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The mechanism of crystallographic ordering in CuPt

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The present paper is primarily a study of the ordering characteristics within the CuPt system, near the CuPt composition, using X-ray diffraction, optical microscopy (in conjunction with polarized light), high-voltage electron microscopy and dilatometry.

In platinum-rich off-stoichiometric alloys, a wide two-phase region consisting of ordered + disordered platelets was established and the phase boundaries were accurately located. For isothermally ordered stoichiometric alloys, in general two categories of diffraction sequences were observed, depending on the annealing temperature. For anneals in the range 620°C $< T <$ 815°C ($= T_c$), a series of broad, asymmetric X-ray line profiles were obtained during the early part of the ordering cycle: this represents a "continuous" reaction. However, when samples were annealed a temperatures lower than 620°C, there was unmistakable micrographic evidence of the coexistence of both the ordered and disordered phases: this represents a "discontinuous" reaction. After making allowances for a number of side-effects which had broadened X-ray reflections at high temperatures, a nucleation-and-growth model is proposed for CuPt at all ordering temperatures.

The parallel microscopic studies also exhibited quite contrasting morphologies above and below 620°C: a lamellar structure is the product at high temperatures, whereas a grain-boundary reaction, generating very coarse domains, is observed at lower temperatures. A modified microstructure was observed for samples annealed at $T <$ 475°C, when ordered spherulites were seen to grow within the grains. Samples cooled slowly through T_c order by a diffusion-controlled shear process.

1. Introduction

The equiatomic alloy CuPt, which has a face-centred cubic structure at high temperatures, acquires an ordered configuration when it is cooled below 815°C. This configuration, or superlattice, is crystallographically unique; no ordered alloy is known to be isomorphous with it. The superlattice of ordered CuPt has a rhombohedral (trigonal) unit cell (Fig. 1), related to the disordered cubic cell by a slight compression along one body-diagonal. Successive close-packed sheets, parallel to (111), consist of pure platinum and pure copper, in alternation; the superlattice is unusual in that the average number of unlike nearest neighbours of a copper or platinum atom is not altered by the transition from the disordered to the ordered configuration, and it is only the proportion of *second*-nearest neighbours which is changed.

Very little is known about the mechanisms of formation of this ordered configuration or about the consequences of that configuration for physical or mechanical properties of the alloy. Accordingly, we decided to examine these mechanisms, and to compare them with what is known about the ordering of a number of other alloys such as CuAu, CoPt, Ni_4Mo, Ni_2V which resemble CuPt in that *their crystalline symmetry changes during ordering*. This group of alloys is to be distinguished from more familiar alloys such as Cu_3Au, FeCo, Ni_3Fe, etc., which are cubic in both the disordered and the ordered configurations. The two kinds of alloys behave differently in a number of respects: the most prominent distinction is the ability of the first category to undergo much more substantial *order-hardening* than the second category.

We have published a preliminary note [1] on

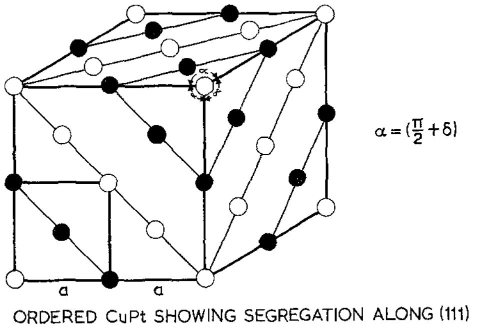

Figure 1 Crystal structure of ordered CuPt. ○ - Cu; ● - Pt.

our examination of the phase-boundaries of copper-platinum alloys of non-stoichiometric composition, and a full account [2] of our study of the mechanical properties of CuPt. The present paper is concerned with the parallel X-ray and microstructural studies.

1.1. Type of transformation

An issue which has excited much interest in connection with the ordering mechanisms of the various alloys listed above is the question whether ordering involves a first-order or a second-order mechanism. The distinction was first applied to ordering alloys by Jones and Sykes [3] in terms of the presence or absence of a latent heat at the critical temperature. Up to now, the term "first-order" has generally been held to imply a well defined nucleation-and-growth mechanism, whereas a "second-order" mechanism implies homogeneous ordering, in which all sites in a crystal at any instant are in an equivalent state of partial order, until the reaction is complete. This was a question which we wished to resolve also in connection with CuPt.

The above use of the terminology based on *orders* of transformation has however in the past caused much confusion and is therefore unsatisfactory. The terminology strictly has meaning only in connection with processes *at* the critical temperature, T_c; yet many experiments on ordering involve anneals at some temperature well below T_c. Really, we are interested in the reaction *mechanisms* more than we are concerned with their thermodynamic expression.

For describing *mechanisms*, it would cause less confusion to use a different terminology, not based on orders of reaction. We propose to use the notation first suggested by Willard Gibbs 100 years ago. Drastic atomic rearrangements within very small volumes are denoted as *type I transformations*, while very small rearrangements spread over large volumes are type II transformations. The first type includes nucleation-and-growth reactions, while the second type embraces homogeneous reactions (of which the early stages of a spinodal decomposition form a special case). The background to these distinctions in connection with ordering alloys has recently been fully documented by one of us [4].

1.2. Evidence from X-ray diffraction

The controversy about the type of transformation involved in ordering has been fuelled by a number of experimental investigations. One approach is to use X-ray diffraction. *Here there is a special advantage in investigating alloys which change symmetry on ordering.* When a cubic alloy on ordering becomes, say, tetragonal (as does CuAu), then the *fundamental* diffraction lines split into pairs or multiplets with substantially different Bragg angles. If a type I transformation is in progress, both the disordered lines and the ordered ones should be simultaneously detectable: if the transformation is of type II, the disordered line gradually broadens and then decomposes into the new lines, and the new and old lines will not be simultaneously detectable while the reaction is in progress. (With alloys such as Cu_3Au, where there is no change in symmetry and hardly any change in lattice parameter on ordering, the fundamental lines of the ordered and disordered forms would be superimposed and therefore could not be distinguished, whatever the type of reaction. In Cu_3Au, the fundamental (111) line is shifted through 1 to 2 min of arc only, whereas for CuAu or CuPt the corresponding lines of the ordered fundamental pair move $\frac{1}{2}$ to 1° from their position in the disordered state.)

This strategy has been used by O'Brien and Kuczynski [5] in connection with CuAu. They took diffraction patterns from heat-treated filings: they found fundamental diffraction lines from the disordered and ordered forms simultaneously present and distinguishable at higher temperatures, and deduced the operation of a nucleation-and-growth (type I) mechanism. At lower ordering temperatures, they were unable to resolve the fundamental lines; they thought that this was due to the presence of large ordering strains in this regime, and that these strains smeared out the lines which would otherwise have been sharp and separate. This X-ray technique, therefore, has its limitations: clear resolution of both sets of lines clearly implies a type I transformation, but lack of resolution does not necessarily imply type II. Similar X-ray studies on NiPt (cubic → tetragonal) by Greenholz *et al* [6] indicated type I transformation at high ordering temperatures (very close to T_c), and Southworth [7] similarly resolved separate ordered and disordered diffraction lines from CoPt (cubic → tetragonal) at low temperatures.

X-ray diffraction from polycrystals or powders can also be used in other ways to give information about an ordering reaction: for instance, analysis of line intensities and profiles can give information about the order parameters, domain size and rms strains, which can then jointly be related to the predictions of models for the ordering reaction. This somewhat indirect approach has been applied to the ordering reaction in Ni_4Mo by Ling and Starke.

1.3. Evidence from metallography

Another experimental approach employed to resolve the question of mechanisms is to use metallography, and to search for distinguishable ordered and disordered phase-fields in alloys which have been partly ordered. Optical, electron and field-ion microscopy have been used. CoPt appears to order by a type I mechanism (Newkirk *et al* [10], using optical microscopy; Penisson *et al* [11], using electron microscopy). Southworth [7], however, has claimed evidence for a type II ("homogeneous") mechanism by field-ion microscopy, in spite of his conflicting X-ray observations. For CuAu I (cubic → tetragonal) which has been examined more than any other non-cubic ordered alloy, the metallographic evidence is ambiguous [12, 13], but for CuAu II (cubic → orthorhombic) there is metallographic evidence for a type I transformation [14]. There is also metallographic evidence for both type I and type II transformations in Ni_4Mo [15] and recently Tanner [16] has likewise demonstrated type I and II mechanisms in Ni_2V.

1.4. Ordering of non-stoichiometric alloys

A matter closely related to the mechanism of ordering in a stoichiometric alloy such as CuPt is the *equilibrium* condition of a non-stoichiometric alloy (e.g. $Cu_{0.42}Pt_{0.58}$) when annealed below its critical temperature for ordering. A type I ordering mechanism would be consistent with the existence of a two-phase field in which ordered and disordered phases of different compositions coexist permanently. (The coexistence of the two forms in a stoichiometric alloy during ordering is purely transient.) However, if ordering takes place throughout by a homogeneous (type II) mechanism, then there is no way for the alloy to divide into two discrete phases with different states of order and there should be no two-phase fields.* This question has received a modest amount of experimental attention: Rhines and Newkirk [17] in the first study devoted to this question, claimed, by X-ray methods, to have identified a two-phase field in off-stoichiometric alloys near the Cu_3Au composition, while Marcinkowski and Zwell [18] by electron microscopy observed ordered islands in a disordered matrix in the same alloy. Noble and Fairhurst [19] by optical microscopy established a broad stable two-phase region between ordered and disordered phases near Cd_3Mg. The very complicated family of iron-aluminium alloys, most recently examined by Okamoto and Beck [20] and Swann *et al* [21], show two-phase fields in parts of the phase-diagram and an absence of such fields in other parts. Type II transformation must be presumed, for instance, in the FeAl → Fe_3Al transition.

1.5 Disperse ordering

The matter is complicated by the existence of a special category of two-phase field in ordering alloys, termed "disperse ordering" by Warlimont and described by him in a series of papers on Fe-Al and Cu-Al alloys (the most recent by Warlimont *et al* [22], concerned with Cu-Mn alloys). This state consists of an extremely fine dispersion of coherent ordered particles in a disordered matrix. It was formerly believed to represent a form of short-range order, termed the "K-state". The fine dispersion is stable and immune to the normal process of Ostwald ripening. The origin of this peculiar condition has been analysed theoretically by Aubauer [23] and is attributed to the presence of internal elastic strains whose magnitude increases with the size of the dispersion, so that the growth of the particles would increase the total energy of the system in spite of the reduction in total interfacial area. The generation of this form of stable micro-

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*This conclusion would not hold good if only the *nucleation* stage of ordering takes place homogeneously – say by spinodal decomposition – and the domains then grow heterogeneously into the residual disordered matrix.

structure does not appear to be inconsistent with the operation of a type I ordering mechanism.

