Electron Microscope Study of the β” Martensite (wedge-shaped) in Cu-Sn Alloy

By Hirofumi Morikawa***, Ken’ichi Shimizu**, and Zenji Nishiyama***

An electron microscope study was made on the wedge-shaped martensite β” in Cu-24.5wt%Sn alloy, which was produced by quenching into water and then dipping in liquid nitrogen. From the diffraction patterns it is found that the β” martensite has a close-packed orthorhombic structure of AB’ stacking. Its electron microstructure consists of lamellae parallel to the (121) plane, and spots due to the (121) twin are observed in the diffraction pattern. From these facts it is concluded that the β” martensite has twin faults due to the transformation. Moreover there are finer striations within them. These striations are thought to be contrasts of stacking faults parallel to (121) planes. 

The crystal orientation relationships between the β” martensite and the parent phase are (001)β”//(110)β1 and [210]β”//[111]β1.

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I. Introduction

In order to obtain data on the mechanism of the martensite transformation, experiments were made using Cu-24.5wt%Sn alloy. As already reported briefly, this alloy has two kinds of martensite, β’ and β”(1). The former banded martensite β’ which is produced by water quenching has an orthorhombic close-packed structure of AB’AC’ stacking, accompanied by a number of stacking faults (spacing about 100 Å) on planes parallel to the (122)(2). It is considered that this structure is formed by a shear in a [1'PO]β1 direction on the (110)β1 plane and a shuffling in the opposite direction on every two layers (β1: Parent phase(3)). The shear with the shuffling corresponds to the lattice change of the martensite transformation, and the stacking faults constitute the lattice invariant shear to maintain an invariant plane as a habit plane. The manner of shuffling in β’ of this alloy is different from that in β’ of Cu–Al alloy(4), which has an orthorhombic close-packed structure of AB’ CB’CA’BA’BC’BC’AC’AB’ stacking. Furthermore, these two β’ martensites are subjected to the lattice invariant shear along the plane of different index—

(122) in Cu-Sn and (001) in Cu–Al alloy. As formerly stated (2), such a difference is considered to be due to the condition that in the Cu–Sn alloy the resolved shear stress on (122) for relaxing the shape change due to the lattice change of transformation is greater than that on (001), but in the Cu–Al alloy the reverse holds good.

Another kind of martensite, wedge-shaped β” which forms when sub-zero cooled after quenching remains obscure in many respects. Isaščev found orthorhombic martensites (a=4.55Å, b=5.36Å, c=4.31Å) in a 25.5wt%Sn alloy cooled in liquid nitrogen(5). Soejima et al. concluded, on the basis of their X-ray data that lens-shaped martensites in 24.8wt%Sn alloy obtained by cooling in liquid nitrogen have an orthorhombic structure (a=4.558Å, b=5.402Å, c=4.358Å)(6). However, they did not make clear the internal structure and the nature of the martensites and their orientations relevant to the parent phase.

In the present paper description will be given of the result of detailed analysis by electron microscopy on the wedge-shaped martensites β” . While this full paper was being prepared for publication, Warlimont et al.(7) reported that they found stacking faults and twin faults in the martensites of this alloy.

II. Experimental Procedure

The specimen used was the same material (24.50wt%Sn (14.80at%Sn)) as in the study of β’ martensite. When the specimen was sub-zero cooled after quenching from 700°C, wedge-shaped martensites were formed. From the specimen containing such martensite —

sites, thin foils were prepared by electrolytic or chemical polishing for electron microscopic observation. The electron microscope HU-11 equipped with a tilting device was used at an operating voltage of 100 kV. The details were given in a previous paper(3) which dealt with preliminary experiments in the present study.

III. Experimental Results

1. Optical micrographs

Photo. 1(a) is an optical micrograph of the etched surface of the alloy quenched from 700°C into water at 0°C. This micrograph shows line (band) markings due to β' martensite crystals, as evidenced in the first paper(2). When cooled to the liquid nitrogen temperature, this specimen was transformed suddenly with noises, giving rise to wedge-shaped relieves on the surface, as shown in Photo. 1(b) taken from the same area as in (a). Photo. 1(c) is its re-etched structure which clearly reveals the wedge-shaped crystals of β" martensite. Since such martensites were not yet formed at -73°C, the Ms temperature seems to lie between -73°C and -196°C.

