Study of the Ordered Structures of the Au–Mn System by High-Voltage–High-Resolution Electron Microscopy. III. Two-Dimensional Antiphase Structure of Au₃Mn Type

BY O. TERASAKI AND D. WATANABE
Department of Physics, Faculty of Science, Tohoku University, Sendai 980, Japan

(Received 18 August 1981; accepted 15 December 1981)

Abstract

High-resolution structure images of the 23.5 and 24 at.% Mn alloys annealed at 573 K were studied by 1 MV electron microscopy. It was shown that the 24 at.% Mn alloy consists of two-dimensional antiphase structure (2d-APS) of Au₃Mn with the boundaries parallel to the (100) and (010) planes. The average domain sizes were measured as $M_1 = 1.04$ and $M_2 = 2.41$, and an orthorhombic structure model with $M_1 = 1$ and $M_2 = 2.5$ was proposed for the ideal structure of the 2d-Au₃Mn. From the 23.5 at.% Mn alloy, the structures corresponding to the intermediate state between the 2d-Au₃Mn and the 2d-APS(I), which consists of lozenge- and parallelogram-shaped domains and exists in the alloys with 21–23 at.% Mn, were observed. It was concluded that the statistical order of appearance of the stable ordered phases with increasing Mn content in the composition range of 20–24 at.% Mn is Au₄Mn→Au₂₂Mn₀→Au₃₂Mn₀→2d-APS(I)→2d-Au₃Mn (so-called Watanabe structure).

1. Introduction

One of the authors studied the crystal structures of the Au–Mn system by electron diffraction, using thin evaporated single-crystalline alloy films, about twenty years ago and proposed a two-dimensional antiphase structure (2d-APS) model of Au₃Mn type, which is based on the $L1_2$ structure and has the two first-kind antiphase boundaries (APB's) parallel to the (100) and (010) planes (Watanabe, 1960). The same diffraction patterns as those observed by Watanabe were then observed by several investigators from evaporated films (Sato, Toth, Shirane & Cox, 1966; Yamamoto, 1980) as well as from the bulk specimens (Sato, Toth & Honjo, 1967), and the structure is called the 2d-Au₃Mn and sometimes the Watanabe structure.

Recently, Van Tendeloo, De Ridder & Amelinckx (1978) studied the ordering of the Au₄Mn alloy by electron diffraction and dark-field electron microscopy. They observed diffraction patterns similar to those observed by Watanabe in the stable state, using well annealed bulk specimens. This work formed part II of the present study (Terasaki, Watanabe, Hiraga, Shindo & Hirabayashi, 1981) and confirmed that the 2d-APS's do exist in the stable state, using well annealed bulk specimens. From the 23.5 at.% Mn alloy, the structures corresponding to the intermediate state between the 2d-Au₃Mn and the 2d-APS(I), which consists of lozenge- and parallelogram-shaped domains and exists in the alloys with 21–23 at.% Mn, were observed. It was concluded that the statistical order of appearance of the stable ordered phases with increasing Mn content in the composition range of 20–24 at.% Mn is Au₄Mn→Au₂₂Mn₀→Au₃₂Mn₀→2d-APS(I)→2d-Au₃Mn (so-called Watanabe structure).

In the present paper, it is shown that the structure gradually changes from 2d-APS(I) as the Mn content increases from 22.6 at.% Mn and the 24 at.% Mn alloy consists mainly of the 2d-Au₃Mn structure with boundaries parallel to the (100) and (010) planes.

II. Experimental

The method of sample preparation is the same as in part II. Two samples with nominal compositions 23.5 and 24 at.% Mn were prepared and annealed for ordering at 573 K for 33 days. We know from the previous work (part II) that Mn content of the samples is decreased by 0.3–0.5 at.% from the nominal composition, probably due to high volatilization of Mn in the sample preparation. For example, the Mn content of the 23 at.% Mn alloy was determined at 22.6 at.% Mn by chemical analysis with the permanganate titration method after ammonium persulfate oxidation (standard deviation was 0.1 at.% Mn). In the present paper, specimen composition is described in terms of nominal composition.

