Two- and Three-Dimensional Grain Growth in the Cu–Al–Mn Shape Memory Alloy

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The normal grain growth behaviors at 750, 800 and 900°C in block and sheet samples of Cu–Al–Mn shape memory alloy with the bcc single-phase structure were investigated. The grain growth exponents, n, evaluated in the two- and three-dimensional grain growths were found to be larger than those in most other metals and were located between 10 and 18. Furthermore, the two-dimensional growth in thin sheet samples was much slower than the three-dimensional growth in block samples due to the grooves formed along grain boundaries on the specimen surface, these grooves constituting a hindrance to the movement.

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1. Introduction

Most materials currently used as practical shape memory alloys (SMAs) are Ni–Ti because of its good shape memory properties, including fatigue property and high corrosion resistance; however, their high cost, low cold-workability and the allergenic potency of Ni may be obstacles for wider applications. Although Cu-based SMAs such as Cu–Zn–Al are commercially attractive because of their low cost and high thermal and electrical conductivities, conventional Cu alloys generally show only limited recoverable strain due to a low degree of the L2₁ order.³

In polycrystalline Cu-based SMAs, the transformation strain is strongly dependent on the orientation, and the superelasticity is known to be improved by an increase of grain size relative to the thickness of sheets due to relaxation of the grain constraint from neighboring grains in the stress-induced martensitic transformation.⁶–¹² However, conventional Cu-based alloys show only limited recoverable strain and a low fatigue strength since a coarse grain structure easily causes an intergranular fracture.⁹,¹³ For ductile Cu–Al–Mn-based SMAs, meanwhile, their superelastic behavior has been systematically investigated for wire samples in a range of 0.66 < d/D < 7 (480–1480 µm in wire diameter D, and 60–7000 µm in mean grain diameter d)¹⁰ and for sheet samples in the range of 0.18 < d/θ < 15.4 (about 250 µm in thickness θ, and 50–4000 µm in mean grain diameter d).¹⁵ It was found that with increasing relative grain size, the superelastic strain increases due to a decline in the elastic constraint from surrounding grains and that an excellent shape recovery of 7–9% strain can be achieved in a bamboo structure in the Cu–Al–Mn thin wires or sheets for large d/D or d/θ. Consequently, a mean grain size larger relative to the cross section area of specimens is required to obtain excellent superelasticity. Thin sheets with a thickness of about 0.2 mm are being practically utilized as ingrown nail treatment clips;¹⁶ however, demands for SMAs with larger dimensions are recently increasing for seismic devices including dampers and isolators, which can dissipate mechanical energy and perfectly recover a large deformation strain.¹⁷–²⁰ We have succeeded in fabricating Cu–Al–Mn bars 4 and 8 mm in diameter, these bars being characterized by excellent superelasticity in the bamboo structure.²¹–²³ Thus, control of mean grain size is very important to improve the SM properties of Cu–Al–Mn alloys and the basic grain growth behavior must be examined.

The topological aspects of grain structure, namely, three-dimensional (3-D) and two-dimensional (2-D) grain structure need to be considered. When grains grow and become larger than the sheet thickness, the grain structure changes from 3-D to 2-D and the contribution of surface energy to grain growth becomes significant in the 2-D growth. A thermal grooving along grain boundary, which is formed on a free surface due to tension balance between the free surface and the grain boundary, is sometimes observed in the 2-D structure. This grooving may pin the grain boundary migration,²⁴,²⁵ and it has been reported that normal grain growth stagnates when the mean grain size reaches 2 or 3 times the sheet (or film) thickness.²⁶–²⁸

We have recently reported normal grain growth of the β (A2) single phase for Cu–Al–Mn alloy sheets with a thickness of 1 mm.²⁹ However, since the average grain diameter was located in the range between 300 and 1200 µm comparable to the specimen thickness, the 3-D and 2-D grain growth modes coexisted and the growth behavior was too complicated to be quantitatively analyzed. Consequently, it is needed to investigate the grain growth behavior separately in the 3-D and 2-D modes. In the present study, the normal grain growth behavior in the Cu–Al–Mn alloy was examined for block samples with the 3-D grain structure and for thin sheet samples with the 2-D grain structure. While, as mentioned above, the difference of grain growth behavior between the 3-D and 2-D modes has been proposed based on the results

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of different materials with either of the modes, the present experiments with one material with the same composition can provide us a direct evidence of the effect of the topological aspect on grain growth.

