that coherence between ordered and disordered phases is lost) when the volume of the ordered material is increased too much.

4.2. Order-Hardening

Our basic problem in this section is connected with explaining the order-hardening curves obtained on *quenched* samples ordered at different temperatures and considering some possible mechanisms that can satisfactorily account for the relatively small increase in hardness for the cold-worked material.

Ordered CuAuI, unlike the better-known Cu_3Au, can have both superlattice dislocations and single dislocations. Dislocations having Burgers vector $\frac{1}{2}<110>$ can move singly as they do not destroy order, while $\frac{1}{2}<101>$ and $\frac{1}{2}<011>$ dislocations must move in pairs. Further, deformation by twinning on $\{111\}$ planes is possible; but again only one of the three possible Burgers vectors of the partial dislocations concerned with this twinning ($\frac{1}{6}<112>$) preserves order and so is admissible in the superlattice. Such twinning on $\{111\}$ planes has been observed by us [10] on grown CuAu single crystals which were strained while they were transformed, and Pashley [20] also reports observing these twins during deformation. These differences in the dislocation arrangements between cubic and non-cubic superlattices should lead therefore to a different deformation behaviour when a non-cubic superlattice is formed from a cubic disordered lattice. At low temperatures of ordering (e.g. 150° C), the yield stress of the alloy is increased. This can be thought of as due to dislocations having to change their character when they travel from the disordered matrix to the ordered nuclei. Apart from the yield-stress measurements, the influence of ordering is felt more strongly on the work-hardening behaviour as exemplified by the microhardness values.

An additional argument involving work-hardening remains to be considered. If we consider an edge dislocation travelling on the slip plane from the disordered matrix to the ordered nuclei, then it may have to acquire a superlattice character at the interface (the probability of this being necessary is 66.6%) to proceed further, and should then also leave a sessile interface dislocation. This situation is closely similar to that of a dislocation passing a boundary where it encounters a sudden change in the lattice parameter. This has been considered in detail by Fleischer [21]. His argument is briefly as follows.

As the Burgers vectors are different either side of the boundary, the dislocation leaves an interface sessile dislocation at the boundary. Subsequent dislocations travelling on the same plane have the stress field of the interface dislocations to overcome, and each new dislocation will add another interface dislocation. As more and more dislocations move, the resistance offered by the interface dislocations will increase progressively.

If we apply this model for our present discussions, then it can be seen easily that the counter-stress resisting the passage of further dislocations should increase considerably as the duration of order-annealing is increased. First of all, there should be a significant increase in the lattice parameter misfit at the interface as the degree of tetragonality increases from a c/a ratio of unity to about 0.92. Secondly, the shear modulus also should exhibit a maximum during intermediate order; experiments by Rohl [22] on Young's modulus during ordering of CuAu have confirmed this possibility. According to Fleischer's theory, the counter-stress increases if the shear modulus increases. This can satisfactorily account for the increase in the hardness of the alloy, so long as the ordered and disordered phases are coherent with each other. At 150° C, the period of coherence is long as the growth rate is low, and hence there is a slow but continuous rise in hardness as the period is increased. Because of the low growth rate, the elastic stress is still not large enough to induce twinning, and so the second stage of hardness curve is not present. At higher temperatures, however, the growth rate of ordered nuclei is so high that ordering is accompanied by twinning. The consequent reduction in strain energy reduces the effective volume of the interface, and moreover coherence is progressively lost. After an initial rise, hardness values therefore drop after longer ordering anneals. For alloys annealed at 350° C, the growth rate is so high that the maximum in hardness is reached very quickly.

Fleischer's model is a simplified one, in that it is applicable only for an edge dislocation travelling across an interface when slip planes on both sides of the interface are parallel. When these conditions are not both fulfilled, immobile jogs would have to be created by dislocations at the interface. The interaction of these jogs should also lead to considerable hardening, as has been suggested for cubic superlattices.

We shall conclude this section by considering why cold-worked CuAu does not order-harden more than the quenched alloys, as happens with cubic superlattices [4]. The possibility that nucleation of ordered structure occurs in the vicinity of dislocations has been considered in detail by Hunt and Pashley [23], who have also provided some experimental evidence for this happening. Such a preferred nucleation may possibly be responsible for this apparent lack of order-hardening in cold-worked CuAu. For an edge dislocation in an isotropic medium, maximum tensile or compressive strain occurs in direction of Burgers vector. This implies that, if nucleation of order takes place near a dislocation such that the Burgers vector is along the direction of maximum strain of the ordered nuclei, then a great reduction in strain energy is achieved. At 150° C, because of the extensive nucleation and very low growth rate at this temperature, there would be extensive strain relief and no significant elastic strain would be introduced. Indeed, the hardness values at this temperature remain more or less constant. This situation changes with increase in ordering temperature since this increases the growth rate. The compensation offered by dislocations for reduction in strain energy clearly would be insufficient now, and a marked hardening would therefore be observed, although it should still be less than for quenched alloys.

4.3. Relief of Ordering Stresses in CuAu

Among various relief mechanisms that were found operating on ordered CuAu, twinning has probably received the maximum attention [14, 18, 19]. It has been shown that twinning on {101} planes alternates the c axis along two mutually perpendicular directions and thus reduces the misfit stresses. Hirabayashi and Weissmann [14] detected two stages of twinning in their electron microscope observations and these were termed as *microtwinning* and *macrotwinning*. They attributed the microtwinning during the early stages of ordering to short-range "tetragonal stresses", and the macrotwinning to long-range stresses created as a result of different c-axis orientations. The latter twinning has been observed by other workers [18, 19] also.