1.6. Non-stoichiometric Cu-Pt alloys

Because of the interest aroused by these recent studies of non-stoichiometric alloys, we have examined the equilibrium state of platinum-rich non-stoichiometric Cu-Pt alloys, as well as the transient state of stoichiometric CuPt.

1.7. Earlier work on Cu-Pt alloys

Following the early X-ray survey of the Cu-Pt system by Linde [24], a more detailed investigation by X-ray diffraction of stoichiometric CuPt was carried out by Walker [25]. He established, *inter alia*, the variation of equilibrium degree of order with temperature: there is a sharp jump in the order parameter at the critical temperature. The only reported attempt at a micrographic examination of CuPt, by transmission electron microscopy, was by Corke *et al* [26]. The extreme difficulty of thinning the alloy appears to have discouraged further attempts, though some TEM photographs of ordered and deformed CuPt have been published very recently [27]. No optical micrography has yet been attempted. The theory of the curious ordering found in CuPt has been discussed by Fournet [28] and by Clapp and Moss [29].

The ordered CuPt superlattice has a unit cell doubled with respect to the disordered lattice. The lattice parameter is in fact almost precisely doubled, while the interaxial angle increases from 90 to 91.03° at full order.

2. Experimental methods

Three alloys were prepared from 5N copper and 5N platinum by melting in a cold-hearth induction furnace, under argon. The compositions were CuPt, $Cu_{0.46}Pt_{0.54}$ and $Cu_{0.42}Pt_{0.58}$. The alloys were homogenized for a week at 1300°C and the homogeneity confirmed by electron microprobe analysis. The alloys were too brittle for any cold-work to be feasible as an aid to homogenization.

X-ray diffraction was performed both by diffractometer, with sieved filings, and by powder camera, using Cu$K\alpha$ radiation. Since attention was to be concentrated on profiles of clusters of closely adjacent diffraction lines, it was desirable to avoid complications due to the Cu$K\alpha_1/\alpha_2$ doublet, and this was achieved on the Siemens diffractometer by monochromatizing the *diffracted* beam by means of a curved quartz crystal. In this way the $K\alpha_2$ component could be entirely removed; this was confirmed by tests with a gold standard specimen. Powder photographs were made with unmonochromatized Cu$K\alpha$ radiation.

Preparation of foil samples for electron microscopy at 100 kV was attempted by using the electrolytic thinning technique described by Corke *et al* [26]. (Some delay was caused by an error in the published description of the electrolyte: the correct electrolyte composition is 100 ml saturated $CaCl_2$ solution, 73 ml distilled water, 4.5 ml conc. HCl, 25 ml conc. $HClO_4$, 1 g $CuNO_3$.) In spite of sustained attempts, neither Corke nor we succeeded in preparing more than a very few electron-transparent samples of indifferent quality. The problem arose out of the ready electrolytic passivation of the alloy surface.

Towards the end of the investigation, time on a high-voltage electron microscope became available, and a number of samples were examined on this instrument, operated at 700 kV. The samples were again thinned in Corke's electrolyte, which gave good results when the samples were examined with the more penetrating electrons.

Optical microscopy also at first posed serious difficulties, because the same passivation problem made electrolytic polishing impracticable, in spite of attempts with several electrolytes, superimposed a.c. and other devices. Electrolytic preparation was necessary because we thought it unlikely that a suitable etchant would be found to delineate the ordered regions. Since, however, ordered CuPt has a strongly anisotropic crystal structure (alternate sheets of Cu and Pt normal to the three-fold axis), we thought it likely that this phase would respond strongly to plane-polarized light. For such response to be successfully exploited, a completely strain-free surface is necessary, as was found for instance in early experiments on uranium [30]. A mechanically polished surface cannot be used without further treatment.

To overcome this impasse, we developed the thermal polishing method, already briefly described [31]. In outline, a mechanically polished specimen is sealed *in vacuo* in a Vycor or silica tube and heated at 900 to 1000°C for at least 2 h. This leads to differential evaporation of the high points of the mechanically polished surface (as evidenced by the deposition of a metallic mirror), and the end-point is a strain-free specular surface, marred only by small pits at the sites of blow-holes. The surface thus prepared is very sensitive to polarized light after the specimen, sealed *in vacuo*, has been subjected to a further heat-treatment to order it. It is possible by this technique to give a sample repeated ordering anneals and to compare the appearance of the same field of view using polarized light after each treatment.

Samples were photographed under polarized light on a Zeiss Ultraphot microscope, using ultrarapid Kodak Royal-X Pan film (1250 ASA) since the reflected light intensity was very low.

Some samples were examined by multiple-beam interferometry to test for surface tilts after ordering anneals. This was done by means of a Unitron convex glass reference surface covered with a multicoat partially reflecting layer. (This technique has been exhaustively explained by Tolansky [32].)

3. Observations: X-ray diffraction

3.1. Mechanisms at stoichiometry

Monochromatic radiation was employed to study changes in the diffraction line profiles as ordering progressed: the $(111)_\text{D}$ reflection was normally used for this purpose since it has the highest intensity and this particular reflection splits into a $(22\bar{2})/(222)$ doublet upon ordering, with an ideal intensity ratio of 3:1. The Miller indices change because the size of the unit cell doubles, while the intensity ratio results from the rhombohedral geometry: one of the four body diagonals (and the family of planes normal to it) is structurally different from the other three. (The $(22\bar{2})/(222)$ symbolism is a convenient shorthand. The (222) planes are normal to the trigonal axis and have a smaller *d*-spacing and come at a higher Bragg angle; $(22\bar{2})$, $(2\bar{2}2)$ and $(\bar{2}22)$ each have the same but a larger *d* than

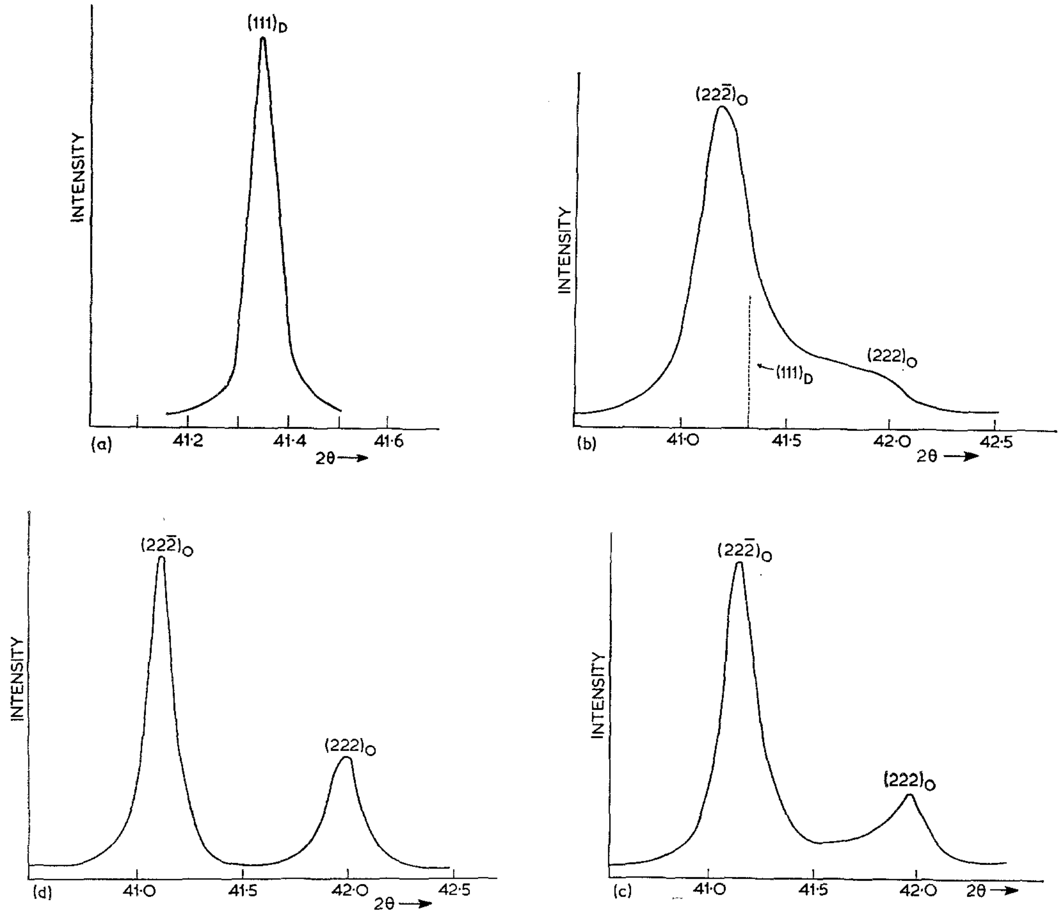

Figure 2 X-ray diffractometer line profiles of stoichiometric CuPt, taken with monochromated Cu$K\alpha_1$. (a) Disordered: quenched from 860°C. (b) Ordered 15 min at 665° C. (c) Ordered 30 min at 665°C. (d) Ordered 4000 min at 665°C.

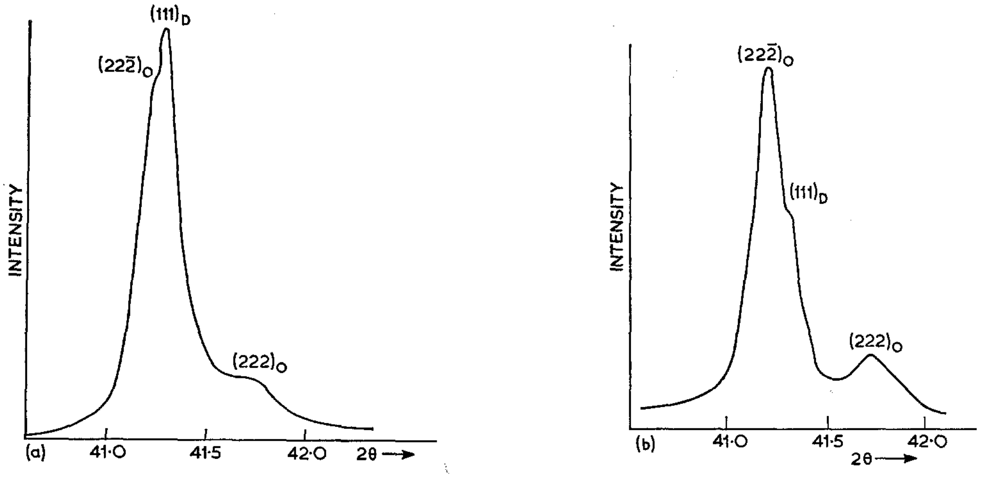

Figure 3 X-ray diffractometer line profiles of stoichiometric CuPt, taken with monochromated Cu$K\alpha_1$. (a) Quenched from 860° C and ordered 90 sec at 765° C. (b) Ordered 3 min at 765° C.

