oxygen present in your apparatus, so that the material you studied was an oxychloride? Such an oxy-chloride would more likely assume a spinel structure than would cuprous chloride.

A. GoswAMI: We have considered the possibilities of the formation of cuprous oxychloride. Known oxychloride does not have a spinel structure. But, as the film was too thin, we are not sure of its composition and it could not be subjected to chemical analysis. We don't even know the composition of the film.

S. OGAWA: Isn't there any possibility that your spinels were caused by oxides? How high was your vacuum?

A. Goswami: Since we took pure cuprous chloride, the oxide was not present in the original compound. But during evaporation it dissociated to Cu_3Cl_4 and Cu, we believe. We are not sure of the formation of oxide, since no chemical analysis could be carried out on the film. Vacuum was $\simeq 1 \times 10^{-2}$ mmHg.

JOURNAL OF THE PHYSICAL SOCIETY OF JAPAN Vol. 17, SUPPLEMENT B-II, 1962 PROCEEDINGS OF INTERNATIONAL CONFERENCE ON MAGNETISM AND CRYSTALLOGRAPHY, 1961, Vol. II

On the Anti-Phase Domain Structures in Ordered Alloys

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Recent studies on the anti-phase domain structures in ordered alloys by electron diffraction and electron microscopy are surveyed.

In the course of the ordering of alloys, domains out of phase with each other in their manner of ordering will arise. Such antiphase domains will affect the aspect of super-



Fig. 1. Electron diffraction pattern of a partially ordered Cu₃Au.

lattice reflections in diffraction patterns. This diffraction effect was confirmed on a partially ordered Cu_3Au by X-ray diffraction¹⁾, but the electron diffraction work by Raether²⁾ more clearly showed characteristic shapes of superlattice spots caused by the formation of anti-phase domains in this alloy, as shown in Fig. 1. Well oriented evaporated films were used in this case. Such anti-phase domains will increase in size as the ordering proceeds by atomic diffusion and at last domain boundaries will vanish. In fact,



Fig. 2. Isothermal growth of anti-phase domains in $\mathrm{Cu}_3\mathrm{Au}.$

it was observed from diffraction patterns that they grow up quickly with temperature rise²⁾ and slowly with the lapse of time even at comparatively low temperatures.³⁾ Fig. 2 shows isothermal curves of the growing.

On the other hand, there are many ordered alloys which possess anti-phase domains in their equilibrium state of order. Domains are definite in their size throughout the lattice in these alloys, that is, change of step in the atomic ordering takes place periodically after each few unit cells. Therefore, the lattice period becomes longer along the direction of domain alignment. Clear splittings of superlattice reflections are characteristic of this periodic anti-phase structure, and a typical example is seen in the diffraction



Fig. 3. Electron diffraction pattern of CuAu (II).

pattern of CuAu (II)⁴⁾, as shown in Fig. 3. In this case, the fundamental structure, Cu-Au (I), is composed of alternate gold and copper layers, and the period of changes of step, i.e. the domain size is five times the unit cell (Fig. 4). Thus the lattice period becomes ten times the original unit cell along the direction of domain alignment. The domain size seems not to change with temperature but to considerably change with composition. Evaporated films grown epitaxially on cleavage faces of rocksalt are very suitable for studying this structure and are often used, because electron diffraction patterns obtained from them reveal the intensity distribution in a reciprocal plane with little distortion. The domain size can easily be found from the separation in split superlattice reflections, i.e. the former is inversely proportional to the latter, and even a single diffraction pattern can provide much information on the atomic arrangement. Thus many ordered alloys with periodic anti-phase structure, such as $Ag_{3}Mg^{5}$, $Au_{3}Zn(H)^{6}$, $Pd_{3}Mn^{7}$, Cu₃Pd⁸⁾, Au₄Zn⁶⁾, Au₃Mn⁹⁾ etc., besides CuAu (II), have been studied in our laboratory, us-



Fig. 4. Structure of CuAu (II).



Fig. 5. Anti-phase in A₃B type face-centered lattice.

ing single-crystalline evaporated films.