2. Electron microscope observation

Photo. 2 is a typical example of electron micrographs showing the inner part of a wedge-shaped β" martensite with internal twin lamellae, within which are found striations due to stacking faults of alternate inclinations for alternate twins (S.F. and S.F. (T)).

It is seen by careful observation that each twin lamella has abundant striations whose directions are the same in the twins of the same kind. Such striations are contrasts due to stacking faults, as will be shown later.

Photos. 3(a)~6(a) are electron micrographs showing β" martensites in different specimens, and Photos. (b)'s represent the diffraction patterns of (a)'s, respectively. All the micrographs reveal twin lamellae and stacking fault fringes similar to those in Photo. 2.

Photo. 3(b) is the pattern with a two-fold symmetry which is quite similar to a reciprocal lattice plane containing the c* axis of a hcp crystal. Furthermore the interplanar spacing corresponding to the shortest distance OQ (Table 1) is of the order of the length of the c axis of ordinary hcp metal crystals. These facts show that the period of stacking of atomic planes in the c direction is twice the interlayer spacing in the same way as in the hcp crystal.

The diffraction pattern in Photo. 4(b) consists of two groups of spots, indicating that the β" martensite under observation consists of crystals of two kinds of orientation. These two groups are symmetrical about AB to each other, and spot P is common to the two groups. These facts suggest that the two groups of spots are twin-related and that the atomic plane corresponding to spot P is the twin plane. Since the direction OP is perpendicular to the lamellae in (a), the latter are interpreted as twin faults.

Photo. 5(b) has weak spots at regular positions besides strong fundamental reflections, indicating that the β" martensite has a superlattice structure.
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Photo. 3 (a) Electron micrograph showing the inside of a $\beta''$ martensite with internal twin lamellae. Arrows T.F., S.F. and S.F. (T) indicate the (121), (121) and (121)$_T$ traces on the specimen surface, respectively. These notations are also used in the following micrographs.

(b) Electron diffraction pattern of (a), [210] zone. Note that almost all spots are elongated in the direction of OS (Fig. 1), accompanied by narrow streaks in the direction of OQ.

(c) Electron diffraction pattern of an area near (a), displaying [210] zone approximately. The narrow streaks cannot be observed in this pattern.

IV. Analysis of Diffraction Patterns
An experiment\(^{(8)}\) was previously made by electron microscopy to clarify the crystal structure of the parent phase of $\beta''$ martensites, with the conclusion that it had a Fe$_3$Al type superlattice $\beta_1$ in the retained state.


Photo. 4 (a) E.M. showing the inside of a $\beta''$ martensite
(b) Electron diffraction pattern of (a), [101] and [101]$_T$ zones, (T means twin)

Photo. 5 (a) E.M. showing the inside of a $\beta''$ martensite
(b) Electron diffraction pattern of (a), [111] zone
1. Proposal for the lattice type of $\beta''$ martensite

On the basis of the shear mechanism of martensite transformation, the transformation from a bcc crystal to a close-packed structure may safely be assumed to occur by one of the shears, of which simple ones are illustrated in Fig. 7 in the preceding paper. In these mechanisms the shearing plane is (110) and the shearing direction is [110], as observed in $\beta''$ martensites in Cu-Al and Cu-Sn alloys, in which type (ii) and type (iv) are realized, respectively. If the $\beta''$ martensite in the present case is also assumed to have a close-packed structure, type (iii), $AB'$, will be selected, taking account of the two-layer period found in Photo. 3(b). This lattice can be produced by shears along the (110) plane in the [110] direction with shufflings on alternate layers.

2. Structure factor of $AB'$ lattice

The structure factor of $AB'$ lattice assumed above (with a stoichiometric composition) is calculated as follows:

Fundamental spots:

$$ \frac{1}{4} (3f_{cu} + f_{sn}) [1 + \exp 2\pi i \left( \frac{1}{2} k \right) + \exp 2\pi i \left( \frac{1}{2} h \right)] $$

Superlattice spots:

$$ (f_{sn} - f_{cu}) \left[ 1 + \exp 2\pi i \left( \frac{1}{3} h + \frac{1}{2} k + \frac{1}{2} l \right) \right] $$

where $f_{cu}$ and $f_{sn}$ are the atom form factors of Cu and Sn atoms, respectively, and $h, k, l$ are the indices of reflections referred to the orthorhombic lattice whose axes correspond to [110], [001] and [110] of the parent cubic lattice. Fig. 5 shows the intensity distribution in the reciprocal lattice calculated by the above formulae.