$d_{(222)}$ and lower θ, and combine to form the stronger peak.)

The previously disordered and quenched samples were isothermally annealed at 665° C, in the first instance. This temperature was high enough for equilibrium to be attained within about 70 h, and at the same time was low enough to allow the ordering reaction to be conveniently "frozen" at different stages. Diffraction patterns were made from filings quenched after various annealing periods.

Fig. 2 shows the behaviour as a disordered sample is progressively annealed for the times indicated. The perfect symmetry of the disordered peak is destroyed after 15 min at 665° C. Apart from the asymmetrical excess intensity of the $(22\bar{2})_O$* towards higher Bragg angles, the area under the $(22\bar{2})_O$ peak was found to be considerably greater than the expected value, relative to the $(222)_O$ peak. After 30 min at 665° C, the ordered $(22\bar{2})/(222)$ doublet was clearly resolved, but the $(22\bar{2})_O$ peak was still asymmetrical, skewed towards the higher Bragg angle side. This skewness had, however, disappeared after 4000 min at 665° C; now the $(222)_O/(22\bar{2})_O$ intensity ratio matches the predicted 1:3 value.

Attempts were made to resolve analytically the composite profile after 15 min anneal, by using the known line positions of all three lines and the 3/1 ratio of integrated intensities of the order doublet. The assumption was made that the total excess component of the intensity under the $(22\bar{2})_O$ peak on the high-angle side of the maximum was a contribution from the residual *disordered* phase. However, though the presence of the disordered phase together with the ordered phase is implied by the overall profile, its analytical separation from the ordered doublet proved impracticable owing to a number of extraneous line-broadening factors (discussed below).

Fig. 3 shows the corresponding diffractometer profiles for an alloy annealed at 765° C. At this temperature, the diffraction lines from the ordered and disordered phases are somewhat more clearly distinguished during the ordering process. Nevertheless, in spite of a reduced line width, the lines of the two phases are still not sharply resolved. Note that the angular separation between the (222) and $(22\bar{2})$ components of the ordered phase is smaller than in Fig. 2, because at the higher ordering temperature the degree of order is smaller; correspondingly the rhombohedral distortion of the initially cubic unit cell is less pronounced. This is in accord with the findings of Walker [25]. Again, attempts to resolve the profiles analytically into the constituent lines were unsuccessful.

The implication of the patterns of Figs. 2 and 3 is that ordered and disordered phases do coexist during the ordering reaction, but that the diffraction lines of the ordered phase are *initially* quite close to the lines from the disordered phase.

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*The suffix "O" refers to the ordered components, and the suffix "D" to the disordered component.

This implies that the ordered phase initially has a degree of order much less than the equilibrium degree eventually achieved at that temperature.

Further, in order to establish whether or not the 665 and 765°C profiles were representative of all temperatures, Debye-Scherrer diffraction photography using only a Ni filter to remove β radiation, combined with microdensitometry, was employed to study expeditiously a wide range of ordering temperatures. It was found that for $620°\mathrm{C} < T < T_c$, the microdensitometer traces were analogous in their appearance to the diffractometer profiles of Figs. 2 and 3. Such a sequence has in the past been termed a "continuous" mode. However, for several temperatures below 620°C, a quite different "discontinuous" sequence was recorded. For instance, Fig. 4a shows a sequence of $(220)_\mathrm{D} \rightarrow (440)_\mathrm{O}/(4\bar{4}0)_\mathrm{O}$ profiles for anneals at 500°C. Though at the commencement of the reaction the rhombohedral lines do not appear quite in their final positions, yet the ordered and disordered diffraction lines are very clearly resolved, evidence of an unmistakable two-phase structure.

We believe that the distinction between the continuous and discontinuous modes of ordering is only apparent. At the highest temperature used (765°C), strains are small and lines are sharp, so that there is moderately clear resolution of the two phases, even though the angular separation of the order-doublet is small. In the range 600 to 700°C approximately, the doublet separation is greater, but large strains lead to broad lines and very poor resolution. At lower temperatures, the doublet separation is larger still, and (for reasons later revealed by the metallography) strains are small in the early stages of ordering and so the X-ray resolution is clear. Allowing for these various factors, the

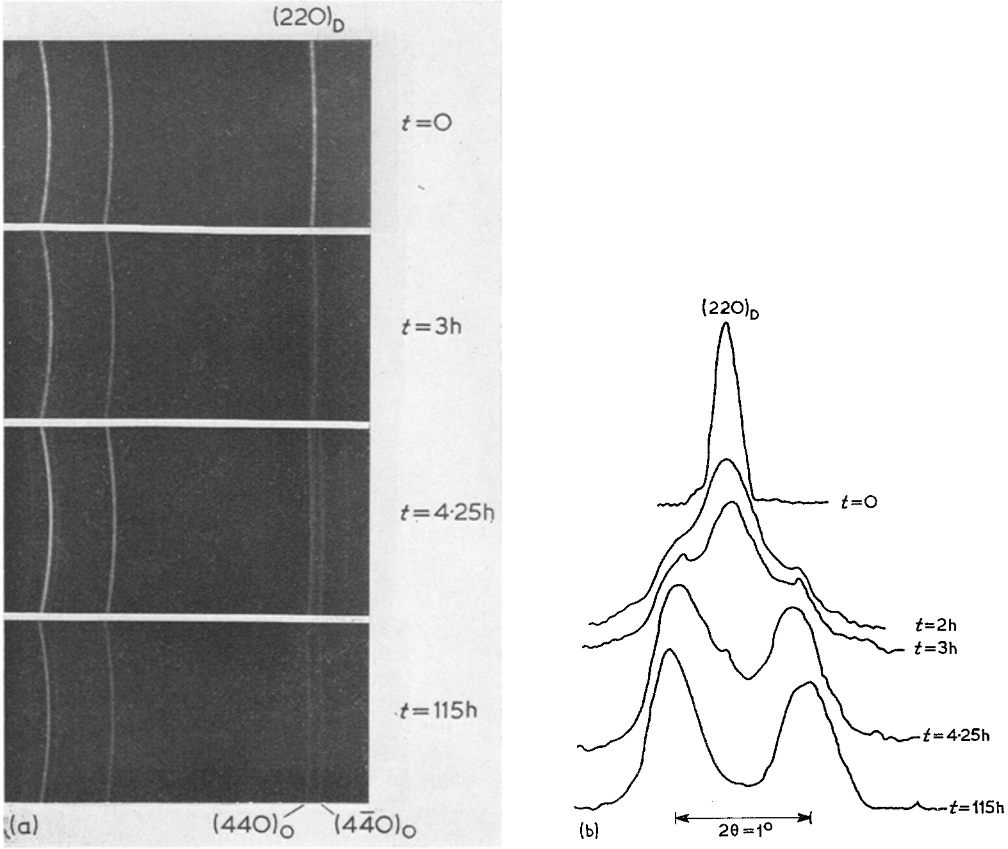

Figure 4 (a) Low-angle portions of Debye-Scherrer photographs (Cu$K\alpha$) of stoichiometric CuPt annealed at 500°C for various times. (b) Corresponding photometertraces of $(220)_\mathrm{D}$-$(440)_\mathrm{O}/(4\bar{4}0)_\mathrm{O}$ group of lines.

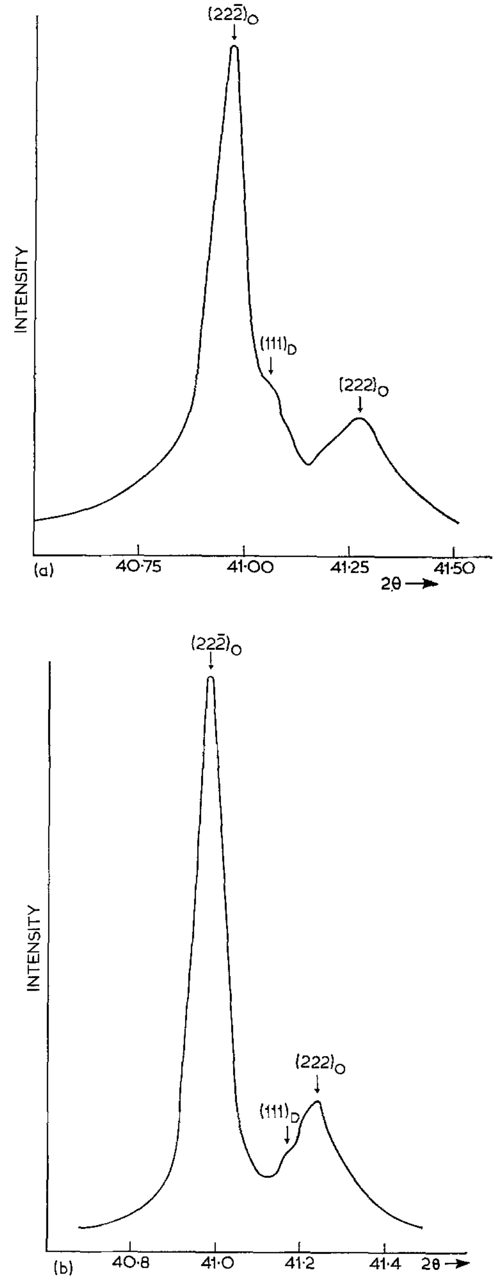

Figure 5 X-ray diffractometer line profiles of $Cu_{0.42}Pt_{0.58}$, taken with monochromated Cu$K\alpha_1$. (a) Quenched from 860° C, annealed to equilibrium at 740° C. (b) Quenched from 860° C, annealed to equilibrium at 770° C.

X-ray results indicate for all annealing temperatures that ordering in stoichiometric CuPt takes place by a type I reaction.