Electron microscope observations in this present investigation are in general conformity with the results of Hirabayashi and Weissmann. However, it is possible that these microtwins may be due to accidents in growth rather than mechanical deformation. If they were mechanical twins then the stress relief provided by them should have resulted in a drop in hardness values. Further, electrical-resistivity measurements by other workers do not show this onset of twinning. After only about 15 min of annealing at low ordering temperatures, order would not have reached completion, and so it is doubtful whether sufficient misfit stresses have been built up to activate twinning.

It is more likely that these twins are of the growth type. The likelihood of different ordered nuclei having different (i.e. mutually perpendicular c axes) c sub-lattices has already been mentioned. In structure and appearance, both these c-domain boundaries and $\{101\}$ twins would be the same with one exception: while the composition plane of the twins would be $\{101\}$, that of the domain boundary would not correspond to $\{101\}$ necessarily. But it can be seen that the $\{101\}$ plane is the least distorted plane between two nuclei having c axes at 90° to each other. It is possible, therefore, that the c domains adjust their interface so as to have it parallel to $\{101\}$. After this has happened, it is not possible to distinguish the c-domain interfaces from $\{101\}$ twins created due to tetragonality strain.

Since these twins have not been the result of misfit stresses, and have been distributed on the ordered matrix by the chance of the nuclei having different c axes near each other, they clearly cannot provide any large relief for stresses built up during ordering. Hence, on further order-annealing, macrotwinning occurs. This serves to explain why one does not observe microtwins on evaporated CuAu films. Here, because of surface-energy considerations, only one c orientation forms on ordering, and so there are no other c axes to form growth twins. If it were only due to tetragonality even within a single domain, then there would be profuse twinning even after short ordering anneals of thin films.

In addition to twinning, stress-induced boundary migration and fracture along grain boundaries were found to operate to relieve the stress built up during ordering. These last two processes were found exclusively in polycrystals. Repeated ordering of *single crystals* produced no signs of recrystallisation or cracks. Though ordered single crystals were often found to be bent or even curled, they always returned to their original single-crystal state after disordering, with one exception – they now contained a large number of $\{111\}$ twins*.

Besides twinning, which is common to both single and polycrystals as a mode of stress relief, we have to consider why recrystallisation takes place in polycrystals. This is closely similar to the well-known process of strain-induced boundary migration. Where two adjacent grains are in substantially different states of internal strain, the less strained one is apt to grow at the expense of the other. This appears to have happened in CuAu. Various types of grains produced during such processes have been discussed recently by Cahn [24]. Both multigrain nucleation and single-boundary migration have been observed by us during the present experiments.

Though this seems to be the first report of the occurrence of spontaneous recrystallisation in ordered CuAu, similar observations have been made by Newkirk *et al* [25] on CoPt alloys. They found a large number of new grains along grain boundaries, and these were swallowed up as the period of annealing was increased.

Stress relief by grain-boundary migration is strictly possible only as long as the boundary migration is rapid in relation to the building up of misfit stresses. At higher ordering temperatures, the rate of ordering is so high that internal strains build up rapidly to large values in the grains either side of the boundaries. Clearly, grain-boundary migration cannot be as rapid as to cope with this build-up of strains. Further, migration of boundaries in a completely ordered matrix would impose complex patterns of atom movements, and this in turn might slow the migration. At high ordering temperatures, fracture along grain boundaries provides the only mode of stress relief. Fracture seems to have originated at three-grain junctions and spread more or less continuously along the boundaries. It has been demonstrated [26] that, if grain-boundary migration occurs, then grain-boundary fracture does not occur, and this principle is applicable to CuAu. Boundary migration tends to dissipate the stress concentrations built up by localised shear in the boundaries, and thus the right condition for fracture nucleation does not occur. At moderate ordering temperatures, therefore, only grain-boundary migration was observed and no fracture. However, fracture in ordered CuAu

*Though stress relief is obtained predominantly by $\{101\}$ twinning and to only a small extent by $\{111\}$ twinning, $\{101\}$ twins disappear when the crystal is disordered, as $\{101\}$ is a mirror plane in the disordered state.

has been observed earlier by Kohara and Kuczynski [8], who found that ordering at 350° C was accompanied by fracture along grain boundaries.

The microstructural appearance of the spontaneous fracture is similar to creep rupture observed in polycrystals, and, as the stress systems have been built up only at grain junctions (within grains, they vary rapidly in sign and magnitude), no transcrystalline cracks have been observed. Cold-worked and ordered specimens were found to contain no traces of fracture, and with continued order-annealing they were found to recrystallise. With recrystallisation, grain-boundary migration could have reduced the stress build-up for fracture nucleation.

It is likely that there is a definite relationship between grain size and fracture, as some observers have not observed fracture during ordering at all. To test the correctness of this view, a systematic study on the interrelation between grain size and incidence of fracture is under way.

5. Summary

Order-hardening of CuAu has been studied on both quenched and cold-worked CuAu at different temperatures.

Quench-aged alloys hardened far more than strain-aged alloys. This difference has been interpreted as due to a preferential nucleation of ordered platelets in the vicinity of dislocations present in the cold-worked structure.

Different stress-relief mechanisms were found to operate for quench-aged alloys. In addition to twinning, recrystallisation and fracture along grain boundaries have been observed at higher ordering temperatures. No fracture has been observed in cold-worked and ordered alloys.

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