These ordered alloys of A₃B type have a common fundamental structure, which is represented by the unit cell of Cu₃Au. In this structure the B atom can occupy any of basic positions, as shown in Fig. four When a set of several cells neigh-5a. another in which the B atom bours occupies a different position from that in the former set, an anti-phase relation occurs. There are two kinds of out-of-step vector in this case, i.e., one is such that two B atoms at the boundary do not occupy nearest neighbor positions (Fig. 5b). This is called "outof-step vector of the first kind." The other is that which allows two B atoms at the boundary to come into contact with each other (Fig. 5c), and this is "out-of-step vector of the second kind." When anti-phase domains are aligned only along one direction, this is called one-dimensional anti-phase structure. There are three possible orientations of the one-dimensional structure in the lattice. No one-dimensional domains connected by the second kind of vector, however, have ever been observed. Ag₃Mg, Au₃-Zn (H), Pd₃Mn and Cu₃Pd (α'') with less Pd content possess the one-dimensional structure. Fig. 6 shows a diffraction pattern of Cu₃Pd (α'') . Slight elongation or contraction takes place along the alignment direction of domains in most cases.

Cu₃Pd (α'') with more Pd content, Au₄Zn, some of ternary alloys Cu-Au-Zn¹⁰ and Au₃-



Fig. 6. Electron diffraction pattern of $Cu_3Pd(\alpha'')$ with one-dimensional anti-phase domains.

Mn, on the other hand, exhibit a two-dimensional structure. That is to say, the antiphase relation takes place simultaneously along two [100] directions, which leads to the formation of a coherent two-dimensional domain structure. In this case the second kind out-of-step vector is allowed. Diffraction patterns caused by the two-dimensional structure were theoretically treated by Perio Tournarie on ordered Cu₃Au type and alloy¹¹⁾. The treatment is rigorous, and the distribution of the diffracted amplitude in any (001) reicprocal plane can be defor all possible combinations termined of the two kinds of out-of-step vector. In actual cases, however, only two types two-dimentional structure have of the been found. The structure found in Cu₃Pd (α'') , Au₄Zn and some of Cu-Au-Zn alloys is characterized by both the first and second kind vectors along the two alignment direc-



Fig. 7. Two-dimensional domain in Cu_3Pd (α'') with excess Pd content. Domain sizes are assumed to be 5 and 4 along x and z directions, respectively.



Fig. 8. Two-dimensional domain in Au₃Mn. Domain sizes are assumed to be 1 and 2 along x and y directions, respectively.

tions, as shown in Fig. 7, while anti-phase domains in Au₃Mn and some of Cu–Au–Zn alloys are combined only by the first kind vector along both directions, as shown in Fig. 8. Figs. 9 and 10 are diffraction patterns of Cu₃Pd(α'') with more Pd content and Au₃Mn, respectively. There are also several possible orientations of the two-dimensional structure in the lattice. The structure in which the anti-phase relation takes place simultaneously along three directions has so far not been observed in any ordered alloy.

The periodic anti-phase structure has the following two remarkable features: The first is the apparent non-integrality of domain size estimated from diffraction patterns. For example, the domain size in CuAu (II), meas-



Fig. 9. Electron diffraction pattern of Cu₃Pd (α'') with two-dimensional anti-phase domains.



Fig. 10. Electron diffraction pattern of Au_3Mn (Watanabe⁹⁾).

ured in the original unit cell, continuously increases from 5 to 6 with deviation of composition from 50: $50^{12/4}$. It is continuously decreased in Ag₃Mg with increasing Mg content⁵⁾, as shown in Fig. 11a, and also in Cu₃-Pd (α'') with increasing Pd content^{8) 13)}, as shown Fig. 11b, taking fractional values. This non-integrality is conceivable as mixing integral values, and Fujiwara¹⁴⁾ showed theoretically that sharp diffraction maxima result from such a mixture of different domain sizes, using his anti-phase function, as shown



Fig. 11. Change of domain size in Ag₃Mg (a) and Cu₃Pd (α'') (b).



Fig. 12. Anti-phase function as defined by Fujiwara¹⁴).

in Fig. 12. Fig. 13 is the result of his calculation, showing peaks at positions corresponding to a non-integral domain size. He remarked that some irregularity in mixture might be allowed in this case, provided that different sizes of domain were uniformly distributed, although a regular uniform structure would naturally be a proper one. The difference between a strictly regular



Fig. 13. Intensity distribution given by numerical calculation of Fujiwara.¹⁴⁾ M=1.80, N=72, uniform regular arrangement.

uniform structure and a uniform structure including some irregularity can be distinguished only by the most precise measurement of intensity. Perio and Tournarie¹¹⁾ also studied this problem theoretically, using their "creneau" function. Their mathematical treatment is a beautiful generalization of Fujiwara's and seems to necessitate a little corrections to the diffracted amplitudes calculated by the latter author in some cases.

