The Second Martensitic Transformation Stress-Induced in Cu–Zn–Al Alloy Single Crystals

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The martensite to martensite transformation, $\beta'_1 \rightarrow \alpha'_1$, stress-induced secondly in single crystals of Cu–Zn–Al alloys is crystallographically studied in detail. The transformation proceeds by a simple shear on the basal plane of $\beta'_1$ martensite with the 9R long period stacking structure to form the 3R stacking structure of fct. The crystallographic orientation relations are obtained to be (001)$_{\beta'}$/ (111)$_{\alpha'}$ and [100]$_{\beta'}$/[112]$_{\alpha'}$. Two types of stress-strain curve, “two-stage type” and “stress-drop type”, are observed in the tensile test depending upon the tensile direction and testing temperature. In the former case, the $\alpha'_1$ martensites are transformed after completing the first transformation $\beta_1 \rightarrow \beta'_1$, while in the latter, two variant crystals of $\beta'_1$ cross each other to produce the $\alpha'_1$ martensite inside. The drop in stress level is well understood by considering the smaller critical resolved shear stress for the second transformation, $\tau_{\alpha'}$, as compared with that for the first one, $\tau_{\beta'}$.

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I. Introduction

The two step transformation, $\beta_1 \rightarrow \beta'_1 \rightarrow \alpha'_1$, is stress-induced in Cu–Zn base alloys(1)–(3) as well as in Cu–Al–Ni alloys(4). Contrary to the case in Cu–Al–Ni(5), the $\alpha'_1$ martensites are easily produced and often retained at room temperature upon unloading in Cu–Zn(6)–(7) and Cu–Zn–Al alloy(2) having the electron-atom ratio, $e/a$, of 1.40. The nature of $\alpha'_1$ martensite, which is sensitive to the composition of the alloy(3)–(8), is to be closely related to the character of the pseudoelasticity and shape memory effect in this alloy system. In a previous work studying the reversible shape memory effect(9)–(11), it has been verified that the second transformation, $\beta'_1 \rightarrow \alpha'_1$, is easy to occur as compared with the first one, $\beta_1 \rightarrow \beta'_1$, provided another variant of $\beta'_1$ is cooperatively induced with $\alpha'_1$ and also that the $\alpha'_1$ martensite is stable for the reverse transformation.

To study the character of $\alpha'_1$ martensite further, a series of investigations are planned and performed using the single crystal tensile test by the present authors. A large number of stress-strain (S-S) curves are analysed for Cu–Zn–Al single crystals with different orientations, temperatures and alloy compositions(12) in relation to the two-step transformation. In the present paper, the basic crystallographic relations in the second transformation are first established, and then the morphological change is analysed with respect to the structural change in the specimen. Different types of S-S curves are obtained depending upon the orientation of the tensile axis and the relative magnitude of the critical resolved shear stress of the first and second transformations.

II. Experimental Procedure

Two kinds of alloys, containing 31.0 at%Zn and 4.5 at%Al (Ingot A) and 31.6 at%Zn and 4.2 at%Al (Ingot B) were prepared by melting pure materials in quartz capsules in argon atmosphere. Single crystals of $\beta_1$ matrix phase were grown by a modified Bridgman method. Slabs 1 mm thick with large grains about 7 mm in size cut from Ingot A by a spark machine were polished electrolytically in a solution of supersaturated phosphoric-cromic acid at room
temperature. Thin specimens about $20 \times 4.5 \times 0.1\text{mm}$ in size (Specimen A-1) were pulled by a small manual tensile equipment. During the extension observations were made on the top surface of the specimen by a stereoscopic microscope. At the same time the structural change was examined associated with the transformation by the transmission Pseudo-Kossel (P.K.) X-ray technique\(^{(13)}(14)\).

Twenty tensile specimens about $7.5 \times 2 \times 1\text{mm}$ in size with different orientations were cut from the single crystal of Ingot B by the spark machine. The tensile directions were determined by the back-reflection Laue method, as shown in Fig. 1. Tensile tests were carried out with an Instron-type testing machine at a strain rate of about $2\%/\text{min}$, the morphological change due to the transformation being recorded in a VTR through a TV camera.

