On the Crystal Structure of the Banded Martensite in Cu-24.5 wt %Sn Alloy*

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The crystal structure and internal defects of the banded martensite in a quenched Cu-24.5 wt %Sn alloy have already been investigated by Nishiyama et al. However, since their results are rather unexpected in some respects, the crystal structure and the morphology were reexamined by means of electron microscopy and selected area electron diffraction. Consequently, the following different results were obtained. (1) The crystal structure of the banded martensites was a 18R type long period stacking order structure with a stacking sequence of AB'CB'CA'CA'BA'BC'BC'AC'AB'. (2) The internal defects of the martensites were stacking faults on the basal plane. (3) The habit plane of the martensites was close to the $(\bar{1}44)_{\beta_1}$ plane, consistent with the result of Greninger and Mooradian, which was determined by the two-surface analysis in bulk specimens. (4) The orientation relationship between matrix and martensite was consistent with the Kajiwara-Nishiyama relationship found in a thermally formed β'_1 Cu-Al martensite. (5) These results were compared with the so-called phenomenological theory, and good agreement was obtained between them.

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I. Introduction

The β phase alloys in the Cu-Sn system transform martensitically by quenching and subsequent cooling. The morphology and crystal structure of martensites depend upon the composition of the alloys concerned⁽¹⁾, like those in the Cu-Al system. Nishiyama et al.⁽²⁾⁽³⁾ reported two types of martensites in the alloy of 24.5 wt %Sn, that is, the banded β' martensite obtained by quenching into water at 0°C and the wedge-shaped β'' martensite obtained by further cooling to a lower temperature. According to their investigation, the crystal structure, internal defects and habit plane of the former are the 4H type long period stacking order structure, stacking faults on the $(122)_{4H}$ plane and the $(\bar{2}2\bar{3})_{\beta_1}$ plane respectively, while those of the latter are the 2H type stacking order structure, $(121)_{2H}$ twins and the habit plane not indexed. Although there is no problem in their results on the latter martensite, there are some unusual points for

the former martensite in the following respects.

(i) Almost all of banded martensites in other Cu-based alloys have a 18 R or 9 R type structure, and the 4H type is not found in their martensites.

(ii) The most probable stacking faults in long period stacking order structures are the ones on the basal plane. However, the ones they found are those on the $(122)_{4H}$ plane and no stacking faults were found on the basal plane.

(iii) The reported habit plane $(\bar{2}2\bar{3})_{\beta_1}$ is inconsistent with that reported by Greninger and Mooradian⁽⁴⁾ which has been determined by the two-surface analysis in bulk specimens.

Furthermore, they could not take diffraction patterns containing the c^* axis, which were unambiguous verification of the structure proposed.

Thus, the present investigation was undertaken to take diffraction patterns containing the c^* axis and to reexamine the above unusual points using alloys with the similar composition, and it was carried out by the methods of electron microscopy and selected area electron diffraction. As a possible crystal structure of the banded β' martensites, the following four long period stacking order structures were assumed in the same way as the previous

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workers⁽²⁾ did:

- (i) AB'(2H) $a=4.558\text{\AA}$, $b=5.402\text{\AA}$,
 $c=4.358\text{\AA}$,
- (ii) AB'AC'(4H) $a=4.558\text{\AA}$, $b=5.402\text{\AA}$,
 $c=8.716\text{\AA}$,
- (iii) AB'CB'CA'CA'BA'BC'BC'AC'AB'
(18R)
 $a=4.558\text{\AA}$, $b=5.402\text{\AA}$, $c=39.22\text{\AA}$,
- (iv) AB'CA'BC'(6R)
 $a=4.558\text{\AA}$, $b=5.402\text{\AA}$, $c=13.07\text{\AA}$.

The lattice parameters for each structure shown above were computed from those of β'' martensite determined by Soejima et al.⁽⁵⁾, by assuming that the size of the basal plane and the d-spacing between neighboring basal planes are unchanged from those of the concerned β' martensite.