The second feature of the periodic antiphase structure is the formation of "satellites" flanking intense reflections. These satellites can clearly be seen, e.g., around the direct spot on the diffraction pattern of CuAu (II) in Fig. 3. They are observable to the third order on the original photographic plate. Their separation from the relevant main spot is the same as that between two neighboring split spots of superlattice reflections, {110}. According to our opinion, this fact suggests that a lattice period as large as the domain size exists in the structure.

This means that the lattice with the periodic anti-phase structure is modulated by a periodic change of scattering factor or of lattice spacing or of both. Ogawa and Watanabe previously assumed this modulation to be based on a periodic error of the spacing at domain boundary in case of CuAu (II)4). Glossop and Pashley¹⁵⁾ considered, however, not such a modulation but double diffraction to be the origin of the satellites. Ogawa, Watanabe, Watanabe and Komoda took a diffraction patterns of oblique incidence of CuAu (II) as well as CuAu with some Zn content, tilting the film around the crystallographic axis^{16) 17)}. Fig. 14 shows a pattern of the latter. The satellites lying on the axis of rotation still remained, while split superlattice reflections vanished. This fact means that a greater part of the intensity of the satellites is certainly ascribed to the said modulation, although a smaller part may be caused by double diffraction. This was proved by Watanabe to be true also in case of Au₃Mn¹⁸⁾. Perio and Tournarie¹⁹⁾ considered that only a periodic change of composi-



Fig. 14. Electron diffraction pattern of a Cu-Au-Zn alloy. The film was tilted. [110] incidence.



Fig. 15. Density modulation in CuAu (II) estimated by Perio and Tournarie¹⁹⁾ from the electron diffraction pattern obtained by Glossop and Pashley.¹⁵⁾

tion, i.e., a modulation of density causes the satellites to occur. A departure from stoichiometric composition increase the intensity of the satellites. They estimated the amplitude of the density modulation from the observed intensity of the satellites in CuAu (II). Fig. 15 is the result of their estimation. Watanabe¹⁸⁾ gave this problem a deliberate consideration in case of Au₃Mn, making a two-dimensional Fourier map, and concluded both periodic changes of lattice spacing and scattering factor to exist in this case. According to him, it is suggested that some distortion in the distribution of valence electrons exists at domain boundaries. The distortion will lead to the periodic error of potential distribution which may involve both types of the lattice modulation. Thus the satellites at small $\sin \theta / \lambda$ are fairly intense in electron diffraction patterns, while they may be much diminished in intensity in X-ray diffraction patterns. Cowley²⁰⁾ presented recently a statistical theory on order parameters. According to his theory, there is a fluctuation in average composition in the equilibrium state of order in Cu₃Au type alloys. This is realized, if atom pairs of the same kind are somewhat increased at antiphase boundaries. Such a periodic fluctuation of composition may lead to the occurrence of the satellites. To sum up, however, it seems impossible at present to determine which theory is capable of exactly explaining the origin of the satellites.

Anti-phase domains in evaporated films can be observed in electron micrographs of bright field or dark field, using the satellites around the direct spot or superlattice split spots themselves. By the bright field technique Ogawa, Watanabe, Watanabe and Komoda¹⁶⁾ first



Fig. 16. Electron micrograph of the domain alignment in CuAu (II).

observed the domain distribution in CuAu(II) as parallel lines with intervals of 20 Å in electron micrographs. Fig. 16 shows such lines. This interval coincided well with the domain size in this alloy. Some imperfections were found in the line system, as indicated by the arrow. A mixture of domain sizes leading to an apparent non-integral size was examined by measuring each line interval, and a histogram obtained showed two peaks. at neighboring integral values (Fig. 17). A mixing mode was also examined, but a further deliberated study seems necessary to draw a definite conclusion. Pashley and Presland²¹⁾, on the other hand, obtained a histogram showing a peak at a half integral domain size which was near to the value estimated from diffraction observations (Fig. 18). They







Fig. 18. Histogram of the line spacings in CuAu (II), measured on a dark field image by Pashley and Presland.²¹⁾

considered that the domain size should be measured not by the original unit cell but by the interplanar spacing.