III. Experimental Results

1. Morphology and change in crystal structure

Figure 2 shows a morphological change on the top surface of Specimen A-1 upon loading, the deformation increasing from (a) to (d). The transmission P.K. photographs were taken as represented in Fig. 3(a) to (d) corresponding to Fig. 2(a) to (d), respectively. Main deficient lines, black in Fig. 3, have been indexed, as shown in the key diagrams, Fig. 3(a') to (d'). Figure 2(a) represents a $\beta'_1$ matrix crystal. The corresponding P.K. pattern, Fig. 3(a), shows that the lattice parameter $a_0=0.294\text{nm}$ and that the top surface is parallel to $(317)_{\beta'_1}$. The $\beta'_1$ martensites were produced upon loading the specimen in $[321]_{\beta'_1}$ direction\(^\dagger\), as shown in Fig. 2(b), in which the traces of habit plane, $(12\ 2\ 11)_{\beta'_1}$, are indicated by arrows. The P.K. pattern in Fig. 3(b) was successfully indexed in $\beta'_1$ as a 9R structure\(^\dagger\dagger\) pattern, the lattice parameters being $a_{\beta'_1}=0.446\text{nm}$, $b_{\beta'_1}=0.266\text{nm}$ and $c_{\beta'_1}=1.92\text{nm}$. The orientation relationship

\[ \beta'_1 \]  

\[ \text{Fig. 1 Tensile directions of the specimens examined.} \]

\[ \text{Fig. 2 Macroscopic change upon tensile loading in Cu–31.0 at\%Zn–4.5 at\%Al alloy. The deformation increases from (a) to (d); } \beta'_1, \alpha'_1. \]

\[ \text{† The tensile direction w[u_1, u_2, u_3]_{\beta'_1} is always designated so as to satisfy the condition that } u_1>0, u_2<0, u_3<0 \text{ and } u_1>|u_2|>|u_3| \text{ in this series of experiments.} \]

\[ \text{†† Detailed investigations\(^{(15)}(16)\) have concluded that the } \beta'_1 \text{ martensite has a modified 9R structure which has a slightly inclined c-axis with respect to the basal plane. However, the lattice parameters were determined by assuming the orthorhombic 9R structure in the present work.} \]
between the $\beta_1$ matrix and $\beta'_1$ martensite was obtained as $(101)_{\beta_1}/(\bar{1}14)_{\beta'_1}$ and $[\bar{1}11]_{\beta_1}/[110]_{\beta'_1}$, which is called Relation (A) hereafter.

After the $\beta_1 \rightarrow \beta'_1$ transformation had been completed in the whole region of the specimen, $\alpha'_1$ martensite plates were formed parallel to the basal plane $(001)_{\beta'_1}$ on further loading, as shown in Fig. 2(c). New deficient lines appeared in the P.K. pattern, Fig. 3(c), corresponding to the $\alpha'_1$ plates as illustrated by the dotted lines in the key diagram (c'). Finally the whole region was transformed to the $\alpha'_1$ martensite with a 3R structure which showed the P.K. pattern in Fig. 3(d) and (d'). The lattice parameters of the $\alpha'_1$ martensite were obtained to be $a_{\alpha'_1} = 0.376 \text{ nm}$ and $c_{\alpha'_1} = 0.358 \text{ nm}$. The orientation relationship between the $\alpha'_1$ and $\beta'_1$ martensites, $(001)_{\beta'_1}/(111)_{\alpha'_1}$ and $[100]_{\beta'_1}/[112]_{\alpha'_1}$, called the Relation (B), was derived by comparing Fig. 3(b) with (d). The interplanar spacing of $(009)_{\beta'_1}$ was equal to that of $(111)_{\alpha'_1}$ and so was the length of $[010]_{\beta'_1}$ to that of $(1/2)[110]_{\alpha'_1}$.

