Macroscopic Shape Change due to the Bainitic Transformation in Cu–Zn–Al Alloys

By K. Takezawa* and S. Sato*

An elongation strain as large as 5.5% was obtained in Cu–Zn–Al shape memory alloys upon heating under stress at moderate temperature. The amount and behavior of shape change strongly depended on the heating temperature, tensile direction, and amount of applied stress. The morphological examination revealed that the shape change was attributed to the formation of particular variants of bainite crystals. The shape change is thought to be produced by the martensitic process in the bainitic transformation. On the other hand, the shape change was found to occur after an incubation period and to fit with a curve by the Austin–Ricketts equation which represents the kinetics of a diffusion-controlled transformation. The activation energy obtained from the Arrhenius plot of the shape change, $8.7 \times 10^4$ J/mol, was almost the same as that of the diffusion of Zn atoms in the matrix crystal. Hence, the shape change is obviously controlled by a diffusion process. Nevertheless, this fact may not be contrary to the interpretation that the shape change is produced by the shear process, because the diffusion is thought to be necessary to prepare suitable surrounding conditions for the nucleation and growth of bainite crystals to be transformed by the shear process.

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I. Introduction

The bainitic transformation takes place in Cu–Zn(1)–(7) and Cu–Zn–Al(8)–(12) shape memory alloys during isothermal heat-treatment at moderate temperature. When a particular stress is retained in or a small amount of stress is applied to the matrix crystals, this transformation is often accompanied by a macroscopic shape change. The phenomenon has been called the reverse shape memory effect(8)(12)(13), which is irreversible and quite different from the usual mechanical behavior of the shape memory phenomena due to the martensitic transformation, such as SME(14)–(16), RSM(17)–(19), PE(14)(20)–(22). However, this shape change(8)(13)(16) is thought to be caused by the martensitic nature involved in the bainitic transformation. As a matter of fact, the martensite and bainite have very similar crystal structures, crystallographic orientation relationships, habit planes and inner faulted structures.

On the other hand, the following experimental facts support that the bainitic transformation possesses a diffusion-controlled nature(23)(24): (1) The transformation starts after an incubation period. (2) The transformation proceeds with a compositional change. (3) The isothermal change in the amount of bainite fits with a curve with the Johnson-Mehl style. Therefore, the bainitic transformation has been considered as a phase transition which possesses the both natures together or which has an intermediate character between the two. Even though the bainitic transformation has originally been found in Fe–C alloys(23)–(25), similar transformations in nonferrous alloys such as Cu–Zn(1), Cu–Sn(26) and Ag–Cd(27) are recently believed to have the bainitic nature. However, questions arise as follows: (a) What kinds of mutual interaction operate between the both reactions? (2) Can both reactions take place at the same time? (3) How is the eutectic or precipitate reaction related to the bainitic transformation? These questions have never been answered and the de-
tailed mechanism of the bainitic transformation is still unknown.

To answer these questions, the present authors have so far performed various investigations on Cu-Zn base alloys, a part of which being described in this paper.

II. Experimental Procedure

Cu–31.6 at% Zn–4.2 at% Al and Cu–28.9 at% Zn–6.1 at% Al alloys were prepared by melting 99.99% pure materials at 1473 K in quartz capsules in argon atmosphere. Ingots were homogenized for 3.6 ks at 1143 K after cooling the melts from 1473 K to this temperature. Thin plate specimens 0.2 or 0.3 mm which were obtained from the ingots by repeating hot and cold rolling, re-homogenized at 1143 K and followed by quenching to room temperature. Single crystals were grown in argon-filled quartz capsules by a modified Bridgmann method.

A quasi-quantitative examination was performed with a bending mode on the shape change due to the bainitic transformation during heating. Polycrystalline ribbons of Cu–31.6 at% Zn–4.2at% Al alloy with a dimension of $47.5 \times 10.0 \times 0.3 \, \text{mm}^3$ were bent to a circular form with a radius of $r=10 \, \text{mm}$ or 20 mm and then fixed outside by a steel wire. The constrained specimen was then isothermally heated in a silicon oil bath at temperatures below 523 K or in a salt or lead bath above 523 K. As for a measurement of shape change with tensile mode, single crystals or polycrystalline plates of Cu–28.9 at% Zn–6.1 at% Al alloy with a dimension of about $13 \times 2.0 \times 0.2 \, \text{mm}^3$ were slightly loaded by a small tensile equipment in a bath as shown in Fig. 1, and measured the elongation during heating at various temperatures.