If Zn is added to CuAu and a suitable heat-treatment is imposed, Cu-Au-Zn alloys isomorphous with CuAu (II) are formed¹⁰¹¹⁷¹. The domain size is decreased with increasing Zn content in this case. Smaller domains in these Cu-Au-Zn alloys also revealed themselves in electron micrographs, down to a line interval of 8 Å (Fig. 19).



Fig. 19. Electron micrograph of the domain alignment in a Cu-Au-Zn alloy. The line spacing is about 8Å.

By the dark field technique Glossop and Pashley¹⁵⁾ obtained the line system with more contrast in micrographs of CuAu (II) and succeeded in observing clearly various imperfections of the lines. They explained well these imperfections by the relation between dislocation and anti-phase boundary. By their continuous observation on CuAu films heated in the microscope the details of the transition from CuAu (I) to CuAu (II) were revealed. These observations were so excellent and remarkable that they contributed much to increasing universal interest in the antiphase structure. Evaporated films employed by Glossop and Pashley seems to have been fairly uniform in thickness. They prepared the films not directly on rocksalt cleavage faces but on thick silver films epitaxially grown on these faces. This technique may be useful in making the film thickness uniform.

Ogawa and Watanabe²²⁾ made observation on the distribution of two-dimensional domains of Cu₃Pd (α'') using the dark field technique. The (010)_{eub} and (110)_{eub} diffraction spots groups were used to form images. Several systems of parallel lines observed showed two definite values of the line intervals, which coincided with the two side lengths of the two-dimensional domain estimated by electron diffraction. Fig. 20 is an example. The two values of the line intervals varied from film to film due to the composition change and were 12 to 16 Å and 15 to 26 Å, respectively. Crossing lines obtained by using the (010)_{eub} group revealed most intuitively the two-dimensional domain. An



Fig. 20. Electron micrograph of Cu_3Pd (α'') with two-dimensional domains, taken by the dark field technique using the (010) spots group. The two values of the line intervals are 16 and 26Å.



Fig. 21. Crossing lines obtained from twodimensional domains of Cu₃Pd (α''). The (010) spots group was used.

example is seen in Fig. 21.

The image contrast of domain boundaries in the above cases was formed when electrons were incident in parallel with the boundaries. The theory of image formation in such a case seems to be lacking at present.

As is described at the beginning of the present paper, anti-phase domains exist in a partially ordered Cu₃Au. They seem unstable, and splits of superlattice spots are very diffuse, unlike those arising from the periodic anti-phase structure. Fisher and Marcinkowski²³⁾ observed electron-microscopically the domain distribution in thin sections of electropolished Cu₃Au, chiefly by means of the bright field technique. The specimens were ordered by annealing at a temperature near $T_{\rm c}$ or by slow cooling, and hence the domain size estimated from line breadth of X-ray diffraction was considerably larger and 500~1000 Å. This large size did not give rise to any appreciable diffuseness of superlattice spots in the electron diffraction pattern. Electron micrographs obtained showed irregular maze-like images of domain boundaries. A random distribution of domains as deduced from micrographs may give rise to those diffuse splits of superlattice spots in the diffraction pattern which are discernible at small domain size. Changes of step can be thought of as a kind of stacking fault, and images of domain boundaries should, therefore, give similar contrast to those of stacking faults. If the boundaries make a large angle with the incident direction of electrons and the contrast is formed by superlattice reflections, interference fringes will be expected also in the present case. The extinction distance is, however, much larger, about 1000 Å for 100 kV electrons, owing to small structure amplitudes of superlattice reflections. Notwithstanding, Fisher and Marcinkowski could observe the boundary contrast to change with varying thickness and varying incident angle, and even the fringe contrast was found in some cases.

The boundary images in Cu₃Au were observed also in evaporated films by Yamaguchi, Watanabe and Ogawa²⁴⁾, the dark field technique being used. In this case irregular boundaries were seen for a smaller value of mean domain size, about 70 Å in Fig. 22a, as well as for a larger values, 350 Å in Fig. 22b.