High-resolution images were taken with the 1 MV electron microscope under the condition that the
positions of the Mn atoms projected along the beam direction are observed as bright dots (Terasaki, Watanabe, Hiraga, Shindo & Hirabayashi, 1980; Hiraga, Shindo, Hirabayashi, Terasaki & Watanabe, 1980).

III. Results

III-1 Electron diffraction patterns

Diffraction patterns obtained from the 23.5 and 24 at.% Mn alloys annealed at 573 K are shown in Figs. 1 and 2, respectively, which exhibit the characteristic features of 2d-APS in the present system. Fig. 1 corresponds to the intensity distribution in the (001) reciprocal-lattice section, whereas the pattern in Fig. 2 is not of single domain orientation but of a superposition of different orientation variants and it is seen from the positions of superlattice spots that the fundamental face-centred cell is distorted slightly to tetragonal with $c/a < 1$. No new long period is detected along the [001] direction. It is to be noted that the configuration of superlattice spots is different from that of the 2d-APS(I) and corresponds to that of the Watanabe structure; fine superlattice spots characteristic of the 2d-APS(I), represented by open circles in Fig. 3(b) of part II, are not observed. The average domain sizes, $M_1$ and $M_2$, along the [100] and [010] directions defined in the Watanabe structure (Watanabe, 1960) were measured on the diffraction patterns; $M_1 = 1.13$, $M_2 = 2.42$ and $M_1 = 1.04$, $M_2 = 2.41$ for the 23.5 and 24 at.% Mn alloys respectively.

III-2 High-resolution images

(a) Au–24 at.% Mn alloy: High-resolution image taken with the [001] incidence from the Au–24 at.% Mn is shown in Fig. 3(a) and the enlarged image in Fig. 3(b). A schematic illustration of the upper part of Fig. 3(b) is given in Fig. 3(c). In the [100] direction are seen the dark, broad fringes of average spacing of about 10 Å, which correspond to the APB’s parallel to the (010) plane, in contrast with the images obtained from the 21–23 at.% Mn alloys (part II). It is remarkable that the dots with a separation of 2.9 Å, corresponding to the nearest neighbour pairs (NNP) of Mn atoms, are clearly seen at the boundaries, and the structure is considered as the 1d-APS based on the $D_{0_{22}}$ structure with boundaries parallel to the (010).

Over most of Fig. 3(b), the APS’s exist periodically and an idealized structure model is derived, as shown in Fig. 4, where Au and Mn atoms are represented by open and solid circles respectively, and large and small circles are at two different levels along the [001] direction. It has an orthorhombic symmetry with the space group $Pamm$ (No. 51) and lattice constants $A = 2a (= 8.12 \text{Å})$, $B = 5b (= 20.30 \text{Å})$ and $C = c (= 4.04 \text{Å})$, and contains 30 Au and 10 Mn atoms in the unit cell. This structure can be described as the 1d-APS of $D_{0_{22}}$, where the antiphase vectors, $(a + c)/2$ and $(-a + e)/2$, are operative alternately at every 2.5 (= $M_2$) cells of $D_{0_{22}}$ structure, or it may be understood as the 2d-Au$_3$Mn structure with $M_1 = 1$ and $M_2 = 2.5$.