Morphological and structural examinations were made on the specimens in the above experiments by optical and electron microscopy as well as electron diffraction. Thin specimens were prepared for transmission electron microscopy by jet polishing. A Hitachi HU-650 electron microscope was used at 650 kV.

III. Experimental Results

1. The shape change with bending mode

Figure 2 shows an example of the shape change during heating at 473 K. A ribbon was first heated for 1.2 ks at 473 K under constraint with a circular form of $r=20 \, \text{mm}$. (a) represents the shape of ribbon at room temper-

![Fig. 2 Observed shape change with bending mode in Cu–31.6 at% Zn–4.2 at% Al. After pre-heating for 1.2 ks at 473 K under bending constraint ($r=20 \, \text{mm}$), (a) without constraint, (b) just after heating (a) at 473 K, (c) after heating (a) for 6 ks at 473 K.](image)
ature after removing the steel wire for con-
straint. Almost all of the strain introduced by
bending was retained in (a). When the ribbon
(a) was heated again to 473 K, it was unwound†
a little bit as shown in (b). However, as the
heating was continued at 473 K, the ribbon (b)
became automatically wound and finally the
shape (c) was reached after 6 ks. This shape
deformation from (b) to (c) corresponds to the
reverse shape memory effect.

A similar experiment was performed with
another ribbon, outside of which was con-
strained by a steel wire to a circular form of
r = 10 mm. The constraint ribbon was then put
in a bath at a moderate temperature. Since the
constraint force was relaxed due to the shape
change as described above, the wound ribbon
fell off the steel wire after a certain period of
time. The measured periods are plotted in Fig.
3. Although the temperature below which the
bainitic transformation would be expected is
about 720 K in this alloy(2), the shape change
was clearly recognized at temperatures higher
than it. The activation energy was calculated to
be \(8.7 \times 10^4 \text{ J/mol}\) from the Arrhenius plot us-
using the data below 573 K at which the period
was long enough to measure‡. The obtained
value is very close to the activation energy of
diffusion of Zn atoms in the \(\beta_1\) phase of a Cu-
Zn alloy measured by Kuper et al.\(^{(28)}\), \(7.9 \times 10^4\)
J/mol.

2. The shape change with tensile mode

Figure 4 shows an isothermal change in the
elongation strain measured in a polycrystalline
specimen of Cu-28.9 at\% Zn-6.1 at\% Al alloy
under a tensile stress of 124 MPa during
heating at 473 K. In this measurement, the
elongation definitely started after an incuba-
tion period, \(\tau_0\) of 900 s. On the other hand in
the electrical resistivity measurements, almost
the same variations were recorded with time.
Accordingly, it is understood that the
measured strain is proportional to the amount
of transformation products, i.e. bainites, dur-
ing the heat-treatment. The ultimate value of
strain in Fig. 4 was more than 5.5%, which is
almost the same as the maximum value so far
measured on SME or PE in the polycrystalline
specimen of the present alloy. Consequently, it
is to be understood that the bainitic transfor-
mation possesses the martensitic nature.

Two curves calculated from the empirical
formulae for a diffusion-controlled transforma-
tion process by Johnson, Mehl and Avrami
and by Austin and Ricketts\(^{(23)(24)}\) are drawn in

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† The change from (a) to (b) is attributed to the reversi-
ble shape memory effect\(^{(18)}\), which is caused by the pre-
heating at 473 K. It should be mentioned that the
reversible shape memory effect (RSM) is quite different
from the reverse shape memory effect.