3.2. Transformation in non-stoichiometric alloys

Following this study of the *transient* mechanism of $Cu_{0.5}Pt_{0.5}$, attention was next focused on the phase behaviour *off*-stoichiometry under equilibrium conditions. Filings of the 42 at. % Cu alloy were annealed at three different temperatures: 740, 755 and 770° C. Once more crystal-monochromated Cu$K\alpha$ radiation was used and the $(1\,1\,1)_D$ line profiles constructed. A short account of the early stages of this work has already been published [1].

At an angle of $2\theta = 41.05^\circ$ a very distinct discontinuity was observed on the $(22\bar{2})_O$ peak for an annealing temperature of 740° C (Fig. 5). This discontinuity shifted its position to higher Bragg angles with increasing annealing temperature, until for 770° C the kink in the profile formed on the $(222)_O$ branch of the doublet. This irregularity in the profile can only be attributed to the presence of the $(1\,1\,1)_D$ peak which is expected to occur within such a range of Bragg angles. The positions of the $(1\,1\,1)_D$ Bragg reflections were accurately located from the line profiles, and were used to determine the lattice parameter of the disordered phase. Since it is a low-angle reflection, the position of the $(1\,1\,1)_D$ line is inherently subject to a systematic error; nevertheless, its high intensity and small broadening made it more suitable for the present purpose than lines at higher angles. To correct for the systematic error in position of $(1\,1\,1)_D$, the true value of the cell constant a_0 was determined for a 42 at. % Cu alloy, which had been disordered and quenched, by means of the usual a versus $\sin^2\theta$ extrapolation used in diffractometry. For this disordered 42 at. % alloy, a correction Δa was established, where Δa is the difference between the true a_0 and the apparent value of a determined from the position of the $(1\,1\,1)_D$ line.

Next, the apparent values of a determined for the two-phase 42% alloys annealed at various temperatures, were corrected by adding Δa to each apparent a, deduced solely from the $(1\,1\,1)_D$ line. This corrected value of a_0 was combined with the calibration by Schneider and Esch [33] for the lattice parameter as a function of composition for disordered Cu-Pt alloys.

So, finally, for each annealing condition, a different copper concentration in the disordered component of the sample resulted. These concentrations were used to locate the "disordus" boundary on the phase diagram, while the "ordus" curve was located by means of dilatometric heating runs on a 46 at. % Cu and the

50 at. % Cu alloys. Additional points on the "disordus" boundary were also obtained by dilatometric cooling runs. The results were plotted on the partial phase diagram shown in Fig. 6. This phase-diagram also shows several points deduced from a study of isotherms representing equilibria between a series of Cu-Pt alloys and an oxygen atmosphere of variable pressure [34].

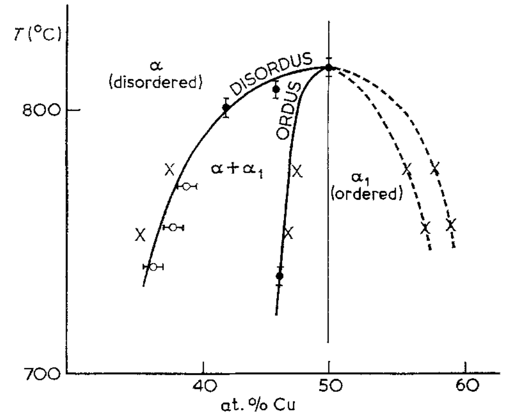

Figure 6 Partial phase diagram of Cu-Pt system showing limits of order/disorder two-phase field. ● Dilatometric points, ○ points from X-ray diffraction, × Points from study by Assayag and Dodé [34].

A further experiment was performed to test whether the two-phase region shown in Fig. 6 is indeed a classical two-phase region, as suggested by the diffractometry results. Filings of the alloy containing 46 at. % copper were equilibrated at 780° C by two distinct routes: (a) the alloy was disordered at 860° C, quenched, and then annealed at 780° C; (b) the alloy was fully ordered at 685° C in the *single*-phase field, then heated to 780° C and held there. (These temperatures are maked in Fig. 6.) Debye-Scherrer photographs were prepared of samples after different annealing periods. Over 300 h were needed to attain equilibrium in each case. The end-result for both treatments, though starting from quite different points of departure, was an identical two-phase structure: this is what would be expected for a classical (Gibbsian) two-phase region.

The steps *en route* to the final structures were interesting. The disordered sample first ordered almost completely, then partially disordered again: the final diffraction pattern showed evidence of more strain than the intermediate highly ordered stage. A rather similar sequence has been observed in Fe-Al alloys by Warlimont [35]. The initially fully ordered sample changed monotonically towards the final two-phase structure. For case (a) it appears that a "metastable" ordered phase forms initially from the disordered phase, and then decomposes to give a stable two-phase structure.

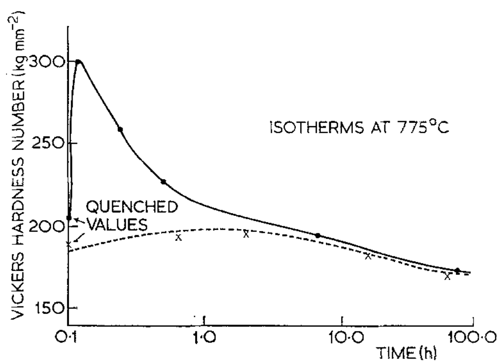

Figure 7 Hardness isotherms for Cu$_{0.46}$Pt$_{0.54}$ annealed at 775° C, in two-phase field. Arrows indicate as-quenched hardness values. Solid line: initially disordered. Dashed line: ordered in single phase region at 675° C.

The behaviour of the alloy in the two distinct starting conditions is consistent with the changes of hardness of the same alloy (Fig. 7). The final hardness is the same for both starting conditions, but not the approach to that final hardness.

4. Observations: metallography

4.1. Stoichiometric alloys

4.1.1. High temperatures

As mentioned above, two general types of X-ray sequences were observed, depending on whether the ordering was carried out above or below 620° C. When samples were isothermally heat-treated above 620° C, a lamellar morphology resulted. In the early stages of the ordering process at 700° C, the contrast under polarized light was diffuse (Fig. 8a), but with prolonged annealing a coarse twinned structure became visible (Fig. 8b), as the anisotropy within the sample increased. The ordered alloys incorporated considerable internal strains, which sometimes resulted in intergranular fracture [2].

4.1.2. Intermediate temperatures

At 550° C (i.e. in the middle of the temperature interval which gave clear X-ray resolution between the two phases, during the ordering process), fully ordered domains were seen to originate at grain boundaries and other surface imperfections (pores, scratches) and these domains were seen to grow into the grain bulks. The same specimen area is shown in Fig. 9 after increasing annealing times at 550° C. Since no etching is required, the polarized-light technique allowed such sequences to be readily followed. Growth has occurred on both sides of one of the grain boundaries and, unlike the plate structure of Fig. 8, no contrast was observed from within the grain bulks. No growths were ever observed emerging from annealing twin interfaces. Fig. 9 is typical of many fields which were photographed in the course of this study.

Polarized-light microscopy, apart from providing information regarding domain morphologies, also permitted a qualitative analysis of the domain orientations. At no stage of the growth process were more than four orientations of the ordered regions in any one grain seen to exist;

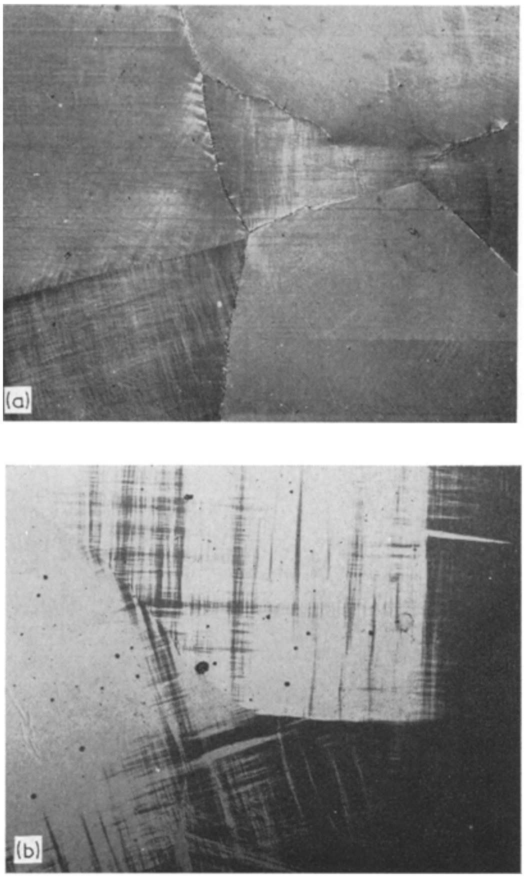

Figure 8 Stoichiometric CuPt, thermally polished at 900°C, quenched and ordered at 700°C for (a) 1 h, (b) 20 h. Viewed under polarized light; × 108.

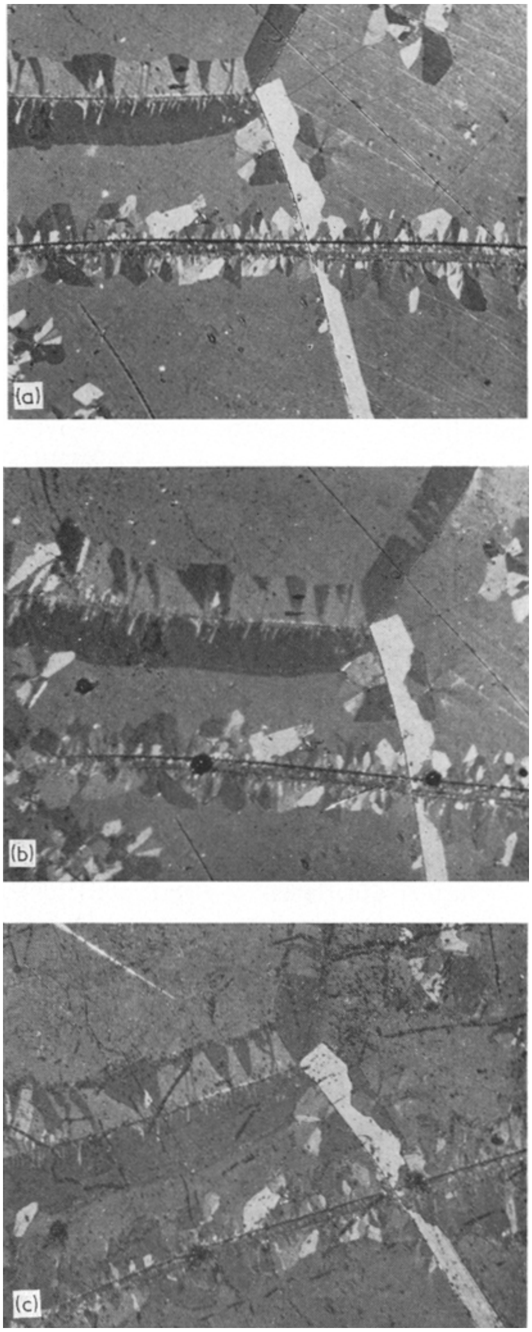

Figure 9 Stoichiometric CuPt, thermally polished at 900°C, quenched and ordered at 550°C for (a) 85 h, (b) 157 h, (c) 412 h. Viewed under polarized light. Shows growth of heterogeneously nucleated domains; × 108.