3. Correspondence of observed diffraction patterns to calculated reciprocal lattice planes in the $AB'$ model

Referring to Fig. 5, it is easily recognized that the diffraction pattern in Photo. 3(b) corresponds to the [210] zone, as illustrated in Fig. 1.

The diffraction pattern of Photo. 4(b) has two groups of spots, matrix spots (P, Q, R, etc.) and twin spots (Pt, Qt, Rt, etc.), corresponding to the [101] zone, as shown in Fig. 2.

Photos. 5(b) and 6(b) correspond to the [111] and [021] zones, respectively, as illustrated in Figs. 3 and 4. Extra spots appearing in these photographs will be explained later.

4. Plane of internal twin

The parallel lamellae were almost always observed in the micrographs shown above and twin spots were observed in the diffraction patterns as seen in Photo. 4(b). Using the directions of the lamellae and the diffraction patterns, one-face analysis could be carried out for the twin plane. The normal of the trace of the twin plane on the specimen surface is shown in a stereograph, Fig. 6, which shows that all arcs indicating the normals intersect at (121) within

* In the present paper, the (uvw) zone means a diffraction pattern corresponding to the reciprocal lattice plane perpendicular to the zone axis (uvw) and passing through the origin.

** In Figs. 1−4, solid and open circles represent fundamental and superlattice reflections, respectively.
Table 1  Data of lattice spacing

<table>
<thead>
<tr>
<th>Photo. No.</th>
<th>Spot mark</th>
<th>Measured spacing (Å)*</th>
<th>Zone axis</th>
<th>Spot index</th>
<th>Spacing from X-ray data (Å)**</th>
<th>(3)</th>
<th>(6)</th>
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<tr>
<td>3</td>
<td>P</td>
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<td>[210]</td>
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<td>2.324</td>
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<tr>
<td></td>
<td>Q</td>
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<td>001</td>
<td>121</td>
<td>4.358</td>
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<td></td>
<td>R</td>
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<td>121</td>
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<td>0.982</td>
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<tr>
<td>4</td>
<td>P</td>
<td>1.988</td>
<td>[101]</td>
<td>121</td>
<td>2.050</td>
<td>0.970</td>
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<tr>
<td></td>
<td>Q</td>
<td>1.978</td>
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<tr>
<td>6</td>
<td>P</td>
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<td>124</td>
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* Corrected for the distortion of diffraction ring from an exact circle
** From the lattice constants obtained by Soejima et al. a=4.558Å, b=5.402Å, c=4.358Å

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Fig. 1  [210] zone in AB' lattice, corresponding to Photos. 3 (b) and (c)

Fig. 2  [101] and [101] zone in AB' lattice, corresponding to Photo. 4(b)

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5. Plane of stacking fault

As described before, every twin lamella in Photo. 2 has striations very similar to those seen in β' martensite, indicative of the existence of plane faults. The direction of the striations is, however, difficult to be measured accurately because of the thinness of twin lamellae, so that the index of the fault plane cannot be determined definitely. Therefore, inversely let us first assume the index of the fault plane and then compare the calculated trace on the specimen surface with the striations observed. If the plane of the faults is assumed to be (121), its calculated trace is as indicated by two arrows in Photos. 3—6; one of them (S.F.) shows the trace in the matrix crystals and the other (S.F. T) that in the twin crystals. These directions approximately coincide with those of

* The normal of specimen (4) deviates slightly from (121), due probably to the inclination of the specimen foil to the incident beam.
striations seen in the above photographs (the direction of S.F. in Photos. 3(a) and 4(a), and that of S.F. (T) in Photo. 5(a)). This fact supports the assumption that the striations are due to (121) plane faults.

The plane faults obtained above may be twin faults or stacking faults. If they were twin faults, diffraction patterns with a 180° rotation symmetry about OQ and OQ', Fig. 2, would appear in addition to the patterns of Photo. 4(b), since this photograph has (121) and (121) spots which would become the twin planes. But such patterns have not been found. From this fact the striations in question are interpreted to be due to stacking faults on (121).