‡ The period of time which was too quick to be
measured is plotted on the ordinate axis at 1 s in Fig.
3.
Suppose that $V$ is the total volume of bainite transformed at time $t$, $V_e$ at the end of transformation, and $V_0$ is the volume of specimen. The volume fraction of bainite transformed at $t$ is $y = V / V_e$. Putting the ultimate elongation strain $\varepsilon_e = \varepsilon_e(V_e / V_0)$, where $\varepsilon_t$ is a transformation strain in the transformed region, the elongation strain $\varepsilon$ can be expressed as

$$\varepsilon = \varepsilon(t / V_0) = \varepsilon(t / V_0) y = \varepsilon(y)$$  (1)

Substituting the Johnson-Mehl-Avrami equation, i.e.,

$$y = 1 - \exp\{-k(t - \tau_0)^n\}$$  (2)

into the eq. (1) and setting suitable values of $n$ and $k$ to make a fit with the measured curve, one obtains the dashed line. When the Austin-Ricketts equation, i.e.,

$$y = \left\{ -k(t - \tau_0)^n \right\} / \left[ 1 + \left\{ -k(t - \tau_0)^n \right\} \right]$$  (3)

is tried to make a coincidence with the measured curve the solid line is obtained. The curve by the eq. (3) shows a better fit with the measured points rather than by the eq. (2) over the whole transformation process.

The Johnson-Mehl-Avrami equation has been derived by assuming that the normalized growth rate, $dy/dt$, is proportional to $(1 - y)$, i.e., either a "hard" impingement between the precipitates or a "soft" one associated with the diffusion of solute atoms takes place in the growth kinetics of the transformation. On the other hand, the Austin-Ricketts equation is obtained under the assumption that $dy/dt$ is proportional to $(1 - y)^2$, i.e., the "hard" and "soft" impingements operate simultaneously during the transformation. Therefore, the result of Fig. 4 suggests that the both impingements operate independently at the same time in the bainitic transformation.

Figure 5 shows the elongation curves obtained for three polycrystalline specimens under a stress of 125 MPa during heating at different temperatures. One sees that the incubation period as well as the time necessary to reach the ultimate strain decreases and the growth rate increases with increasing temperature. These facts clearly show that the progress of transformation is controlled by the diffusion of solute atoms, as in the case of Fig. 3 with the bending mode.

The effect of applied stress was also studied, the measured points being plotted in Fig. 6. The solid lines are drawn using eq. (3) so as to fit with the measured points. Even though the
applied stress increases from 66 to 139 MPa, the growth parameter $k$ in eq. (3) associated with the growth rate of bainite does not change too much as $1.8 \times 10^{-4}/s$. Whereas, the shape parameter $n$ decreases a little, from 3.45 to 2.75. The most prominent variation due to the applied stress was recognized in the ultimate values of strain which increased from 2.6 to 5.4%. These facts also suggest that the bainitic transformation is related to the martensitic phase change.

A special examination was further performed to study on the effect of applied stress as follows: A polycrystalline specimen was heated at 473 K under a stress of about 100 MPa. After a few percent of elongation was reached, the stress was reduced to about 1/4 of the initial value without changing the rest. It was clearly observed that the elongation continued upon heating, even though the rate was reduced, as seen in the two examples in Fig. 7. No elongation has been recognized in a preliminary test, when one starts to heat-treat under such a low stress at 473 K. Accordingly, the following two important facts are confirmed: (1) The rate of elongation depends on the amount of applied stress. (2) The elongation continues even when the initial stress is removed. These facts suggest that the stress promotes the formation and growth of particular bainite variants and the preferred growth continues once the variants are preferably formed. This is thought to be the origin of the reverse shape memory effect.

Figure 8 shows elongation curves in the early stage obtained at 483 K for single crystal specimens with different tensile directions as shown in the stereographic triangle. One sees that the growth rate strongly depends on the tensile direction, even though the incubation periods are almost the same, i.e., 650 s, for all the specimens. When $t - \tau_0$ is small, eq. (1) can be approximated by

$$\varepsilon = \varepsilon_0 k^n(t - \tau_0)^n$$

(regardless of which eq. (2) or (3), is used. The values of $n$ in eq. (4) which fits to the measured points in Fig. 8 was obtained to be about 2.0 for all the specimens. The present result supports that the transformation products have a two-dimensional shape in the early stage of transformation and this agrees with the morphological observation so far made (1)-(6) and also as described in the following section.