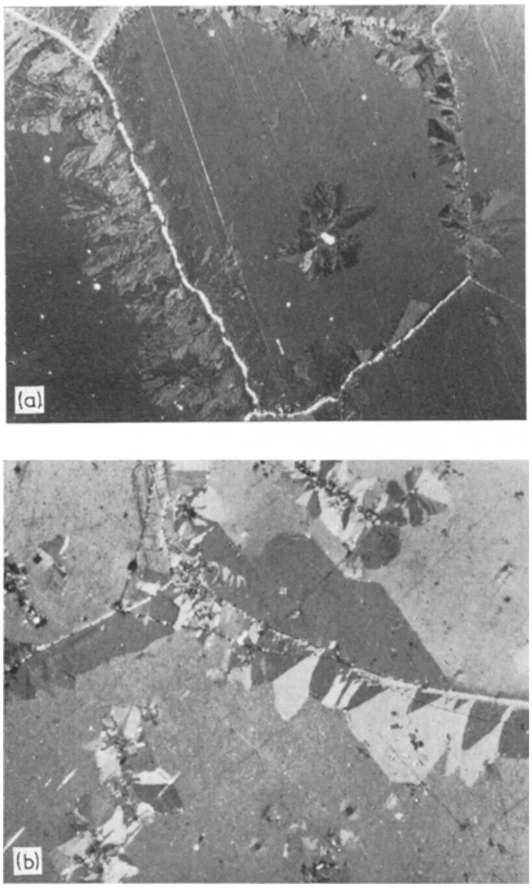

Figure 10 Stoichiometric CuPt, thermally polished at 900° C, quenched and ordered at (a) 450° C, (b) 550° C. Viewed under polarized light. Shows faceted nature of grain-boundary domains; × 108.

i.e. only four colour shades or fewer were ever observed under polarized light within the confines of any one original disordered grain. This is as expected: each body diagonal of the original cubic unit cell can become a rhombohedral axis, so there are four possible ordered domain orientations. Within the lamellar regions, however, only two distinct orientations were visible within an original cubic grain. The grain-boundary domains often exhibited a faceted morphology (Fig. 10) which implied that domains were growing along specific crystallographic planes. The crystallography of such interfaces is now being investigated in more detail by means of a micro-beam Laue technique.

A separate study [2] had established, by means of microhardness measurements, that the interiors of these grains too were ordered. Indeed the grain interiors hardened rapidly while the coarse domains at grain boundaries scarcely hardened at all. The fact that there was no observable optical contrast from the grain interiors must be attributed to the presence of ordered domains so small that they were outside the resolution of optical microscopy. If all domain orientations are present in equal numbers then there should be no resultant optical anisotropy.

With suitably thinned foils, 1 MeV electron microscopy revealed two quite contrasting types of images. It appeared that the same foil, annealed at 550° C, had within it *clear* transparent regions adjacent to areas containing a fine *speckled* distribution (Fig. 11a). A striking example of the two kinds of structures existing side-by-side is given in the bright field micrograph of Fig. 11b. The selected-area diffraction pattern (SADP) from the "fine structure" (Fig. 11a) contained many extra reflections which could be indexed in terms of a superlattice structure. The microdomains in the speckled structure were 100 to 200 Å across.

SADP from a clear featureless region revealed a very simple pattern (Fig. 12); no apparent superlattice spots were seen. Nevertheless, the clear region is uniformly ordered, as can be deduced from the fine splitting of many of the diffraction spots: two ordered variants evidently exist in the field of view. Fig. 13 shows a unit cell of the reciprocal lattice of an ordered single domain of CuPt; from this it can be seen why the diffraction pattern in Fig. 12, though from an ordered crystal, shows no apparent superlattice reflections; the layer ABCD of the reciprocal lattice contains both superlattice and fundamental reflections of *identical* intensity. Each reciprocal lattice spot, fundamental or superlattice, becomes divided into four sub-spots if all four domain variants contribute to a diffraction pattern. Other regions of this type, differently oriented, did show superlattice spots.

The electron micrographs and optical micrographs taken in conjunction show that *CuPt ordered around 550° C consists of coarse domains growing from grain boundaries, surface pores and scratches, while simultaneously a fine "disperse order" structure develops in the grain interior* (the "matrix"). One would expect that the growth of the coarse domains would slow down as the matrix orders in its own fashion, and this was indeed found (Fig. 14).

A further set of experiments was performed in

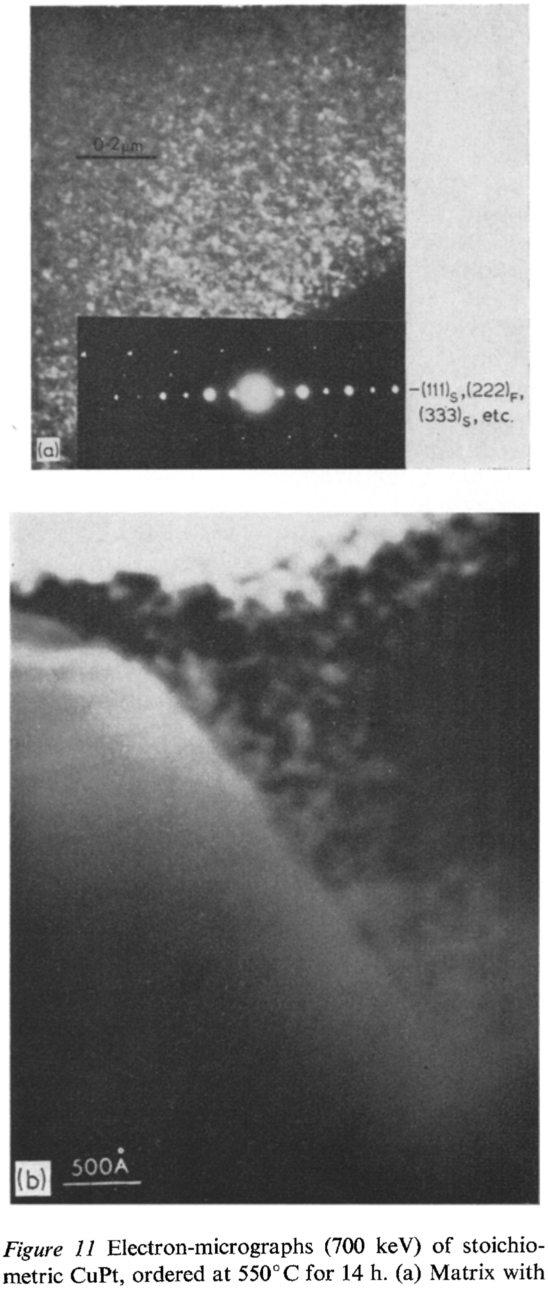

Figure 11 Electron-micrographs (700 keV) of stoichiometric CuPt, ordered at 550°C for 14 h. (a) Matrix with fine ordered/disordered two-phase structure. (b) Matrix plus ordered grain-boundary domains. Marker = 0.2 μm. (Inset shows corresponding SADP, which includes both fundamental and superlattice spots.)

Figure 12 Selected-area diffraction pattern (700 keV) from a grain-boundary domain in stoichiometric CuPt ordered 14 h at 550°C. Note doubling of many spots, indicating that selected area encompasses two ordered orientation variants. This SADP includes no superlattice spots.

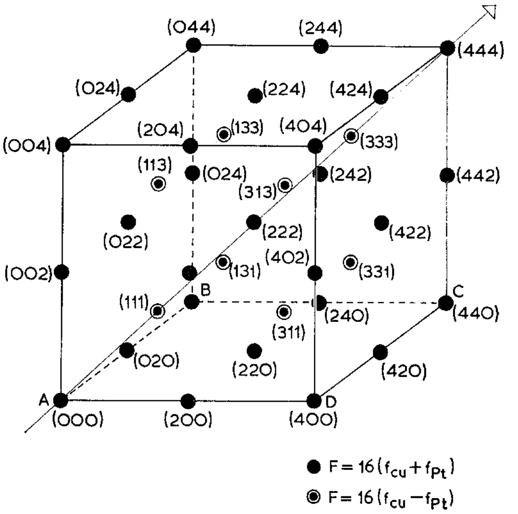

Figure 13 Unit cell of the reciprocal lattice of ordered CuPt. ● Fundamental r.l. points. ⊙ Superlattice r.l. points.

order to investigate the influence of delayed nucleation on subsequent domain growth. As already noted, domains were visible at surface defects, and in particular were always found at scratches (Fig. 9); it was this property which was used for the following experiment: scratch marks were introduced on the specimen when it was in the disordered condition and then at various stages of the annealing programme once ordering had commenced. The observations revealed that domain growth was prolific from scratches introduced in the disordered alloy, whereas scratch marks made after only a few minutes of ordering did not nucleate ordered domains. A micrograph illustrating this is shown in Fig. 15.