However, the whole of the crystal is not covered perfectly with this orthorhombic structure and various kinds of irregularities or modulations are observed in the image. There are many places where the domain has a two-unit-cell width ($M_2 = 2$) in the [010] direction, instead of $M_2 = 2.5$, as can be seen in Fig. 3(c). Such domains do not extend to the grain boundary, but terminate within the grain, thus giving rise to the jogged APS’s. The neighbouring domains have the size of $M_2 = 2.5$ in most places, but sometimes domains with $M_2 = 3$ exist over small areas. Consequently, the sequence of antiphase domains in the [010] direction is different from place to place; in Fig. 3(c), for example, the sequence is

- $2.5$ $2.5$ $2.5$ $2.5$ $2.5$ $2.5$ $2.5$ .... along $A$.
- $2$ $2.5$ $2.5$ $2.5$ $2.5$ $2.5$ $2.5$ $2.5$ .... along $B$.
... 2.5 2.5 2 3 2 3 2.5 .... along C.

The non-integer value of $M_e$ (=2.41) obtained from the diffraction pattern is accounted for by the existence of $M_2 = 2$ domains. The existence of $M_2 = 2$ and 3 domains plays an important role also in explaining the intensity distribution in the observed diffraction pattern. If the whole of the crystal consisted of the orthorhombic superstructure (or the $M_2 = 2.5$ domains), a density modulation would exist along the [001] direction, i.e. the number of Mn atoms at two different levels, $z=0$ and $z=1/2$, would be different, and the superlattice spots, 001, 110, ..., would be expected to appear. However, this is not the case; the density modulation is cancelled by the introduction of the domains with $M_e = 2$ or 3, as easily seen in Fig. 3(c), and the spots, 001, 110, ..., do not appear, in agreement with the observation (see Fig. 2). There are local concentration fluctuations near the jogs of APB's; the Mn-Mn NNP's keep close at the jogs. However, there are the places nearby where they keep away from each other, and therefore the average Mn concentration appears to be about 25 at.~o around the jogs.

There are also some places where the basic unit of the orthorhombic structure deviates from $D0_{22}$ (which

Fig. 3. (a) High-resolution image of Au-24 at.~o Mn alloy. (b) Enlarged image of (a). (c) Atomic arrangement corresponding to the upper part of (b). Open and solid circles represent Au and Mn atoms respectively. Lines of screen-tone indicate the boundaries where the Mn-Mn NNP's are localized.
is the 1d-APS based on the L12 with $M_1 = 1$ and two unit cells of the L12 structure continue along the [100] direction, as indicated by short arrows in Figs. 3(b) and (c). The existence of this kind of deviation explains the non-integer value of $M \approx 1.04$ obtained from the diffraction pattern. Geometrically, the structure on one side of such a place cannot maintain the orthorhombic symmetry if there is no other irregularity around it, as schematically illustrated in Fig. 5; arrangement of the Mn--Mn NNP's in the APB is different from that in the orthorhombic structure. In fact, this kind of APB can be seen in the image, as depicted in Fig. 3(c). It is to be noted also that the APB's near such deviations are of the 2d-APS(I) type and have the Au$_4$Mn-type structure, thus accommodating the deficiency of Mn atoms in the specimen with 24 at.\% Mn.

(b) Au-23.5 at.\% Mn alloy: Images obtained from the 23.5 at.\% Mn alloy consist mainly of regions where lozenge-shaped or parallelogram-shaped domains with the D0$_{22}$ structure are dominant, and regions having the 2d-Au$_3$Mn type structure as described above, resembling the image of the 22.6 at.\% Mn alloy:annealed at 573 K (see part II). In the former regions there is a tendency for the lozenge-shaped domains with \(4 \times 4\) columns of Mn atoms to prevail over the \(3 \times 3\) or \(4 \times 3\) domains, as shown in Fig. 6(a), in contrast with the 2d-APS(I)'s. If the structure is covered completely with the \(4 \times 4\) domains, the composition will be 22.9 at.\% Mn, whereas the structure models proposed for the 2d-APS(I)'s in part II have a composition of about 22.7 at.\% Mn. However, the configuration with \(4 \times 4\) domains only has not been observed. Instead, the shape of lozenge or parallelogram domains changes so that the Mn--Mn NNP's are formed at the APB's, as shown in Fig. 6(b) and (c), which are the enlarged image of a part of Fig. 6(a) and its schematic illustration. The domains extend to some extent along the [100] direction in certain places, and it is suggested that this state represents the first stage of a structure change from the 2d-APS(I) to the 2d-Au$_3$Mn-type structure.

