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Macroscopic shape change of Cu13Zn15Al shape memory alloy on successive heating

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Abstract

The shape change of Cu-13Zn-15Al shape memory alloy on successive heating at a heating rate of 5 °C/min has been studied. The behavior of shape change is strongly temperature dependent. As the heating temperature is below 320 °C, the stabilization phenomenon of the martensite appears, and the first reverse shape memory effect (FRSME) in the Cu-13Zn-15Al alloy occurs due to the martensitic nature transformation that involved in the martensite stabilization process. At the temperature between 320 and 400 °C, the forward shape memory effect (FSME) can be caused by the reverse transformation of the stabilized martensite. The second reverse shape memory effect (SRSME) in the Cu-13Zn-15Al alloy occurs when the ribbon is heated to above 450 °C and subsequently air-cooled to room temperature, this phenomenon attributes to the growth of an asymmetric martensite phase due to the constraining of α-phases distributed along the boundary of the new-formed martensite variants.

Keywords: Cu-13Zn-15Al shape memory alloy; Shape change; Martensite stabilization

1. Introduction

Shape memory alloys (SMAs) have been used in industrial fields for their one-way shape memory effect (OMSME), pseudoelasticity and two-way shape memory effect (TWSME) [1–4]. For the SMA with OMSME, it can revert to its original shape once the low temperature martensite phase or the stress-induced martensite is deformed and heated to A_f (austenite transformation finish temperature). This is created by thermoelastic martensitic transformation (MT). For the SMA with TWSME [3], it may change its shape once the low temperature martensite phase is heated to the high-temperature austenite phase, and reverts to its original shape when it is cooled into martensite again. Sub-structural anisotropy in the parent phase is assumed responsible for TWSME [3,5]. This anisotropy is due to the array of dislocations created by a special thermo-mechanical cycling through the martensitic transformation, either by stress cycling at a fixed temperature, or by temperature cycling at a fixed stress [6–8]. When a particular stress is retained in or a small amount of stress is applied to the matrix crystals, bainitic transformation occurs and it is often accompanied by a macroscopic shape change. This phenomenon has been called the reverse shape memory effect (RSME), which is caused by the martensitic nature involved in the bainitic transformation [9]. Besides OMSME, TWSME and RSME in the Cu-based shape memory alloy, a particular shape change in Cu13Zn15Al shape memory alloy on successive heating has been discovered by the present authors. The investigation contributes to interpreting the shape change.

2. Experimental procedure

The alloy Cu-13Zn-15Al (at%) was induced melted, cast into flat ingots and then homogenized at 850 °C for 24 h and finally rolled to 1 mm thickness plate. Ribbons of the alloy with a dimension of 50.0 mm × 5.0 mm × 0.5 mm were obtained from rolling strips, then re-homogenized at 850 °C for 10 min and followed by water-quenching. A quasi-quantitative examination was performed with a bending mode on the shape change caused by the transformation during heating. The quenched ribbons were bent to “U”-form with a radius of 26.5 mm.

The in situ X-ray diffraction measurement were performed on a D-Max2500 diffractometer with CuK_α radiation. The particle size of the powder specimen is less than 44 μm. The X-ray profiles were measured at various temperature at the heating rate of 5 °C/min. To reduce the influence of ageing during profile measurements, the counter scanning was limited to certain interested ranges. The scanning rate was 0.02°/s. The powder was solution-treated at 850 °C for 10 min in a sealed quartz tube filled with argon prior to water-quenching. The

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metallographic specimen was mechanically polished and followed by electropolished in a mixing solution of CH_3CH_2OH and H_3PO_4 with a volume ratio of 1:1. Incandescent and polarized light was used in turn to display the surface state of the sample.

3. Experimental results

3.1. Electrical resistivity measurement

The resistivity of quenched Cu-13Zn-15Al sample as a function of temperature is measured and the result is shown in Fig. 1. The heating rate is 5 °C/min. With the increasing temperature, the resistivity increases, and it deviates from linear relation, reaches the maximum at about 320 °C and then decreases and the reverse transformation of martensite occurs. So a small peak at about 320 °C can be observed. The resistivity increases again at the temperature above 380 °C. For the "U" -form ribbons treated at 200, 220, 240, 260 °C oil baths respectively, the reversible shape memory effect occurs in the ribbon undergoing the 240 °C oil bath. Therefore, the A_s of the alloy is between 220 and 240 °C, which means that the nartensite is stabilized by heating at rate of 5 °C/min [10].