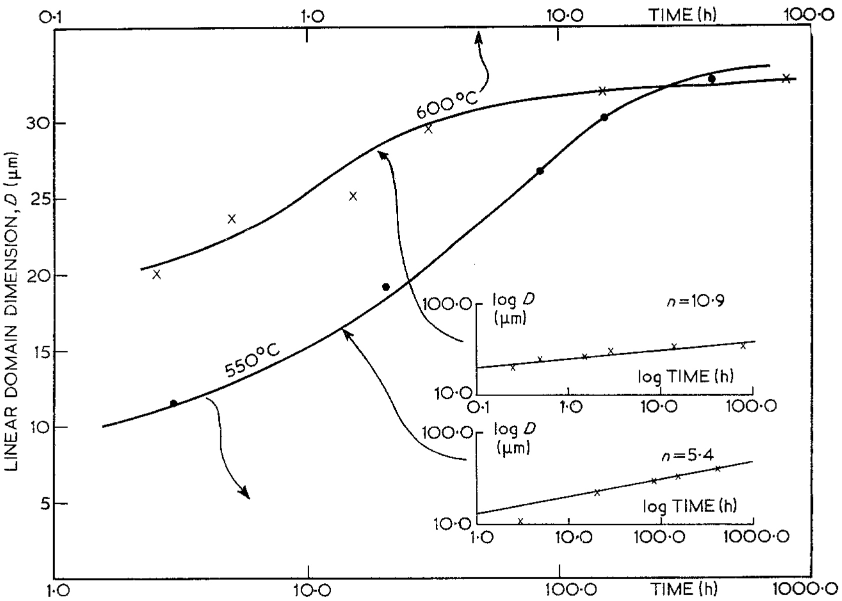

Figure 14 Isothermal growth of individual grain-boundary domains in stoichiometric CuPt ordered at 550 or 600°C.

It is to be noted that Fig. 15 indicates a rapid inhibition of the domain-*nucleating* function of a scratch, whereas Fig. 14 records the more gradual decay of the rate of *growth* of an existing domain.

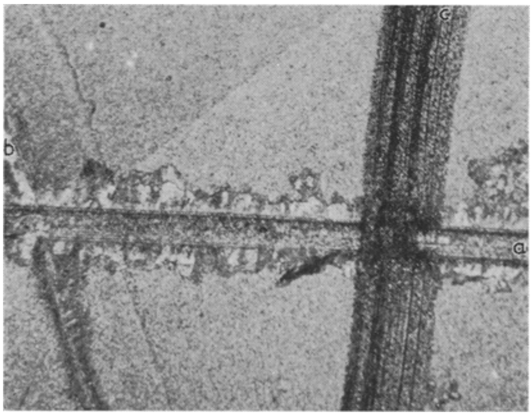

Figure 15 Polarized-light micrograph of thermally polished stoichiometric CuPt annealed 13¾ h at 550°C. The three scratches were made (a) in the disordered state, (b) after 30 min ordering, (c) after 70 min ordering, × 108.

4.1.3. Low temperatures

When annealing was carried out at even lower temperatures, below 475°C, a modification of the grain-boundary morphology resulted. Though there was again unmistakably a grain-boundary reaction forming ordered domains (Fig. 16a), this time the grain interiors too had developed clearly visible ordered structures. The latter took the form of rosettes (spherulites) and were sometimes nucleated at some surface irregularity (as before), but also at random locations, apparently without any nucleation aid. The general appearance of the surface was that of a dense population of anisotropic areas, even after relatively short anneals at such low temperatures. Upon further annealing, the spherulites increased their dimensions and grew into the optically anisotropic matrix, until the entire specimen surface was littered with them as in Fig. 16b. The matrix was again much harder than the rosettes, indicating that disperse ordering was again in progress.

4.1.4. Continuous cooling

A final annealing programme consisted of transforming stoichiometric samples of CuPt by continuous cooling at 3°C h^{-1} from above T_c, through T_c /815°C), to about 300°C, followed by quenching. Remarkable morphologies resulted and bore crystallographic relationships with the parent grain, as seen in Fig. 17a. The structure was densely twinned. Fig. 17b provides an excellent example of the paired nature of the variants comprising an order twin: families of

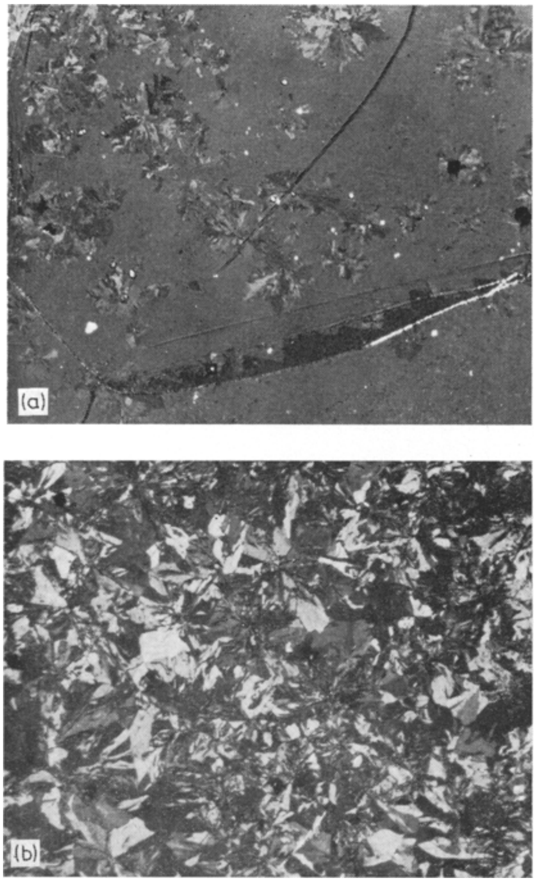

Figure 16 Stoichiometric CuPt, thermally polished at 900°C, quenched and ordered for (a) 23 h at 350°C, (b) 228 h at 475°C. Viewed under polarized light (a) × 54, (b) × 108.

*micro*twins are contained within a *macro*twinned region. When such slowly cooled samples were viewed under ordinary light, considerable surface relief was evident. It proved possible to measure the amount of shear of the polished surface by multiple-beam interferometry (MBI). The shear was clearly associated with individual macrotwins. Some of the macrotwins had sufficient dimensions to allow the use of MBI and a typical interferogram corresponding to the area in Fig. 17a is shown in Fig. 17c. From the characteristics of the fringes in the various macrotwins, it was possible to calculate a value for the relative shear between adjacent lamellae. Only a proportion of the twins were suitably oriented to show substantial surface shear, and only such twins were measured. The results showed that the shear angle for twins in a number of grains, which showed considerable shear under ordinary light, varied from 1.20 to 1.24°. Table I summarizes the combined conclusions

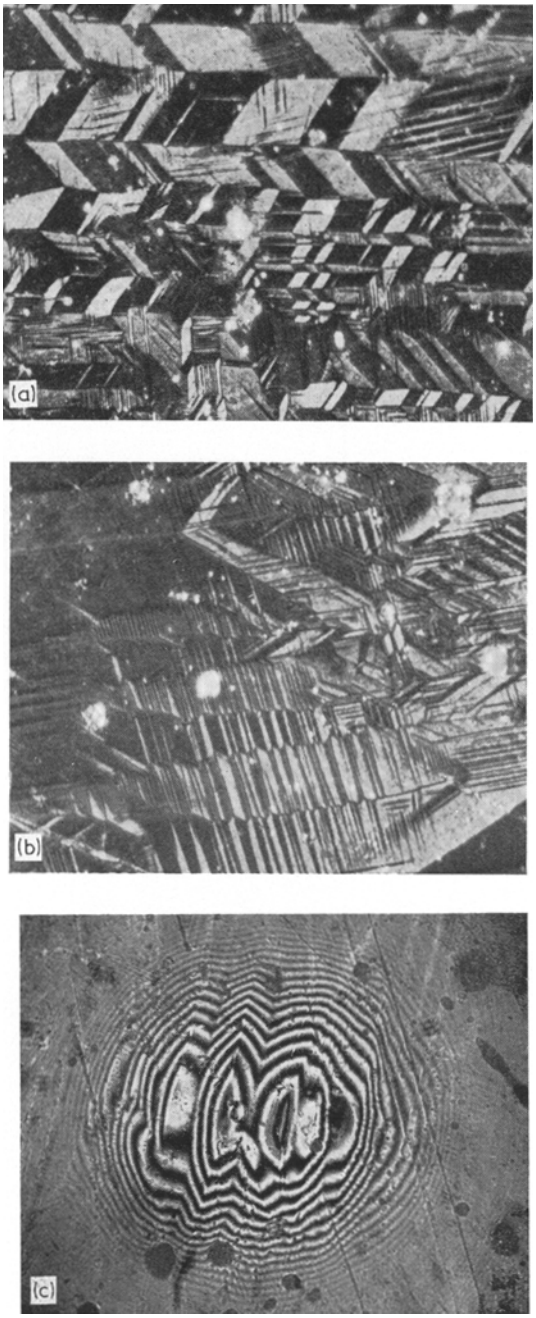

Figure 17 Stoichiometric CuPt, thermally polished at 900°C and continuously cooled at 3°C h^{-1} to about 300°C. (a) and (b) viewed by polarized light; × 190. (c) Multiple-beam interferogram, showing surface tilts associated with macrotwins shown in (a) above × 100.

TABLE I Domain characteristics in stoichiometric CuPt

Temperature (° C)	Morphology of domains	Ordering mechanism from X-ray diffraction	Max. no. of orientations under polarized light
$T > 620$	Lamellar	Continuous	2
$620 > T > 475$	Grain-boundary	Discontinuous	4
$T < 475$	Grain-boundary + rosettes	Discontinuous	4
Slow cooling through T_c	Lamellar (micro- and macrotwinned)	—	2

from X-ray and metallographic examination at different temperatures.

4.2. Non-stoichiometric alloys

When platinum-rich samples were annealed at high temperatures in the two-phase field and viewed under polarized light, they bore a remarkable resemblance to the lamellar morphology already cited above. In fact, the morphological appearance was indistinguishable from that resulting from a stoichiometric high-temperature reaction, except that the lamellae were on average slightly coarser (Fig. 18a). However, when a platinum-rich sample (in this instance it was slow-cooled) was investigated by means of 1 MeV electron microscopy, a two-phase structure was clearly visible (Fig. 18b). This micrograph shows the presence of ordered platelets separated by disordered platelets, the former set being distinguishable by the strong characteristic APB contrast. Fig. 18c shows a view of an ordered *lamella* imaged by means of a superlattice reflection. The disordered part of the field is not in contrast. Platinum-rich samples isothermally annealed at high temperatures in the two-phase field showed a plate structure with subsidiary speckling like that in Fig. 11a.