### 2. Stress-strain curves

Two different types of the stress-strain (S-S) curves were observed with the associated morphological changes in the tensile test of Cu–Zn–Al single crystals, depending upon the crystallographic tensile direction and testing temperature. A typical example of the first type is shown in Fig. 4 together with the morphological change. A single crystal specimen (B-1) was pulled in $[4\bar{3}1]_{\beta_1}$ direction at room temperature in this case. The tensile direction was close to that in the structural study in Figs. 2 and 3 as described in III.1.

Upon loading, no morphological change appeared, until the yield point (b) was reached. At (b) where a critical stress necessary to produce the $\beta'_1$ martensite was reached, apparent plastic deformation started by the formation of $\beta'_1$ martensite which was stress-induced at the upper region of the specimen, as seen in (b). The deformation proceeded by the successive nucleation and growth, (c) to (d), of the martensite with no remarkable increase in stress, until point (e) was reached, where the transformation was almost completed. The stress-induced $\beta'_1$ martensite has the habit plane of $(12\bar{2}11)_{\beta_1}$, and this variant is called $\beta'_1(1)$ hereafter. As soon as the $\beta'_1(1)$ martensite touched the grip ends of the specimen, (e), a rapid increase in stress occurred, until a second yielding at (f) associated with the formation of the $\alpha'_1$ martensite took place.

Upon unloading, the $\beta'_1(1)$ was first transformed reverse to $\beta_1$ matrix starting at a lower part of the specimen, as seen in (h), without any change in the $\alpha'_1$ martensite until the step (i) was reached, where the transformation front

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† These values are in accord with those so far obtained in the previous work using the rotation photographs.*
moving upward touched the $\alpha'$ martensite. On further unloading, the $\beta'$(I) still continued making reversion to the matrix cutting through the $\alpha'$ martensite, (j), and disappeared as in (k). However, the traces of $\alpha'$ martensite still remained, even though they contained a large amount of striations inside. The retained traces of $\alpha'$ martensite became thinner on further unloading and finally disappeared as in (l) and (m). After complete unloading there remained
the striations inside the old $\alpha'_1$ traces on the specimen surface as well as a small amount of strain in the S-S curve. This type of S-S curve is called the two-stage type.

Figure 5 shows the second type of the S-S curve accompanied with a series of macroscopic metallographs. A single crystal (B-2) was pulled in $[8\bar{2}1]_p$ direction at room temperature. One
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sees a quite different shape as compared with the first one not only for loading but also for unloading.

A part of the $\beta_1$ matrix crystal (a) was initially transformed to the $\beta'_1(1)$ martensites with $(12 \bar{2} 11)_{\beta_1}$ habit plane similarly to the first type as seen in (b). However, corresponding to the formation of another martensite variant having $(12 1 12)_{\beta_1}$ habit plane crossing the initial $\beta'_1(1)$, which is designated as $\beta'_1(2)$ hereafter, the stress level in the S-S curve suddenly decreased as in (c) to (d). A trace analysis concluded that the crossed region between the variants, $\beta'_1(1)$ and $\beta'_1(2)$, had already been transformed to the $\alpha'_1$ martensite. An X-ray examination using the back-Laue method has confirmed that the crossed region is of fct structure. The crossing structure on the surface continued to grow as in (d) to (f) under a constant stress level on further extension.

Upon unloading, the reverse transformation took place in a reverse order of the forward one as in the morphological change in (f) to (g). The stress decreased more rapidly as compared with the first case, and after complete unloading at (h) the crossing structure still retained on the surface. This structure disappeared by a small uncontrolled stress which was possibly applied to the specimen when removed from the tensile machine, as shown in (i). We call the second type of S-S curve the stress-drop type.

The following conclusion was drawn by the tensile tests at room temperature using twenty single crystals with different tensile directions: i) When the tensile direction is close to $[100]_{\beta_1}$, the stress-drop type with a narrow plateau and a large amount of drop is observed. ii) As the tensile direction is apart from $[100]_{\beta_1}$ to $[110]_{\beta_1}$, the amount of the stress-drop decreases gradually and reaches zero at about 20° from $[100]_{\beta_1}$. iii) If the tensile direction is near $[110]_{\beta_1}$, the two-stage type S-S curve is obtained. iv) The second yield stress becomes higher, as the axis approaches $[110]_{\beta_1}$, and at $[110]_{\beta_1}$ it is too high to be measured.