3. The morphological examination

Figure 9 shows an example of the morphological change in a polycrystalline specimen observed during heating at 473 K under a tensile stress of 100 MPa. The optical micrographs taken at various stages during heating are named (a) to (d) as marked by arrows on the diagram showing the macroscopic shape change. Photo. (a) is taken just after the
incubation period and not much products can be seen in such an early stage of transformation. One sees typical bainite pairs with particular variants having \{12 11 2\} and \{12 11 2\} habit planes\(^\dagger\), stucked together with an obtuse angle, here and there. It is noticed that they have several crystallographic orientations. In Photo. (b) where about 40% of transformation has taken place, the number of bainite plates remarkably increases comparing with (a). At point (c) where the gradient of elongation curve starts to decrease, very large amounts of bainite plates are seen with complicated morphology. The observed area is noticed to be highly occupied by the bainite products. In the final stage (d), the transformation has almost finished but the morphology looks unchanged from (c). The most important nature in (d) would be that the number of variant is reduced. One sees almost two directions of traces with two variants having \{12 11 2\} and \{12 2 11\} habit planes.

In Figure 10 are shown two photographs of bainite taken from the single crystal

\(^\dagger\) The symbol \{hkl\} is used in the general case. The relation between the indices in the first and second habit planes is only important.

\(^\ddagger\) The tensile direction \([uvw]\) is indexed such that \(u \geq v \geq w\).
sponding to these variants were not only the largest ones among all possible variants in No. 2 but also larger than those in No. 5. It was verified that the observed variants of bainite are only those which have positive Schmid factors and that the larger the factor, the higher is measured the rate of shape deformation during heat-treatment.

Figure 11 shows a histogram showing the appearance of bainite variants with \((h k l)\), which have a positive Schmid factor, indicated on the vertical axis. The diagram was constructed by examining the trace of bainite variants appearing in twenty five single crystal specimens treated similarly as in Fig. 8. The variants having \((12 \overline{1} 1)\) and \((12 \overline{2} \overline{1})\) habit planes were the most frequently observed, i.e., in twenty among twenty five specimens.

Figure 12(a) and (b) are examples of electron micrographs showing bainite plates in the specimen in Fig. 9. Figure 12(a) is taken of the specimen heat-treated for 300 s after point (c). Most of the bainites, parallel to each other, are of the same variant, named A, probably having the habit plane of \((12 \overline{1} 1)\). The variant having \((12 \overline{2} 11)\) habit plane, B, which appears in pair with the variant A often in the early stage of treatment are retained here and there. The growth kinetics with the parameter \(n=2\) in eq. (4) is to be consistent with the morphology in Fig. 12(a). In Fig. 12(b) are seen complicated bainite patterns consisting of crossed two variants, probably with \((12 \overline{1} 1)\) and \((12 11 \overline{2})\). This photograph was taken after the elongation (d) in Fig. 9. Because of the enough heat-treatment, almost all of fine defects in the bainite plates as seen in Fig. 12(a) are removed in this stage. This change supports that the 9R bainite transforms to fcc(6) after the enough treatment.

IV. Discussion

The ultimate elongation strain as large as 5.5% was measured during the isothermal heat-treatment at moderate temperature under an applied stress. This amount is almost the same as that followed by SME or PE associated with the martensitic transformation. This fact would be one of the most important

\[ \text{Fig. 11 A histogram showing the appearance of bainite variants.} \]

\[ \text{Fig. 12 Electron micrographs showing bainite plates. (a) and (b) are taken at (c) and (d) in Fig. 9, respectively.} \]

\[ \text{† It has been reported in (8) that the variant of bainite with \((12 \overline{1} 1)\) habit plane is the most frequently observed one. A large number of observation has been made after the ICOMAT-82 and finally the histogram in Fig. 11 is obtained.} \]
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Evidences which support the bainitic transformation to take place with a shear process as in the martensitic transformation.