Taking the optical and electron micrographs in conjunction, we conclude that the areas which showed a uniform shade under the *optical* microscope must consist of tiny ordered domains (optically unresolvable), *predominantly of the same orientation*, set in a disordered cubic matrix: i.e. any one "macro-domain" actually consists of microdomains having mainly or entirely one out of the four possible orientations. This should be contrasted with the optically isotropic grain matrix in the stoichiometric samples annealed at 550° C (Fig. 9); these showed no optical contrast, presumably because all four domain orientations were present in roughly equal numbers, and the domain size was again so small (even smaller than in non-stoichiometric alloys) that no optical resolution was possible.

5. Discussion of observations

The X-ray diffraction investigation presented in the preceding section indicates that the stoichiometric alloy when annealed isothermally at various temperatures, orders by a type I reaction, though the metallography has shown that the details of the reaction vary greatly with the annealing temperature. As we have seen earlier, the degree of resolution of the distinct diffraction lines from the disordered and ordered phases depends on several factors which themselves vary with temperature and time: (a) degree of rhombohedral distortion of the unit cell, which is linked to the value of the order parameter and in turn affects the angular separation of the "order doublet"; (b) the existence of a range of values of the order parameter present instantaneously in the sample, which must broaden the lines of the ordered phase; (c) the mean short-range lattice strain. All these factors affect fundamental line profiles, while the mean domain size also affects superlattice lines. We have carried out an investigation to separate out the lattice strain from domain size at various stages of isothermal anneal by the systematic measurement of widths of both fundamental and superlattice lines, and this is to be reported separately [36].

The sequence of microdensitometer traces for an anneal at 500° C (Fig. 4) shows how tricky it is to disentangle the various factors that affect the X-ray patterns. At this temperature, as we know from the metallography, a small fraction of the volume is rapidly consumed by large, almost strain-free and presumably highly ordered domains (we know they are strain-free because they remain soft). This volume fraction must generate a weak but sharp order-doublet, $(222)/(22\bar{2})$, which, however, is almost masked by the rapid broadening of the disordered peak; this broadening is due to the simultaneous incipient fine-scale ("disperse") ordering of the

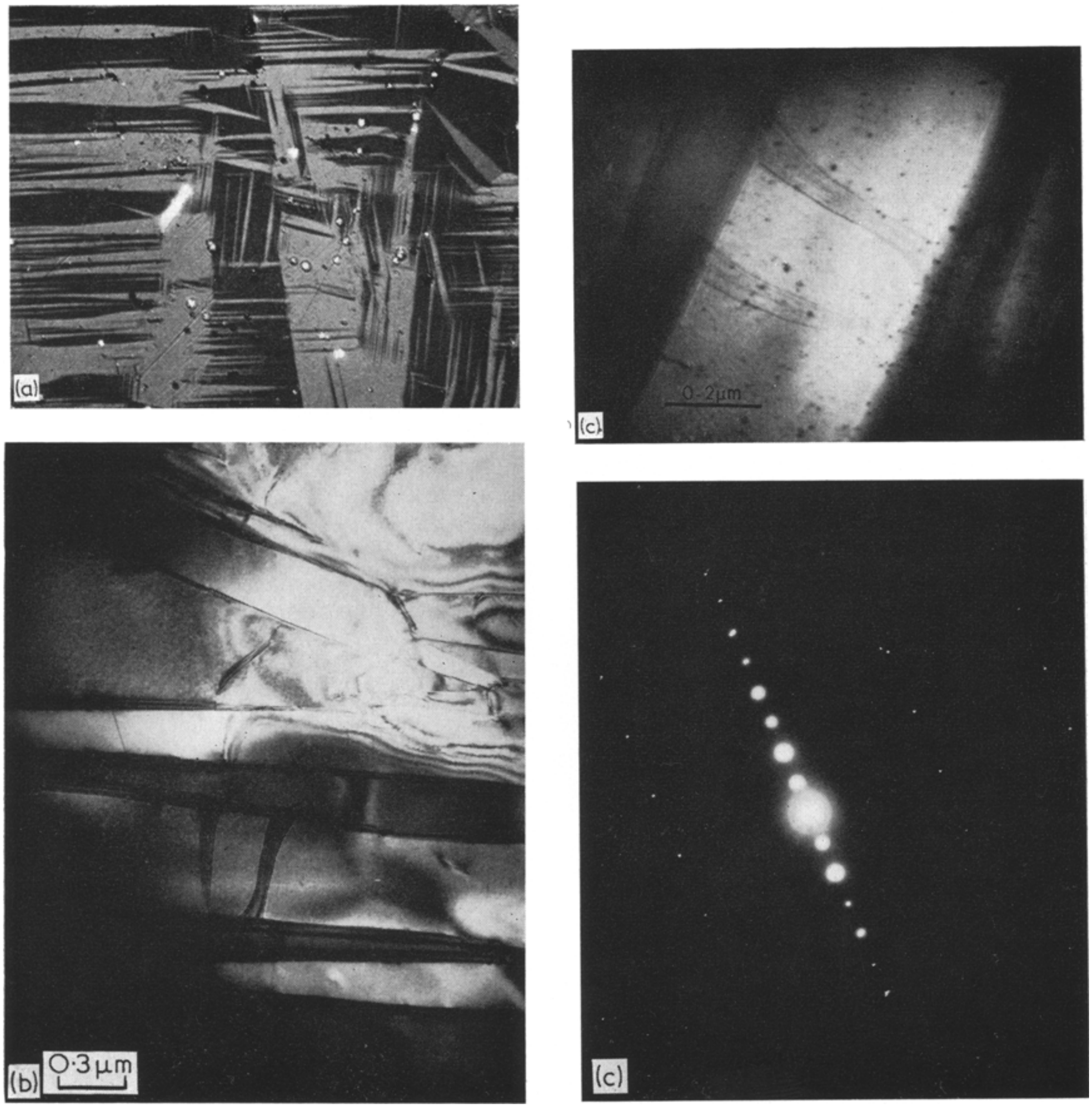

Figure 18 (a) $Cu_{0.46}Pt_{0.54}$, thermally polished at 900°C and quenched, annealed 480 h at 780°C. Viewed by polarized light, × 108. (b) $Cu_{0.42}Pt_{0.58}$ slowly cooled into two-phase region and quenched. Electron-micrograph (700 keV). (c) Same sample as (b), showing an ordered lamella and corresponding SADP. (The small spots represent radiation damage.)

matrix, associated with much hardening and therefore with substantial strain. After long anneals, the strain in the matrix falls slightly as the residual disordered phase disappears, and the ordered doublet sharpens marginally.

In view of these complications, the only reliable conclusion that can be drawn from our X-ray study of the fundamental lines alone is that ordering is always of type I, and further, that a genuine two-phase field comprising ordered and disordered phases exists for non-stoichiometric alloys.

The intermediate and low-temperature morphology pose several distinct problems. Firstly, one would like to understand why coarse domains are so rapidly nucleated not only at grain boundaries but also at scratches and other places, especially pores, where the free surface

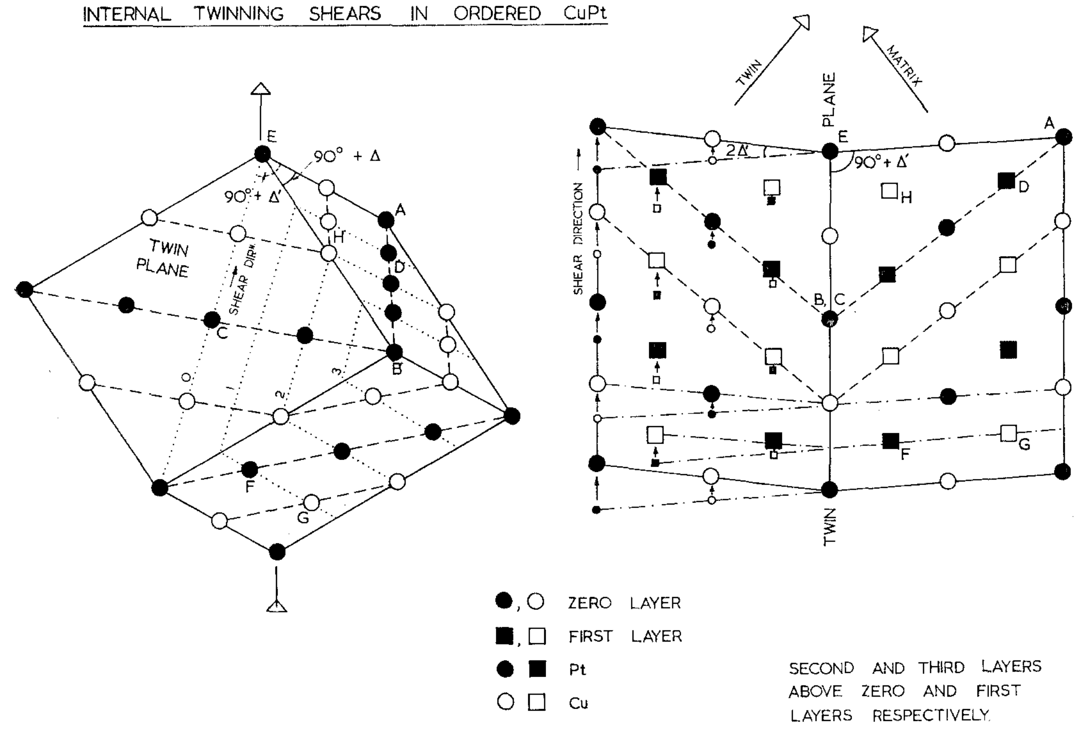

Figure 19 Postulated shear mechanism to account for observed surface tilts on slow-cooled samples of stoichiometric CuPt (compare Fig. 17c).

becomes curved. (This ready nucleation at pores is further accentuated at the lowest ordering temperatures.) Regarding grain boundaries, the first impresssion conveyed by the optical micrographs is that the domains are created by local migration of grain boundaries in the initially disordered polycrystal, each advancing boundary creating an ordered domain as it moves, in the manner observed in Ni_2V by Tanner [16]. However, this seems improbable on further examination, since frequently domains grow into *both* adjacent grains from the same sites on a given boundary. This objection is not, however, conclusive. The alternative is that the domain is simply heterogeneously nucleated at the boundary and orders the grain it grows into. The distinction between these two models is that in the first case the ordered domain has the orientation of the neighbouring grain *from* which it has grown, and in the second case the domain has the orientation of the grain *into* which it has grown. (We wish to describe these two modes collectively as a *discontinuous ordering reaction.*) This issue is as yet unresolved and an examination with the aid of an X-ray microbeam Laue camera is in progress to settle it.