The tests were also performed at different temperatures. Figure 6 shows an example of the S-S curves obtained for Specimen B-3 with the tensile axis of $[13 \bar{8} 5]_{\beta_1}$. The S-S curve at 273 K shows the typical two-stage S-S curve as in (a). Nevertheless, at higher temperatures, for example at 362 K, the curve does no longer show any superelastic loop but the stress drop appears as in (b). It was recognized that the first type was obtained just above the Ms temperature and the second type appeared as the temperature increased.

IV. Discussion

It was observed in the present experiment that the habit plane in the second transformation, $\beta'_1 \rightarrow \alpha'_1$, was (001)$_{\beta'_1}$ parallel to (111)$_{\alpha'_1}$. Since these planes are close-packed planes in both structures, it is expected that the second transformation proceeds by a simple shear deformation on the close-packed planes(4)(17)-(19). This mechanism is supported not only by the present investigation using the P.K. patterns with morphological examination but also by the previous work with rotation photographs(9).

As far as the two-stage type S-S curve is
concerned, the morphological change such as in Fig. 4 can be understood as the result of the two-step transformation without difficulty. Because of the special tensile direction in this case, the apparent critical stress for the second transformation is higher than that for the first one, so that one sees the clear two-stage curve as in Cu–Al–Ni alloys(6). However, the stress-drop type S-S curve and the associated morphological change in the present experiment have never been observed in Cu–Al–Ni alloys.

In the following discussion our attention concentrates on this special type of S-S curve.

Using Relation (A) and the lattice parameters shown in III.1, one gets the crystal axes of $\beta_1'$ martensite, $a_\beta$, $b_\beta$ and $c_\beta$, from those of the $\beta_1$ matrix crystal, $a_0$, $b_0$ and $c_0$ as follows:

\[
\begin{pmatrix}
a_\beta \\
b_\beta \\
c_\beta
\end{pmatrix}_1 = \begin{pmatrix}
-1.112 & 1.025 & 0.120 \\
0.092 & -0.005 & 0.900 \\
4.392 & 4.815 & -0.423
\end{pmatrix}_1
\begin{pmatrix}
a_0 \\
b_0 \\
c_0
\end{pmatrix}, \quad (1)
\]

where the suffix 1 indicates the number of variant crystal which we designate $\beta_1'(1)$.

Subsequently, the crystal axes of $\alpha_1'$ martensite transformed from $\beta_1'(1)$, can be expressed from Relation (B) and eq. (1) with the known lattice parameters as

\[
\begin{pmatrix}
a_\alpha \\
b_\alpha \\
c_\alpha
\end{pmatrix}_1 = \begin{pmatrix}
0.001 & 0.905 & -0.904 \\
0.185 & 0.895 & 0.895 \\
1.205 & -0.125 & -0.124
\end{pmatrix}_1
\begin{pmatrix}
a_0 \\
b_0 \\
c_0
\end{pmatrix}, \quad (2)
\]

where $a_\alpha$, $b_\alpha$ and $c_\alpha$ mean the axes of $\alpha_1'$ martensite. It is to be mentioned that only one crystal of $\alpha_1'$, i.e., $\alpha_1'(1)$ martensite can be produced from $\beta_1'(1)$ martensite, because of the nature concerning the crystallographic symmetry of the 9R long period stacking structure.

Similarly, the crystal axes of $\beta_1'(2)$ having the (12 11 2)$_{\beta_1'}$ habit plane and those of $\alpha_1'(2)$ transformed from $\beta_1'(2)$ can be expressed as follows:

\[
\begin{pmatrix}
a_\beta \\
b_\beta \\
c_\beta
\end{pmatrix}_2 = \begin{pmatrix}
-1.112 & 0.120 & 1.025 \\
0.092 & -0.005 & -0.005 \\
4.392 & -0.423 & 4.815
\end{pmatrix}_2
\begin{pmatrix}
a_0 \\
b_0 \\
c_0
\end{pmatrix}, \quad (3)
\]

and

\[
\begin{pmatrix}
a_\alpha \\
b_\alpha \\
c_\alpha
\end{pmatrix}_2 = \begin{pmatrix}
0.001 & -0.904 & 0.905 \\
0.185 & 0.895 & 0.894 \\
1.205 & -0.124 & -0.125
\end{pmatrix}_2
\begin{pmatrix}
a_0 \\
b_0 \\
c_0
\end{pmatrix}. \quad (4)
\]