2. Experimental Procedures

2.1 Materials and processes

Cu–17Al–11.4Mn (at%) alloy was prepared by induction melting under an Ar atmosphere from each pure metal of Cu (99.99% purity), Al (99.7% purity) and Mn (99.9% purity). The ingot was first hot-rolled at 800°C to 15 mm in thickness and then annealed at 600°C for 15 min. The 15-mm thick sheet was cold-rolled to a thickness of 10 mm and then 10-mm cubes were cut from the sheet for investigation of 3-D growth. 10 mm × 8 mm × 0.2 mm or 10 mm × 8 mm × 0.1 mm sheets were cut from the cold-rolled sheet, mirror-polished and used for investigation of 2-D growth. Higher-purity Cu–17Al–11.4Mn alloy was also made by arc melting from highly pure metals of Cu (99.99% purity), Al (99.999% purity) and Mn (99.999% purity). The ingot was hot-rolled to a thickness of 2 mm at 800°C and heat-treated at 600°C for 15 min. For investigation of 3-D growth, the 2-mm thick plate was cold-rolled to a thickness of 1 mm and for 2-D growth, the 1-mm thick plate was cold-rolled to a thickness of 0.5 mm after intermediate annealing at 600°C and then ground to a thickness of 0.2 mm. These plates were finally mirror polished.

Normal grain growth behavior in the β single-phase structure was examined by annealing at 600°C for 30 min in the α (A1) and β two-phase region and subsequent annealing at 750, 800 or 900°C in the β single-phase region for 1 min–120 h, followed by water quenching, where, except for 10 and 1 mm thick specimens, the final annealing was conducted using an quartz capsule evacuated and back-filled with Ar. The microstructure was observed by optical microscope, and the surface profile was analyzed by a laser microscope.

The solidus and α solvus temperatures of Cu–17Al–11.4Mn alloy were determined by differential scanning calorimetry (DSC) at a heating rate of 10°C/min to be 948 and 726°C, respectively.

2.2 Method of quantitative analysis

The mean grain size of the β phase was evaluated by the linear intercept method. The length of a line segment drawn on the optical microscope images, L, is described as follows,

\[ L = N\bar{l}, \]  

where \( N \) is the number of grains on the line segment and \( \bar{l} \) is the average length crossing one grain. In 3-D grain growth, a grain is taken as a sphere with a mean radius of \( \bar{R}_{\text{3D}} \) and the \( \bar{l} \) is given by

\[ \bar{l} = \frac{4}{3} \bar{R}_{\text{3D}}. \]  

Thus, the average grain radius \( \bar{R}_{\text{3D}} \) is described using the eqs. (1) and (2) as

\[ \bar{R}_{\text{3D}} = \frac{3L}{4N}. \]  

In 2-D grain growth, a grain can be approximated as a circular disk with a mean radius of \( \bar{R}_{\text{2D}} \), the \( \bar{l} \) being given by

\[ \bar{l} = \frac{\pi}{2} \bar{R}_{\text{2D}}. \]  

From eqs. (1) and (4), the average grain radius \( \bar{R}_{\text{2D}} \) becomes

\[ \bar{R}_{\text{2D}} = \frac{2L}{\pi N}. \]  

In the present study, the mean radius was evaluated from 55–227 grains (55 ≤ \( N \) ≤ 227) for one condition. The type of growth was normal grain growth in most observations, but grains exceeding \( 9\bar{R}_{\text{3D}}/4 \) for 3-D growth and \( 2\bar{R}_{\text{2D}} \) for 2-D growth in the present study were considered to be grains with abnormal growth. The abnormal grains as well as their affected neighboring grains were excluded from the evaluation.