II. Experimental Procedure

An alloy ingot was prepared by melting oxygen free copper of 99.99% purity and metallic tin of high purity (Pb 0.05%, Cu 0.03%, Fe 0.02%, Sb 0.03%, As 0.02%) together in a high frequency vacuum furnace, and subsequently by casting into a water-cooled copper mold of 19 mm in internal diameter in argon atmosphere. The composition of the ingot was determined by chemical analysis as Cu-24.4 wt%Sn (14.73 at%Sn), and no difference in the composition was detected between the top and the bottom of the ingot. The ingot was then homogenized for 24 hr at 700°C in vacuum, and forged into a square rod with the thickness of 12 mm at temperatures between 550 and 650°C and then rolled into sheets about 0.35 mm thick at temperature between 550 and 650°C. For transmission electron microscopy, small discs of 3 mm in diameter were cut from these sheets by a SERVOMET machine. They were then heat-treated in vacuum such that

$$700^{\circ}\text{C} \times 1 \text{ hr} \rightarrow \text{W.Q. at } 0^{\circ}\text{C}.$$

After polishing thus treated specimens by emery papers up to the thickness of 0.15 mm, they were electropolished by the Bollman method, the electrolyte used being a mixture of nitric acid and methyl alcohol (1: 2) kept at -30°C and the voltage used being 9V.

Then the material deposited on the surface of specimens was removed by a mixture of methyl-alcohol and acetone (1:1) with a small quantity of citric acid, and finally the foil was washed with an aqueous solution of ammonium. Since specimens were electropolished at -30°C , other martensites, which are different from those introduced by quenching, may be introduced during electropolishing. This point was checked by cooling specimens on the cold stage of an optical microscope, and no structural change was observed down to -100°C . Thus, it will be reasonable to conclude that cooling specimens during electropolishing does not produce other martensites in the specimens, except for a few special cases described in Sec. IV.2.

III. Results

1. Crystal structure

The crystal structure of a number of banded martensites corresponding to the acicular feature under optical micrography was investigated by the selected area electron diffraction method, and the diffraction patterns were analyzed assuming that all reflections in the patterns correspond to their reciprocal lattice points. As a result the structure of the banded martensites was identified as the 18R type long period stacking order structure rather than the previous 4H type one. The errors in d-spacings and interplanar angles between the measured and calculated ones were within 1~1.5% and 1.5°, respectively. The intensity distributions were well accounted for qualitatively by the 18R structure as shown in the following, but it was noted that the relative intensity of superlattice spots against fundamental ones was extremely weak in the present alloy system. This point will be discussed later. A typical electron micrograph of the banded martensites is shown in Photo. 1(a). The martensites are characterized by a parallel-sided plate-like morphology consistent with the optical micrograph shown by Nishiyama et al.⁽¹⁾, and by a number of striations due to stacking faults on the basal plane which is evidenced by the trace analysis shown later. The diffraction pattern taken from the framed

Photo. 1 (a) Electron micrograph of banded β' martensites.

(b) Diffraction pattern taken from the framed area in (a). See the text for meaning of symbols in the key diagram (b').

area in (a) is shown in (b), and is consistently indexed by 18R structure as shown in the key diagram, and it was not explainable by the 4H structure, provided that the reflections correspond to the reciprocal lattice points. The meaning of the symbols in the key diagrams of Photos. 1, 2, 3, and 4 (except for Photo. 3(c')) are as follows:

●: fundamental reflections

○: superlattice reflections
 ×: forbidden reflections
 ⊗: reflections due to double diffraction, originally forbidden.

Other typical diffraction patterns taken from these martensites are shown in Photo. 2. Since the diffraction pattern of (a) contains the c^* axis, it unambiguously shows that the structure is the 18R type, the zone axis of this

Photo. 2 Diffraction patterns taken from the several banded β'_1 martensites. Arrows in (d) and (e) indicate very weak superlattice reflections.

pattern being $[010]_{\beta_1'}$.†

The diffraction pattern (b) is also explainable by 18R structure only, and its zone axis is $[231]_{\beta_1'}$. The diffraction patterns (c), (d) and (e) can again be explained consistently only by the 18R structure, and the zone axes of these patterns are $[8\bar{9}1]_{\beta_1'}$, $[\bar{8}0\bar{1}]_{\beta_1'}$ and $[8, \bar{1}2, 1]_{\beta_1'}$, respectively. Although these patterns were not taken from the same martensite, they are related by a rotation around the $(\bar{2}, 0, 16)_{\beta_1'}$ axis in reciprocal space. To repeat, none of the patterns in Photo. 2 can be explained by the structure other than 18R among those structures assumed in Sec. I. In fact, no 4H structure reported Nishiyama et al. was observed in the present investigation.