Since the $\alpha_1'$ martensite has the fct structure, it can be said that the variant 1 crystal has almost the same orientation as the variant 2, i.e., the $\alpha_1'(1)$ is considered to be the same martensite as $\alpha_1'(2)$.

The above result is important to understand the observed crossed structure of two $\beta_1'$ variants to form single $\alpha_1'$ martensite in the crossed region and to consider the origin of stress-drop type S-S curve. As schematically shown in Fig. 7, two habit planes of $\beta_1'(1)$ and $\beta_1'(2)$ to $\beta_1$ matrix crystal, i.e., (12 11 2)$_{\beta_1}$ and (12 11 2)$_{\beta_1}$, are nearly parallel† to (001)$_{\beta_1'(2)}$ // (111)$_{\alpha_1'(1)}$ and (001)$_{\beta_1'(1)}$ // (111)$_{\alpha_1'(1)}$, respectively. In other words, the basal plane of $\beta_1'(1)$ is nearly parallel to the habit plane of $\beta_1'(2)$ and vice versa, and these two planes transform to the close packed planes of $\alpha_1'$ martensite. The two transformations, $\beta_1' \rightarrow \beta_1'(2)$ and $\beta_1'(1) \rightarrow \alpha_1'(1)$, are supposed to occur cooperatively, $\beta_1' \rightarrow \beta_1'(1)$ and $\beta_1'(2) \rightarrow \alpha_1'(1)$ being as well.

The drop in stress-level in the stress-drop type S-S curve appeared corresponding to the formation of the crossed structure of $\beta_1'(1)$ with $\beta_1'(2)$ as shown in III.1. The Schmid factor for the shear of the $\beta_1' \rightarrow \beta_1'(2)$ transformation, which we call the second shear, is calculated to be smaller than that for the first shear of the $\beta_1' \rightarrow \beta_1'(1)$ transformation. The critical resolved shear stress (CRSS) for the $\beta_1' \rightarrow \beta_1'$ transformation, $\tau_{\beta_1}$ should be the same independent of the $\beta_1'$ variant crystals formed. Therefore, the observed drop in stress level must be attributed to the formation of $\alpha_1'$ martensite with a smaller CRSS for the $\beta_1' \rightarrow \alpha_1'$ transformation, $\tau_{\alpha_1'}$, than $\tau_{\beta_1'}(3)$. This result was con-

† A calculation shows that the deviations are about $6^\circ (17)(18)$.

Fig. 7 Schematic figure showing the crossing structure of $\beta_1'(1)$ with $\beta_1'(2)$ martensite and $\alpha_1'$ martensite.
firmed by the tensile test with different temperatures as described in Fig. 6. The temperature dependence of $\tau_p$ and $\tau_s$ is to be studied in detail in the forthcoming paper.

The fact that the type of S-S curve depends on the tensile direction can simply be understood by the Schmid factors of the two shear systems. When the tensile axis is near $[100]_1$, the difference in the Schmid factor between the two shears, i.e., $\beta_1 \rightarrow \beta'_1(1)$ and $\beta_1 \rightarrow \beta'_1(2)$, is small, and therefore both $\beta'_1(2)$ and $\alpha'_1(1)$ can easily be formed to produce the stress-drop. On the other hand, as the tensile direction moves from $[100]_1$ to $[1\overline{1}0]_1$, the Schmid factor for the second shear, $\beta_1 \rightarrow \beta'_1(2)$ and $\beta'_1(1) \rightarrow \alpha'_1(1)$, becomes relatively smaller than that for the first shear, and consequently $\alpha'_1(1)$ is formed inside $\beta'_1(1)$ at a higher stress level, after the $\beta_1 \rightarrow \beta'_1(1)$ transformation has been completed.

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