Fig. 7(a) is another example of the enlarged image of a part of Fig. 6(a) and Fig. 7(b) is the schematic drawing. It appears that the structure corresponds to the intermediate state between the 2d-APS(I) and 2d-Au$_3$Mn structures; while the traces of lozenge- or parallelogram-shaped domains and the APB's having the atomic arrangement of the Au$_4$Mn structure are still recognized clearly, the Mn--Mn NNP's, which have never been observed in the 2d-APS(I), are formed frequently at the boundaries and have a tendency to line up in the [100] direction.

Average domain sizes, $M_1$ and $M_2$, in the [100] and [010] directions can be estimated from the images. It is interesting that the two regions shown in Figs. 6(b) and 7(a) give almost the same values, $M_1 = 1.1$ and $M_2 = 2.4$, being in agreement with those estimated from the diffraction pattern, $M_1 = 1.13$ and $M_2 = 2.42$.

(c) Computer simulation: Calculation of the images was made for the structure model shown in Fig. 4 by the multislice method as a function of specimen thickness near the Scherzer focus condition, using the fast Fourier transform algorithm, as was done in the previous studies (Terasaki et al., 1980; Hiraga et al., 1980; Terasaki, Mikata, Watanabe, Hiraga, Shindo & Hirabayashi, 1982). The results are shown in Fig. 8. A good matching with the observed image is obtained at the thickness of 162 Å; it is shown that the bright dots in the image correspond to the positions of Mn atoms and that the Mn--Mn NNP's with a separation of 2.9 Å can be resolved as two separate dots, as seen in the observed images.

IV. Discussion

In part II it was uncertain whether the 2d-APS(I)'s consisting of lozenge- or parallelogram-shaped do-
mains are stable or not when the Mn content in the alloy increases from 22.6 at.%. One of the possible structures which can accommodate the extra Mn atoms will be the 2d-APS's with larger lozenge or parallelogram domains containing \( n \times n' \) columns of Mn atoms \((n,n'>4)\). If the structure is assumed to consist only of the lozenge-shaped domains \((n=n')\), Mn concentration, \( x_{Mn} \), is given by the relation,

\[
x_{Mn}/100 = n^2/2(n + 1)(2n - 1).
\]

In Fig. 9, \( x_{Mn} \) is plotted against \( n \). For 24 at.\% Mn, for example, \( n \) will be larger than 10.

In the images obtained from the 23.5 and 24 at.\% Mn alloys, however, the lozenge- or parallelogram-shaped domains of the size larger than \( 4 \times 4 \) are not observed. Instead, the domains change shape and extend along the \([100]\) direction, the extra Mn atoms are accommodated at the boundaries by forming the NNP's, and finally the structure transforms into the 2d-Au3Mn type.

In the pairwise interaction model for ordering in binary f.c.c. alloy systems (Kanamori & Kakehashi, 1977), it is expected that the ordered structure in the Au–Mn system approaches the D0\(_{22}\) with increasing Mn content in the composition range from 20 to 25 at.\% by forming larger and larger \( n \times n' \) domains without creating Mn–Mn NNP's if the relation, \( |V_1| \gg |V_i| \), is assumed to hold irrespective of the alloy composition, where \( V_i \) is the interaction constant of the \( i\)th-neighbour interaction. However, a number of the Mn–Mn NNP's are actually formed in the alloys examined in the present study. It is also worth noticing that the atomic arrangement of the Au3Mn type is still preserved in between the Mn–Mn NNP's at the antiphase boundaries, as can be seen in Fig. 3(c). In other words, the number of first- and third-neighbour Mn–Mn pairs increases and the number of second- and fourth-neighbour pairs decreases, compared with those in the D0\(_{22}\) structure. This fact suggests that the relation, \( V_1 \gg |V_i| \), does not hold in alloys containing more than about 23 at.\% Mn. In this respect, it will be interesting to re-examine whether the D0\(_{22}\) structure exists as a stable phase at the stoichiometric composition \( A_3B \), although the diffraction pattern corresponding to D0\(_{22}\) has been observed in the 25 at.\% Mn alloy by Sato \etal (1967).