3. Results and Discussions

3.1 Grain growth behavior

Figures 1(a), 1(c) and 1(e) show the microstructures of specimens with thickness (\( t \)) of 10, 0.2 and 0.1 mm annealed at 900°C for 5 min, respectively. While all the samples had a \( \beta \) single-phase structure, the grain size of 10-mm samples was clearly larger than those of the others. The microstructures of specimens annealed at 900°C for 72 h are shown in Figs. 1(b), 1(d) and 1(f). It is seen that the mean grain size of every specimen increases by the long-time annealing at 900°C. All the data on average grain diameter (2\( \bar{R}_{\text{3D}} \) or 2\( \bar{R}_{\text{2D}} \)) obtained from the specimens annealed at 900°C are plotted in relation to annealing time in Fig. 2, together with our previous data of 1-mm-thick sheets of Cu–17Al–11.4Mn alloy. The average grain size of the 10-mm specimen annealed for 4.32 × 10^5 s (= 120 h) is about 1200 μm, which is sufficiently small compared to the specimen size, and the grain structure mode is 3-D in the whole range of this study. On the contrary, all the mean grain sizes in both the 0.2 and 0.1 mm sheets are over their thickness and the basic structure seems to be in the 2-D mode. In the 1-mm sheets, judging from the microstructural observation from the cross-sectional view, the growth mode is basically 3-D and 2-D until 1 h and over 24 h, respectively. It is seen that the grain growth starts to stagnate when the average grain size exceeds the sheet thickness of 1000 μm. The sheets 0.2 and 0.1 mm in thickness also show slow grain growth in the 2D mode, where the average grain diameter is up to twice the sheet thickness.

The temperature dependences of the normal grain growth in the 0.2-mm sheet samples are shown in Fig. 3, where the average grain diameters (2\( \bar{R}_{\text{3D}} \)) are plotted as a function of annealing time at 900, 800 and 750°C. It is shown that the mean grain size and the growth rate in samples annealed at lower temperatures are basically smaller and lower, respectively, due to lower mobility of the grain boundary by the decrease of diffusion coefficient.

The growth rate in normal grain growth is expressed by the following equation:

\[ \bar{R}^0 - \bar{R}_0^0 = kt, \]  

where \( \bar{R}^0 \) and \( \bar{R}_0^0 \) are average grain radii at annealing time, \( t \) and that at \( t = 0 \), respectively, and \( k \) is constant. The grain
growth exponent, \( n \), is theoretically 2 in a single-phase condition\(^{31} \) but experimentally determined \( n \) is very often larger than 2 even in high purity metals\(^{32} \) due to the solute drag effect, for instance, and is a function of temperature.\(^{33} \)

When \( n = 2 \), the \( k \) is given by

\[
k = \frac{dR^2}{dt}.
\]

(7)

It was found that \( n = 2 \) does not fit the present experimental results in Figs. 3 and 4, but the \( k \) for \( n = 2 \) and for annealing time up to 10 min can be determined to be \( 1.01 \times 10^{-10} \) and \( 1.54 \times 10^{-11} \text{m}^2\text{s}^{-1} \) in 10-mm-thick (3-D) and 0.2-mm-thick (2-D) specimens annealed at 900°C, respectively. The \( k \) in the 2-D specimen is much smaller than that in the 3-D specimen even though the \( k \) in the 2-D is considered to be half of that in the 3-D specimen in theory.\(^{31} \) The \( n \) was determined from the data of Figs. 3 and 4 in the whole time range to be 10 for 10-mm-thick specimen annealed at 900°C (3-D), 11 for the 0.2-
mm-thick specimen at 900°C (2-D), 12 for 0.2 mm thick at 800°C (2-D) and 18 for the 0.2-mm-thick specimen at 750°C (2-D), where the grain radii annealed for 2, 1, 1 and 5 min were used as $R_0$ since a uniform β single-phase structure was observed after those annealing times. The $n$ is larger in 2-D growth than that in 3-D growth, meaning that the growth rate is slower in the 2-D growth. The inverse of the $n$ of Cu–Al–Mn SMA is plotted as a function of annealing temperature normalized by the melting temperature in Fig. 4 compared with other metals. The $n^{-1}$ of the present Cu–Al–Mn alloy is smaller than those of the most other metals, and the normal grain growth rate is found to be extremely slow.