In Photo. 3(b) very narrow streaks can be seen in the direction of OQ. This direction is perpendicular to (001) and not to (121) nor (121). Since the (001) plane is the plane of the first shear of transformation, the above streaks are considered to be due to stacking faults introduced probably by shuffling errors.

6. Comparison of lattice spacings between the present data and X-ray ones in the literature

The spots in the diffraction patterns are consistent with the expectation from the model as far as their relative positions are concerned. On this basis, the indices of their zone axes were assumed as shown in Figs. 1~4. In order to examine whether these indices are correct or not, a quantitative check must be made with the measured lattice spacings. But we cannot obtain the accurate lattice spacings for the same reason as mentioned in section IV-(5) in the preceding paper[8]. Therefore only comparison is to be made for the present measurement with X-ray data in the literature.

Table 1 shows the comparison of the lattice spacings. The 3rd column gives the measured spacings (corrected for the distortion of diffraction rings). The 7th column shows the ratio of the 3rd to the 6th column which is calculated from the X-ray data obtained by Soejima et al. on lens-shaped martensites in Cu-25.5wt%Sn alloy. In each pattern the ratio is approximately constant, supporting the reliability of the assumed indices. There is a small difference in the ratio from one pattern to another, mainly due to the error in the camera constant. The ratio for spot R1 in Photo. 4 is considerably large,
which is probably caused by the difficulty in measurement due to its weakness.

7. Diffraction intensity

In Photo. 3(b) the spots have apparently equal intensities contrary to the calculation, Fig. 1. This seems to be due mainly to equalization by multiple diffraction. On the other hand, less equalization is found in Photo. 3(c) taken from an area which is near (a) and probably tilted slightly. Such an equalization is also recognized in the fundamental spots in Photo. 6(b).

Forbidden reflections (001 etc.) marked by × in Fig. 1 appear as the result of multiple reflections, e.g., (001) = (120) + (121). Such forbidden reflections are also found in Photos. 4(b), 5(b) and 6(b) (marked × in Figs. 2, 3 and 4).

8. Extra spots

As described above, all the fundamental and superlattice spots are observed as expected from the AB' model. Besides these spots, extra ones are found in almost all the patterns. Each of these extra spots can be explained by elongation of a reciprocal lattice point lying near the Ewald sphere. Mark ▲ in Figs. 1~4 corresponds to a fundamental spot and mark ▲ to a superlattice one.

The extra spots in Photo. 5(b) are split, probably due to misorientation of the crystal part.

The spots ▲ in Fig. 4 will be due to enormous elongation of the rel-rods.

9. Crystal orientation relationships

It was seldom to find a region where a β'' crystal appeared together with the retained β phase. Photo. 6(a) is one of such regions and Photo. 6(c) shows a diffraction pattern of the retained β2 phase region near a β'' martensite plate in (a), showing the [113]β2 zone. Plotting this pattern on the stereogram of the β'' martensite crystal, Fig. 7 is obtained, in which marks ● and △ correspond to the main lattice planes of the β'' martensite and the retained β2, respectively. Marks ○ indicate those of β2 expected from the assumption that (001)β''//[110]β2, [210]β''//[111]β2, and marks ▲ indicate those when the second relationship is assumed to be [210]β''//[111]β2. The experiment shows that spot 121β2 is very strong and spots of β'' are comparatively strong, indicating that their ideal reciprocal points lie just on the Ewald sphere. From this consideration and the relative positions of the spots of β'' and β2, it is concluded that the orientation relationships between these two phases are (001)β''//[110]β2, and [210]β''//[111]β2, the latter being better than [210]β''//[111]β2. These are equivalent to Burgers' relationships if the β'' crystal is referred to the hexagonal axes. As all the principal axes of β2 are parallel to those of β''(001), the above relationships can be regarded as those between β'' and β2. These relationships hold good only when the twinning plane is expressed by (121) and the stacking fault plane by (121). They are quite the same as those between β' and β2 when the stacking fault plane is (121)*.

Isaichchev(5) confirmed (101)β''/\{000\}β2 and [111]β''/\{011\}β2, by X-ray observation without consideration of the existence of the plane faults; their relationships are nearly equivalent to those mentioned above.