The nucleation at scratches can be connected with local strain in some way, or it can, as with pores, be simply a matter of surface contour. It is conceivable that a sharply concave curvature injects an abnormally large concentration of vacancies into the alloy beneath (as in the sintering of pores in a powder compact) and the enhanced diffusion caused by this could accelerate nucleation of a domain.

The second problem concerning the coarse domains is their frequently angular morphology. To understand this requires further crystallographic information, which we hope to get by means of the microbeam X-ray camera.

The third problem is to interpret the progressive slowing up of the rate of growth of the coarse domains as exemplified in Fig. 14. It is interesting that when these curves are replotted on a double-log basis (Fig. 14b), they are found to obey the normal domain-coarsening relation

$$D^n - D_0^n = k(t - t_0)$$

where D is the local domain thickness at time t and D_0 at time t_0. Our n value, however, is much higher than the values of 2 to 3 normal for domain coarsening in uniformly ordered alloys such as Cu_3Au, Mg_3Cd and Ni_4Mo. No means are available at present for interpreting this relationship theoretically, but it is plain that domain growth slows down because the progressive disperse ordering of the matrix reduces the driving force for domain growth. The disperse ordering apparently very quickly impedes heterogeneous nucleation of new domains [15].

Finally, this fine-scale disperse ordering requires explanation. It may well be an example of the general phenomenon discussed by Aubauer [23]: the essential feature here is the inhibition of Ostwald ripening by the progressive build-up of elastic strains. However, the examples that Aubauer seeks to interpret all involve the formation of a dispersion of an ordered phase in a matrix of different composition in an off-stoichiometric alloy. Here, however, a stoichiometric alloy is involved; the ordered and disordered phases have the same composition, therefore no long-range diffusion is involved in contrast to Aubauer's model, and the disordered phase should eventually disappear completely. Since it is an essential requirement in Aubauer's theory that the fine stable dispersion of ordered particles must coexist with some residual disordered phase, it is not at present clear what stabilizes the fine dispersion of ordered domains at this late stage: it may be that a small residue of disordered phase remains indefinitely even in this stoichiometric alloy, enveloping the microdomains and hindering their coarsening.

The difference between the two modes of ordering in the same alloy is presumably to be put down to the distinction between heterogeneous and homogeneous nucleation. The large domains become so, simply because easy nucleation sites are sparse, whereas disperse ordering is initiated much more slowly from a multitude of homogeneously activated sites.

The other issue to be discussed is the mechanism of formation of lamellar domains or "order twins", especially the large macrotwins formed by continuous cooling. The large lamellae formed by isothermal annealing at high temperatures come into contrast gradually, as observed in the optical microscope, and no surface shears are seen. These lamellae may well form by linked homogeneous nucleation of groups of small domains of the same orientation, as proposed by Tanner and Ashby [37]; such small domains would then link up, subject to the presence of antiphase domain walls. It is not clear, however, why this mechanism should result in a lamellar morphology rather than some other shape.

The macrotwins formed in slow cooling must form in some co-operative manner, to account for the observed shearing action. We propose the mechanism indicated in Fig. 19. This mechanism requires that macrotwins form along the $\{100\}$ planes: this is in accord with the findings of Corke *et al* [26] and also agrees with our own observations by HVEM. As soon as some order has begun to form in a region of the alloy, the angles between the cube axes begin to deviate from 90°, and thus (100) ceases to be a symmetry plane and becomes a potential composition (K_1) plane for deformation-twinning, with [111] as shear direction. Presumably the driving force for twinning comes from the accumulation of lattice strains arising from the rhombohedral distortion of initially cubic domains. Order-twinning reduces such strains (Syutkin *et al* [13]; Tanner and Ashby [37]). No twins can form until ordering has begun; but twinning will be finished before ordering is complete. We do not know why this shear process is limited to slowly cooled alloys in this system; it may be that shear is initiated only at temperatures close to T_c.

The analysis of atom motions in the plane of shear (Fig. 19, right-hand side) shows that all atoms move to the correct *sites* without subsequent shuffles, but *half* the copper atoms finish up in sites where platinum atoms should be, and vice versa. To correct this, there has to be an exchange between neighbouring atoms after or during the shear: e.g. α and β can interchange. This is quite possible because this process is going on around 800°C, when diffusion is rapid. Once the twins are formed, with atom interchange complete, then the shear angle will increase steadily as the degree of order increases towards unity, because the shear angle is $2\Delta'$ and Δ' is proportional to the deviation from cubicity, Δ (see Fig. 19); Δ in turn increases with the order parameter. For the fully ordered alloy using Walker's [25] values of Δ, the angle Δ' was calculated to be 0.63°, so that the shear angle, $2\Delta'$ (Fig. 19), is 1.26°. This agrees very well with the shear angles, 1.20 to 1.24°, measured for the most highly sheared surfaces (which alone were selected for measurement). The nearest parallel to this kind of orderly transformation is probably the shear process observed for the CuAu (disordered) → CuAu II transformation by Smith and Bowles [14].

6. Conclusions

1. Ordering in stoichiometric CuPt takes place at all temperatures by a type I reaction: during ordering, ordered and disordered phases coexist.
2. Non-stoichiometric, platinum-rich copper-platinum alloys form a stable two-phase region within a broad range of compositions and temperatures.
3. (a) At high temperatures, CuPt forms order-lamellae. (b) At intermediate temperatures, coarse domains form at grain-boundaries, pores and scratches. These domains are not significantly harder than the disordered alloy. The matrix meanwhile orders dispersely into very fine domains arranged in the residual disordered phase: this array is hardened. The growth of the coarse domains into the matrix slows down as the matrix progressively orders. (c) At low temperatures, coarse domains grow in the form of rosettes, predominantly from pores; the matrix still acquires disperse order, but very slowly.

Details of the hardening of the various alloys have been presented elsewhere [2].

4. Alloys slowly cooled through the critical temperature order in the form of coarse macrotwins, internally subdivided by microtwins. The coarse twins shear the free surface, through angles up to about 1.24°. This shear has been tentatively interpreted in terms of a deformation-twinning model, which entails diffusive interchange of half the sheared atoms.

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References

1. R. S. IRANI and R. W. CAHN, *Nature* **226** (1970) 1045.
2. *Idem, Acta Metallurgica* **21** (1973) 757.
3. F. W. JONES and C. SYKES, *J. Inst. Metals* **59** (1936) 257.
4. R. S. IRANI, *Contemporary Physics* **13** (1972) 559.
5. J. L. O'BRIEN and G. C. KUCZYNSKI, *Acta Metallurgica* **7** (1959) 803.
6. M. GREENHOLZ, *J. Mater. Sci.* **7** (1972) 1285.
7. H. N. SOUTHWORTH, *Scripta Met.* **2** (1968) 551.
8. FU-WEN LING and E. A. STARKE, JUN, "Advances in X-ray Analysis", **15** (New York, Plenum Press, 1971) p. 319.
9. *Idem, Scripta Met.* **5** (1971) 741.
10. J. B. NEWKIRK, A. H. GEISLER, D. L. MARTIN, and. R. SMOLUCHOWSKI, *Trans. AIME* **188** (1950) 1249.
11. J. M. PENISSON, A. BOURRET, and P. H. EURIN, *Acta Metallurgica* **19** (1971) 1195.
12. M. HIRABAYASHI and S. WEISSMAN, *ibid* **10** (1962) 25.
13. P. N. SYUTKIN, V. I. SYUTKINA, O. D. SHASHKOV, E. S. YAKOYLEVA, and N. N. BUINOV, Third Bolton Landing Conf. (edited by B. H. Kear, C. T. Sims, N. S. Stoloff and J. H. Westbrook) (Claitors, Baton Rouge, 1970) p. 227.
14. R. SMITH and J. S. BOWLES, *Acta Metallurgica* **8** (1960) 405.
15. B. CHAKRAVARTI, E. A. STARKE, JUN, and B. G. LEFEVRE, *J. Mater. Sci.* **5** (1970) 394.
16. L. E. TANNER, *Acta Metallurgica* **20** (1972) 1197.
17. F. N. RHINES and J. B. NEWKIRK, *Trans. ASM* **45** (1953) 1029.
18. M. J. MARCINKOWSKI and L. ZWELL, *Acta Metallurgica* **11** (1963) 373.
19. F. W. NOBLE and W. FAIRHURST, *J. Mater. Sci.* **7** (1972) 781.
20. H. OKAMOTO and P. A. BECK, *Trans. AIME* **2** (1971) 569.
21. P. R. SWANN, W. R. DUFF, and R. M. FISHER, *Phys. Stat. Sol.* **37** (1970) 577.
22. H. WARLIMONT, K. BERNECKER, and R. LÜCK, *Z. Metallk.* **62** (1971) 816.
23. H. P. AUBAUER, *Acta Metallurgica* **20** (1972) 165; 173.
24. J. O. LINDE, *Ann. Physik.* **30** (1937) 151.
25. C. B. WALKER, *J. Appl. Phys.* **23** (1952) 118.
26. N. T. CORKE, S. AMELINCKZ, and J. VAN LANDUYT *Mat. Res. Bull.* **4** (1969) 289.
27. H. G. PARIS and B. G. LEFEVRE, *Mat. Res. Bull.* **7** (1972) 1109.
28. G. FOURNET, "Phase Stability in Metals and Alloys" (edited by P. S. Rudman, J. Stringer and R. I. Jaffee) (McGraw-Hill, New York, 1967), p. 195.
29. P. C. CLAPP and S. C. MOSS, *Phys. Rev.* **142** (1966) 418; **171**, 754, 764.
30. B. W. MOTT, "Micro-Indentation Hardness Testing" (Butterworth, London, 1956).
31. R. S. IRANI and R. W. CAHN, *Metallography* **4** (1971) 91.
32. S. TOLANSKY, "Multiple-Beam Interference Microscopy of Metals" (Academic Press, London, 1970).
33. A. SCHNEIDER and U. ESCH, *Z. Elektrochem.* **50** (1944) 290.

34. P. ASSAYAG and M. DODÉ, *Compt. Rend.* **239** (1954) 762.
35. H. WARLIMONT, *J. Sheffield Met. Soc.* **7** (1968) 45.
36. R. S. IRANI, FU-WEN LING, and R. W. CAHN, to be published.
37. L. E. TANNER and M. F. ASHBY, *Phys. Stat. Sol.* **33** (1969) 59.

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