### 3.2 Grain growth of higher-purity specimens

As mentioned above, the solute drag effect of impurities is one of the most likely suspects that results in the deceleration of grain growth and the decrease of the $n^{-1}$. Furthermore, the impurity may easily form inclusions and the grain boundaries may possibly be pinned by them. The effect of impurities on grain growth of the Cu–Al–Mn alloy was examined in both thick and thin sheet samples fabricated with Cu (99.99% purity), Al (99.999% purity) and Mn (99.999% purity). The average grain diameters ($2\bar{R}_{3D}$ or $2\bar{R}_{2D}$) of the higher-purity specimens with a thickness of 1 or 0.2 mm annealed at 900°C are shown in Fig. 5, together with those of the lower-purity specimens fabricated with Cu (99.99% purity), Al (99.7% purity) and Mn (99.9% purity) plotted in Fig. 2. No noticeable difference in the growth rate is seen between the higher-purity and lower-purity specimens, although in 0.2 mm specimens, the mean grain sizes in the higher-purity specimens are slightly smaller than those in the lower-purity ones. The reason for this unexpected result is unknown. From these results, it can at least be concluded that the impurity element is not a dominant factor in the extremely low growth rate of the Cu–Al–Mn alloy. Further examinations are required to clarify the origin of this behavior.

### 3.3 Grooving at grain boundaries

Since the 2-D grain growth is much slower than the 3-D growth as shown in Figs. 2 and 5, formation of grain boundary grooving is expected in the present specimens. Figure 6(a) shows a 3D view by a laser microscope of the surface taken from the 0.6 mm sheet specimen annealed at 900°C for 45 h. A groove with a depth of about 3 µm is observed on the surface profile of Fig. 6(b) as indicated by an arrow, and this kind of groove or step between grains was found at other grain boundaries. It has been reported that when the mean grain size reaches 2–3 times the sheet thickness, the grain growth is arrested due to the balance between the driving force of normal grain growth and the pinning force due to grooving, if grooves act as the effective pinning sites. It has also been proposed that the grain diameter $D_{c}$ at which the stagnation occurs in films or sheets with thickness $d$ is given using the size advantage parameter $Z = R/R_{\text{nei}} > 1$ (R: grain radius, $R_{\text{nei}}$: radius of neighboring grains) by

$$Z = R/R_{\text{nei}} > 1$$
$D_c = 2 \left(1 - \frac{1}{Z}\right) \frac{\gamma_s}{\gamma_{gb}} \theta$, \hspace{1cm} (8)

where $\gamma_s$ and $\gamma_{gb}$ are the surface energy and grain boundary energy, respectively. The $Z$ is up to about 1.5–2 in sheets annealed for 72 h in Fig. 1, and therefore, the $D_c$ is predicted to be 2–3 times the thickness using eq. (8) and $\gamma_s/\gamma_{gb} = 3$, which is in agreement with the present result. It can be concluded that the presence of grooves inhibits the migration of the grain boundaries in the 2-D growth mode at least.

It is interesting to note that a step of several micrometers between the neighboring grains is observed on the surface, as shown in Fig. 6. Such a step was frequently observed for many grain boundaries together with a groove in the present specimens. The origin of the formation of step and its effect on grain growth are unknown at present.

4. Conclusion

The normal grain growth behaviors of 3-D and 2-D growth at 900, 800 and 750°C in the Cu–Al–Mn alloy with the β single-phase structure were investigated. The grain growth exponent $n$ was determined to be 10 (900°C, 3-D growth), 11 (900°C, 2-D growth), 12 (800°C, 2-D growth) and 18 (750°C, 2-D growth), values larger than those in most other metals. The growth rate in the 2-D growth is lower than that in the 3-D growth, and in the 2-D growth the stagnation of grain growth occurs at a grain diameter about two times larger than the sheet thickness, which is attributed to the effect the grooves and steps formed along grain boundaries on surface of the specimens.

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