---

**Fig. 6.** (a) High-resolution image of Au-23.5 at.\% Mn alloy. (b) Enlarged image of a part of (a). (c) Atomic arrangement corresponding to the framed area of (b).
On the other hand, it may be also expected that only the orthorhombic structure proposed in Fig. 4 is observed in the 25 at.\% Mn alloy, since it has a stoichiometric composition \(A_3B\). However, in the diffraction patterns and high-resolution images of the 24 at.\% Mn alloy examined in the present study, the 5\(H\) structure, which has long-period stacking order based on \(D_0_{22}\) and appears in the composition with more Mn content than that of the 2d-\(Au_3Mn\) (Sato et al., 1967), is observed in about one third of the specimen area, whereas neither the 5\(H\) nor any other type of structure has been observed in the 23.5 at.\% Mn alloy. This fact suggests that the existence range of the orthorhombic structure is limited to a narrow region near 24 at.\% Mn.

The structure model corresponding to Fig. 4 was derived by Van Tendeloo, Wolf, Van Landuyt & Amelinckx (1978), in the course of an electron-diffraction and dark-field electron-microscopic study of ordering in the \(Au_{1.1}Mn_4\) (26-7 at.\% Mn). According to them, this structure appears as a transitional phase only in the initial stage of ordering \([e.g.\ as\ quenched\ from\ 1173\ K\ or\ after\ a\ very\ short\ anneal\ (less\ than\ 1\ min)\ at\ 823\ K]\) and transforms to the monoclinic structure and then to the fully ordered \(X\)-phase (Belbeoch, Frisby, Gaignebet, Kleinberger & Roulliay, 1976) on further annealing. The present result has shown unambiguously, however, that the 2d-\(Au_3Mn\) structure, consisting mainly of the orthorhombic

![Fig. 8. Calculated images of the orthorhombic structure for thicknesses of 8.1–325 Å. Parameters used for calculation are also shown.](image)

![Fig. 9. Relation between Mn concentration \(x_{Mn}(\%)\) and size of the lozenge-shaped domain \((n \times n)\).](image)
structure, is a stable phase existing in the alloy with ca 24 at.\% Mn at a relatively low temperature of 573 K.

Based on the results of a series of high-resolution electron-microscopic studies (Hiraga, Hirabayashi, Terasaki & Watanabe, 1981; Hiraga et al., 1980; Terasaki et al., 1982) including the present result, it is concluded that the statistical order of appearance of the stable phases with increasing Mn content in the composition range of 20–24 at.\% Mn is

\[
\text{Au}_3\text{Mn} \rightarrow \text{Au}_{12}\text{Mn}_6 \rightarrow \text{Au}_{13}\text{Mn}_6 \rightarrow 2d-\text{APS(I)} \rightarrow 2d-\text{Au}_3\text{Mn (Watanabe structure)},
\]

although varying amounts of these structures coexist in the specimens. It is understood that the orthorhombic structure derived in the present study is an ideal structure for the 2d-Au$_3$Mn. Further investigation will be necessary, however, to clarify the stable structures existing in the alloys containing more than 24 at.\% Mn and the order of appearance with increasing Mn content.

The authors are grateful to Mr H. Ohta and Mr E. Aogaki of the 1 MV Electron Microscope Laboratory, Tohoku University, for their cooperative help in the present study, and also to Mr D. Shindo for his help in computer programming. This work has partly been supported by Grant-in-Aid for Scientific Research from the Ministry of Education, Science and Culture.

References