As mentioned earlier, superlattice spots are observed to be extremely weak in Photo. 2 and often to be hardly visible (i.e. Photo. 2(d) and (e)). Thus, this effect sometimes makes the interpretation of diffraction patterns more complicated. This is observed not only in the martensite phase, but also in the matrix phase. Two reasons are conceivable for the effect. One is due to the off-stoichiometric composition of the alloy. The composition of the present alloy is 14.7 at%Sn as described in Sec. II. Thus, the deviation from the stoichiometric composition (Cu_3Sn) is quite large. The reason for the appearance of DO_3 type structure in the matrix phase in spite of such large off-stoichiometry is that the e/a ratio at this composition is 1.44, which is favourable for producing the so-called electron compounds. The structure factor for superlattice reflections at the stoichiometric composition is $(f_{\text{Sn}} - f_{\text{Cu}})$ (for both the matrix and martensite), while that at an off-stoichiometric composition is $X_{\text{Sn}}(f_{\text{Sn}} - f_{\text{Cu}})$, where f_{Sn} and f_{Cu} are atomic scattering factors for Sn and Cu, respectively, and X_{Sn} is the atomic fraction of Sn atoms occupying the Sn atom sites (obviously, the rest of the Sn atom sites, $(1 - X_{\text{Sn}})$, are occupied by Cu atoms). Thus, the intensity of superlattice reflections at the present composition

decreases by $(14.7/25)^2 = 0.33$ times that at the stoichiometric composition. The second reason is probably related with the phase decomposition⁽⁶⁾ or ω phase transformation⁽⁷⁾ which are reported to occur in the matrix phase. The extra reflections which presumably correspond to these phenomena were also observed in the present alloy, but the nature of these phenomena was not studied in detail in the present investigation.

2. Internal defects

The electron micrographs of banded martensites showed densely distributed parallel striations like those in Photo. 1(a). The trace analyses of these striations are summarized in the $(001)_{\beta_1'}$ stereographic projection of Fig. 1. The arcs in the figure represent the parts of the great circles on which the pole of the plane must lie. Since the arcs gather at the $(001)_{\beta_1'}$ pole, the striations must be due to the stacking faults on the basal plane. Thus, the internal defects of the banded martensite as the lattice invariant shear are concluded to be stacking faults on the basal plane. This result is in sharp contrast to that reported by Nishiyama et al.⁽²⁾

3. Habit plane

The habit plane of the banded martensite was determined by the trace analyses of elec-

Fig. 1 Trace analysis of stacking fault fringes in the $(001)_{\beta_1'}$ stereographic projection. All the trace normals gather at the $(001)_{\beta_1'}$ plane normals.

† The banded martensites were termed β' by Nishiyama et al., but they are termed β_1' in the present paper, since the structure is ordered and is analogous to the β_1' martensite in the Cu-Al system.

Fig. 2 Trace analysis of habit planes. The projection plane is $(001)_{\beta_1}$. All the trace normals come close to the $(144)_{\beta_1}$ plane normal.

tron micrographs and the corresponding diffraction patterns. The result is summarized in the $(001)_{\beta_1}$ stereographic projection of Fig. 2, in which arcs represent the part of the great circles on which the pole of the habit plane must lie. The mean pole for the habit plane is located near $(144)_{\beta_1}$, which is very close to $\{133\}_{\beta_1}$. Thus, the present result is consistent with that determined by the two-surface analysis on bulk specimens by Greninger and Mooradian.⁽⁴⁾