The former value coincided with that estimated from the corresponding diffraction pattern. Fisher and Marcinkowski presented a model of the domain distribution which could explain their observations. In this model boundaries can be formed, whether the outof-step vector is of the first kind or of the second kind. According to our observation on evaporated films, however, the model seems to have to be somewhat corrected, because two micrographs in which the (100) and (110) diffraction spots were used, respectively, gave very different aspects, while these micrographs should be similar to each other, according to their model. Fig. 23 shows an electron micrograph using the (100) spot. In the corrected model, domain boundaries





(b)

Fig. 22. Electron micrographs of antiphase domains in Cu₃Au annealed at 330°C for 3 hrs (a) and at 330°C for 32 hrs (b) after quenching. The (110) spot was used to form dark field images.



Fig. 23. Electron micrograph of anti-phase domains in Cu_3Au annealed at 330°C for 16 hrs after quenched and slowly cooled. The (100) spot was used.

which are formed by changes of step of the second kind are very few, so that gold atoms rarely come to contact. Fisher and Marcinkowski seem to have observed only the images formed by the (110) reflection. The actual domain distribution will be much affected by the existence of dislocations owing to the similarity between Burgers vector and out-of-step vector.

As is clearly understood from the above description, there is a distinct difference between the periodic anti-phase structure and the random distribution of domains in Cu₃Au. In connection with this fact, it should be noted that the former structure was recently found by Scott²⁵⁾ in Cu-Au alloys with a little more gold content than Cu₃Au, using X-rays. The domain size was 9 cells at 31.6 at. % Au. This fact was confirmed in evaporated films by electron diffraction in our laboratory and the electron micrograph showed a regular line system²⁴⁾.

Some theoretical approach to elucidating the origin of periodic anti-phase structure has been made. Schubert²⁶⁾ correlated the frequency of changes of step with the valence electron concentration in various ordered alloys and tried to explain the phenomenon by "Ortskorrelation der Elektronen." A theory taking the second nearest neighbor interaction into account has recently been developed by Adachi²⁷⁾. This theory is at present only crude but seems promising. Toth and Sato²⁸⁾ have very recently presented an excellent theory based on Brillouin zone consideration. This theory can well explain the change of domain size in CuAu (II) with addition of various elements of different valence. The details are given by them in the present Symposium (this volume p. 262).

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JOURNAL OF THE PHYSICAL SOCIETY OF JAPAN VOL. 17, SUPPLEMENT B-II, 1962 PROCEEDINGS OF INTERNATIONAL CONFERENCE ON MAGNETISM AND CRYSTALLOGRAPHY, 1961, VOL. II

On the Long Period Superlattice in Alloys

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To investigate the origin of long period superlattices found in alloys, a detailed study of factors which affect the period of CuAu II was made. Utilizing the thin film technique, the effect of many additional elements in varying concentrations on the domain size of CuAu II was determined using electron diffraction. From the data, a definite relation was found between the electron-atom ratio of alloys and the domain size. There did not appear to be any systematic relation between the data and other factors such as atomic size, weight, etc. From these results, a theory based upon the stabilization of alloy phases at the Brillouin zone boundary was formulated to show the variation of the electron-atom ratio with the domain size. The agreement between theory and experiment is excellent. In addition, the model gives a good explanation of other one and two dimensional superlattices found in A_3B type alloys.

Introduction

The superlattice CuAu II is a modification of the ordered CuAu I structure and is characterized by regular antiphase boundaries at each 5 unit cell lengths in the b-direction. This alloy, at the stoichiometric composition CuAu, exists between the disordered phase and ordered CuAu I phase, whose transition temperatures are 410°C and 380°C respecti-The unit cells of the two ordered velv. structures are shown in Fig. 1. Experimental data indicate that CuAu II is not a transition phase but an equilibrium phase. Consequently the question arises why the alloy prefers to take a complicated antiphase structure instead of the usual simple one.

These long period structures have been found in many alloy systems,¹⁾ and because of their frequent occurrence, their stability should be due to a common origin. This paper discusses the attempts made to understand the origin of long period superlattices, taking CuAu II as a typical example.²⁾

Experimental method and results

One of the characteristics of a long period superlattice is the period or domain size M, as shown in Fig. 1. To investigate the origin of such a superlattice, one should determine what factors affect the period and the stability range.

The domain size can be obtained from the

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