V. Morphology of the β'' Martensites

The β'' martensite crystal is wedge-shaped and has no mid-rib available for the determination of its habit plane.

All the intersections of the internal twins with the specimen surface are revealed as straight lines in the β'' martensites described above. But in Photo. 7(a) and an enlargement (b) of the framed area in (a), the traces of twin interface have kinks, the subtended angle being 14°. From the features of the traces both branches of the twin interfaces constituting the kink appear to be perpendicular to the specimen surface. In such a case, if these twins were of two different variants of (121), the angle between their traces could not be as small as 14°. Furthermore, even if the kink can be interpreted by the occurrence of slips in the β'' martensite it is difficult to explain the facts that the angle is always 14° and each trace is thoroughly straight. From the morphology it can be supposed that those two traces correspond to the traces of particular crystal planes. If the planes are assumed to be (121) and (122), the subtended angle is 17°, and it may be measured as about 14°, if the twin planes are inclined from the direction of the incident beam by a few degrees of angle. Planes (121) and (122), if referred to the hexagonal axes, correspond to (1011) and (1012), respectively, which are usually considered to become twinning planes.

* In β' martensites the stacking fault plane is (122), which becomes (121) if referred to the AB' type lattice.
VI. Discussion

1. The crystal structure of the $\beta''$ martensite

Although for the martensites formed by sub-zero cooling almost all the diffraction patterns were explained to be due to the $\beta''$ martensite of $AB'$ stacking, there was an exception whose pattern could be interpreted to be of $AB'CB'CA'BA'BC'AC'AB'$ stacking as found in $\beta'$ of Cu-Al alloy. The existence of this structure is not improbable, because its morphology was different from others, showing the internal structure that seems to be due to stacking faults and not due to twin faults. The above interpretation, however, requires a more detailed experiment.

2. The lattice invariant shear accompanied by the transformation from $\beta_1$ to $\beta''$

The present experiment showed that the $\beta''$ martensites had internal twins containing stacking faults of another orientation. The existence of these two kinds of faults indicates the occurrence of a double process, as the lattice invariant shear of transformation, as assumed in the case of Fe-30% Ni alloy\(^{(9)}\),


This is probably because the double process may accommodate the strain produced by the lattice change of transformation more sufficiently than a single process.

3. Difficulty in the application of the phenomenological theory to $\beta_1 \rightarrow \beta''$ martensite transformation in Cu-Sn alloy

The phenomenological theory\(^{(10),(11)}\) of martensite transformation is to explain crystallographical relations between a martensite and the parent phase. According to this theory, the shape deformation $P_1$ can be described as $P_1 = \delta RBP$, where $\delta$ is a dilatation and $R$, $B$, and $P$ are the matrix representations for a rigid body rotation, a lattice deformation and a simple shear, respectively. If the lattice invariant shear consists of twinnings and slips on different planes, as in the $\beta''$ martensite of Cu-Sn alloy, the shear matrix can be obtained on the basis of accurate knowledge on the volume ratio of the twin pair and the quantity of slips. It is, however, troublesome to obtain such information from experiment. Thus it is very difficult to evaluate the shape deformation $P_1$ when the martensite has double faults with different planes; namely the current simple phenomenological theory fails.

VII. Conclusion

The wedge-shaped martensite ($\beta''$) in Cu-Sn alloy containing 21.5 wt% Sn has an orthorhombic lattice of $AB'$ type. It is considered that this type of lattice is formed by a shear along (110) planes of the parent $\beta_1$-lattice (Fe$_3$Al), accompanied by shufflings on alternate layers. These shear and shuffling must be involved in the lattice change of martensite transformation. There are, however, some amount of errors in the shuffling.

The $\beta''$ crystal has twin faults on the (121) planes, and each twin crystal contains stacking faults on the (121) planes. Those faults are considered to be due to the lattice invariant shear of transformation.

The orientation relationships between the $\beta''$ martensite and the parent $\beta_1$-phase are

\[ (001)_{\beta''} || (110)_{\beta_1}, \quad \text{and} \quad [210]_{\beta''} || [111]_{\beta_1}, \]

which hold good when the twining plane is expressed as (121) and the stacking fault plane as (121).

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\(^{(10)}\) M. S. Wechsler, D. S. Lieberman and T. A. Read : J. Metals, 5 (1953), 1053.