4. Orientation relationship

Photograph 3(a) is an electron micrograph showing a banded martensite imbedded in the β_1 matrix. The diffraction pattern taken from the martensite region framed with solid lines is shown in Photo. 3(b). The zone axis of this diffraction pattern is $[\bar{2}92]_{\beta_1'}$ as indexed in the key diagram. The diffraction pattern taken from the region containing both martensite and matrix, which is framed with dotted lines, is shown in Photo. 3(c). The zone axis of the matrix is $[111]_{\beta_1}$. Thus, the orientation relationship is easily obtained from this pattern by assuming that the zone axes for the two phases are parallel. That is,

$$(0\bar{1}1)[111]_{\beta_1} // (\bar{1}\bar{2}8)[\bar{2}92]_{\beta_1'}.$$

This orientation relationship is quite close to the Kajiwara-Nishiyama's one which was found for the thermally formed β'_1 Cu-Al

martensite⁽⁸⁾, that is,

$$(0\bar{1}1)[1\bar{1}\bar{1}]_{\beta_1} // (\bar{1}\bar{2}8)[2\bar{1}0]_{\beta_1'}.$$

In fact, the difference between the two orientation relationships is only 1.13° in the rotation around $[0\bar{1}1]_{\beta_1}$ axis. Thus, instead of proposing a new orientation relationship, the present authors take the view that the latter orientation relationship holds in the β'_1 Cu-Sn martensite also within experimental errors, because the latter expression has an advantage over the former from a physical point of view as discussed for the stress-induced β'_1 martensite in Cu-Al-Ni alloy⁽⁹⁾.

IV. Discussion

1. Comparison of the results with the phenomenological theory

The phenomenological theory was applied to the present transformation. Since the 18R structure is associated with shuffling (non-uniform deformation) on the basal plane, the lattice deformation from the DO_3 type matrix to the 18R type martensite can not be represented by a matrix in a strict sense. Thus, the martensite structure was approximated by a uniform monoclinic cell to facilitate the matrix representation. Although the principle of the present treatment is quite similar to that of Kubo and Hirano⁽¹⁰⁾ using the Ross-Crocker's double shear theory, the present calculation was carried out within the framework of the original Bowles-Mackenzie theory⁽¹¹⁾, because the direction and plane of the uniform shear and shuffling for the lattice deformation are the same. Since detailed procedure will be published elsewhere⁽¹²⁾ for β'_1 Cu-Al-Ni martensite, it is not repeated here.

The input data for the calculating are as follows.

- (i) The lattice parameter of the matrix (DO_3 type cell):

$$a_0 = 6.0378 \text{ \AA}^{(13)}$$

The lattice parameters of the martensite:

$$a = 4.558 \text{ \AA}, \quad b = 5.402 \text{ \AA}, \quad c = 39.22 \text{ \AA}$$

- (ii) The lattice correspondence is such that

Photo. 3 (a) Electron micrograph of a banded β_1' martensite.

(b) Diffraction pattern taken from the area framed with solid line in (a).

(c) Diffraction pattern taken from the area framed with dotted line in (a), showing the orientation relationship between β_1' martensite and β_1 matrix. In the key diagram (c'), closed circles (●) and open circles (○) represent the matrix and martensite reflections, respectively.

$$(101)_{\beta_1} \rightarrow (009)_{\beta_1'}, \quad \frac{1}{2}[10\bar{1}]_{\beta_1} \rightarrow [100]_{\beta_1'}, \\ [010]_{\beta_1} \rightarrow [010]_{\beta_1'}$$

- (iii) The lattice invariant shear is a slip in $[\bar{1}01]_{\beta_1}$ direction on $(101)_{\beta_1}$ plane, which is equivalent to the slip $[\bar{1}00][001]_{\beta_1'}$ in the martensite phase.

The results of the calculations are summarized in Fig. 3 and Table 1. As seen from them, the agreement between theory and experiment is very good both in the habit plane and the orientation relationship.

Fig. 3 Stereographic representation of calculated and observed habit plane (p'_1), direction of shape strain (d_1) and the orientation of principal axes (a , b , c), $(\bar{1}\bar{2}8)$ plane and $[\bar{2}10]$ direction of the β'_1 martensite. Points with arrows correspond to the experimentally determined data, and those without arrows correspond to the calculated ones.