Furthermore, the following points were ascertained in Figs. 6 to 8. (1) The increasing rate of strain, and ultimate value of strain are dependent on the magnitude of stress and the crystallographic direction of elongation. (2) When the stress is applied for a certain period of time after an incubation period, the elongation continues even after the stress is substantially removed. (3) The special bainite variants with positive Schmid factors are preferentially produced under the stress. These facts also support that the shear process of transformation works prominently in the bainitic transformation.

On the other hand, the following experimental results clearly suggest that the bainitic transformation proceeds by a diffusion-controlled process. (1) The time necessary to reach a constant strain shown in Fig. 3 can be related with the heating temperature by the Arrhenius equation with an activating energy of $8.7 \times 10^4$ J/mol. The temperature dependence of incubation period in Fig. 5 shows exactly the same manner as the time in Fig. 3. (2) The variations of shape strain in Figs. 4 to 8 are well explained by the Austin-Ricketts equation associated with the precipitation reaction. (3) The incubation period is independent of the applied stress as shown in Fig. 8.

Based upon these results in addition to the fact that the shape change could not be detected without the applied stress, we propose the following broad mechanism of the bainitic transformations in the present case. In ordinary circumstances, the martensitic phase change would not occur on the heating at moderate temperature, because the Ms temperature is lower than the room temperature and the applied stress is smaller than the critical transformation stress. However, at a particular site in the matrix crystal where a concentration of stress and/or a fluctuation of solute atoms exist, the nucleation of phase transformation may occur with a shear process. Actually, it has been observed that the bainite plates are nucleated at small precipitates of zinc oxide or $\alpha$ phase after a certain period of time on heating. Once the bainite crystal is formed martensitically, this may grow by an autocatalytic reaction with a directional diffusion of solute atoms caused by the shear transformation. The matrix crystal is unstable and has a tendency to transform to a close-packed $\alpha$ phase with a low solute concentration. Therefore, the structural change from 9R to fcc and the further growth of bainite plate take place at the same time.

The elongation strain shown in Figs. 4 to 8 indicates that the shape change is associated with the formation of special bainite variants which preferentially release the applied stress. As described in III.3, several variants with positive Schmid factors are formed in the early stage, but as the treatment develops, they are limited to two variants with (12 $\bar{2}$ 11) and (12 11 $\bar{2}$) habit planes. This fact may be understood as a result of some complex interaction between the variants for rearrangement, and/or of the different growth rate of each variant with a different Schmid factor.

When no stress is applied on the isothermal heating, possible 24 variants of 9R bainite would be formed with an equal probability and no shape change could be observed. However, under the stress, particular variants with large positive Schmid factors are produced with different nucleation rates, despite of that only one variant crystal with the largest Schmid factor can be stress-induced in the case of 9R martensite. The rearrangement of bainite variants upon heating is thought to be made by a twinning process as well as in the stress-induced martensites. The most frequently observed bainite variants with (12 $\bar{2}$ 11) and (12 11 $\bar{2}$) habit planes have almost the same crystallographic orientation relationships with respect to the matrix crystal and one of these variants can transfer to the other by a small rotation. Also, the frequently observed variants in pair with {12 11 2} and {12 11 2} habits can be converted by a twinning on the (104)$_{9R}$ plane, similarly as in the martensite case. In Fig. 12(b) two variants can be seen

\footnote{Weiser and Hornbogen reported a decrease in the incubation period with increasing applied stress in their hardness measurements. However, no clear change was measured in the present study.}
crossing each other, the habit plane of one variant being parallel to the fault trace on the basal plane of the other. An electron diffraction study has shown that the crossed region is transformed to a fcc crystal as observed in the study on the two step martensitic transformation\(^{(20)-(22)}\).

The incubation period is measured not to be affected by the applied stress and this is a support of the diffusion-controlled nucleation process in the bainitic transformation. On the other hand, the number of variants nucleated and their growth rates were strongly controlled by the applied stress and this means that the shear process is also important. The diffusion process is thought to play an important role to prepare a necessary condition for the shear transformation. A detailed discussion will be made in the forthcoming paper.

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