2. 2H type martensites formed in thin films

The crystal structure of the banded martensites in the present alloy was identified as 18R type long period stacking order structure as described in Sec. III.1. However, martensites with a different crystal structure were also seldom observed. An example of such martensites is shown in Photo. 4(a), and the diffraction pattern corresponding to the martensite is shown in (b). The diffraction pattern unambiguously shows that it is the 2H type martensite rather than the 18R type as shown in the key diagram, even though there are no twins inside the martensite, which are characteristic of the 2H type martensite. Besides the morphology of this martensite is slightly different from that of β'_1 , since the latter is parallel-sided while the former is wedge-shaped or triangular. Further, the former usually exists near the crack of the specimens. These unusualnesses, along with the rare occasion of the appearance, seem to indicate that they are not representative of the banded martensites in bulk specimens, but that they were introduced during or after the electropolishing in the thin film state.

3. Nature of the β'_1 martensite

The β'_1 martensites are obtained by quenching into water at 0°C the present alloy from the β phase region, as described in Sec. III. So the present authors were tempted to see whether or not these martensites grow with cooling below room temperature. The observation of the specimens on the cooling

Table 1 Comparison of experimental and theoretical results.

	Experimental	Theoretical
Habit plane (p'_1)	$(\bar{1}44)_{\beta_1}$	$\begin{pmatrix} -0.17638 \\ -0.71792 \\ 0.67341 \end{pmatrix}_{\beta_1}$
Orientation relationship	$(0\bar{1}1)_{\beta_1}/(\bar{1}\bar{2}8)_{\beta_1'}$ $[1\bar{1}\bar{1}]_{\beta_1}/[\bar{2}10]_{\beta_1'}$	$(0\bar{1}1)_{\beta_1}$: 1.21° away from $(\bar{1}\bar{2}8)_{\beta_1'}$ $[1\bar{1}\bar{1}]_{\beta_1}$: 0.38° away from $[\bar{2}10]_{\beta_1'}$
Direction of shape strain (d_1)		$\begin{pmatrix} -0.15781 \\ 0.78236 \\ 0.60250 \end{pmatrix}_{\beta_1}$
Magnitude of shape strain (m_1)		0.19506

Photo. 4 (a) Electron micrograph of a martensite which formed in the state of thin foil.
(b) Diffraction pattern taken from the framed area in (a).

stage of an optical microscope showed that neither they grow nor the martensites with the same morphology appear with decreasing temperature down to -100°C , and that the wedge-shaped 2H type martensites (β''), reported by Nishiyama et al.⁽³⁾, appeared with cooling beyond -140°C . Thus, we can conclude that the martensite which appears with cooling in the present alloy is β'' , but that the martensite called β'_1 is induced by stress upon quenching. However, under a different quenching stress, the 4H type martensite may also be produced, because the 4H type structure is conceivable as a one of long period stacking order ones and the energy difference is not so

much between the 4H and the present 18R structures. On account of this, Nishiyama et al. might have observed the 4H type martensites in their quenched Cu-Sn alloys.

It is to be noted that the β'_1 martensite may also appear by thermal cooling, if the Sn content is much lower than that of the present alloy. Warlimont and Härter⁽¹⁾ reported that the β' martensite appears in the composition range of 13.1–<14.0 at%Sn. Although the crystal structure of the β' martensite proposed by them is different from that of the β'_1 martensite described above, we believe that they are the same because a diffraction pattern they showed at a conference⁽¹⁾ was the same as

Photo. 2(a) of the present paper. However, there is a slight difference in microscopic morphology between the β' formed by thermal cooling and the β'_1 induced by quenching stress. The former appears as an aggregate of martensites constituting an self-accomodating system, while the latter appears as individual acicular martensites, each being separated by the matrix (see Fig. 1 of Ref. (1)).

Finally, the present authors would like to point out the similarities between the present Cu-Sn system and the Cu-Al-Ni system⁽⁹⁾, in which the crystal structures are the same in the matrix phase, in the following respects:

(i) The 18R type long period stacking order structure appears in the low solute content, while the 2H type stacking order structure becomes more stable with increasing solute content.

(ii) Even in the composition range where the 2H structure is stable, the 18R type martensite may appear if the alloys are stressed above the M_s temperature, and the structure is the same as that appears thermally in the lower solute content alloys of the same alloy system.

Therefore, even though the present β'_1 martensite was obtained by quenching stress, the same martensite can be expected to be produced under external stresses such as in tensile tests when the stresses are applied at temperatures roughly above the M_s temperature.

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