3.2. Shape change measurement

The shape change of the "U" -form ribbon during heating at a heating rate of 5 °C/min is shown in Fig. 2 (indicated as the dot-line). A three-step shape change can be observed. Below 320 °C, the chard width (CW) of the "U" -form ribbon decreases with temperature (this macroscopic shape change is named as "the first reverse shape memory effect" (FRSME)); between 320 and 400 °C, the CW increases with temperature (this macroscopic shape change is named as "the forward shape memory effect" (FSME)); above 400 °C, the shape does not change with temperature. For the heating temperature below 450 °C, if the ribbon is air-cooled from the heating-state, the CW of the ribbon maintains the same as that in the heating-state. It can be seen that the CW of as heated ribbon is completely coincidence with that of air-cooled one (indicated as the solid-line in Fig. 2). When the ribbon is heated to above 450 °C and subsequently air-cooled to room temperature, the CW of the ribbon decreases again. Such macroscopic shape change is called "the second reverse shape memory effect" (SRSME) (indicated as the solid-line in Fig. 2). If the quenched ribbon is not distorted, the shape change cannot be detected during heating and cooling.

Once the "U" -form ribbon is put into the 500 °C salt bath for 60 s, it stretches and maintains the stretching state after air-cooling.

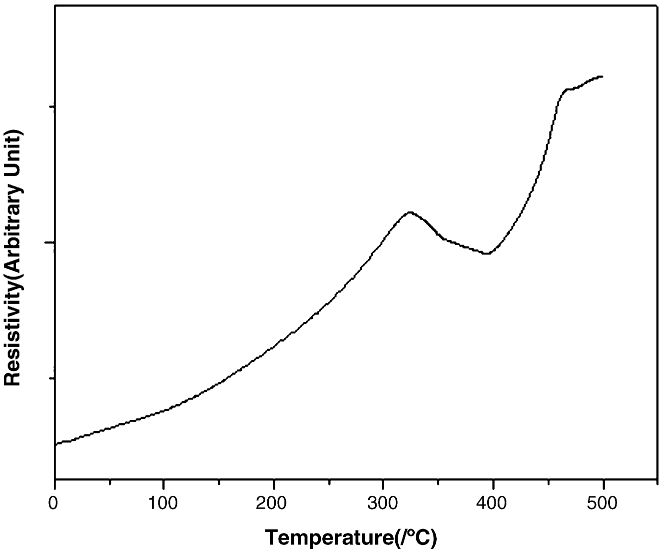

Fig. 1. The Resistivity curves of the Cu-13Zn-15Al alloy with the heating-rate of 5 °C/min.

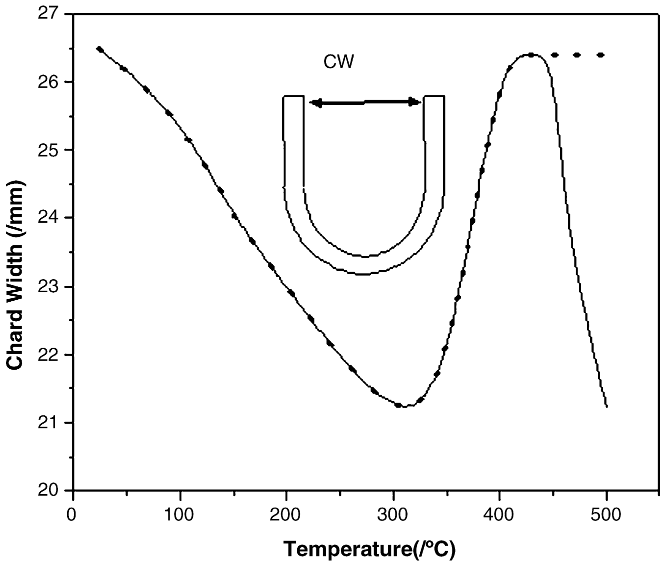

Fig. 2. The relation between the chard width and the temperature; the dot-line: ribbon as heated; the solid-line: ribbon as air-cooled.

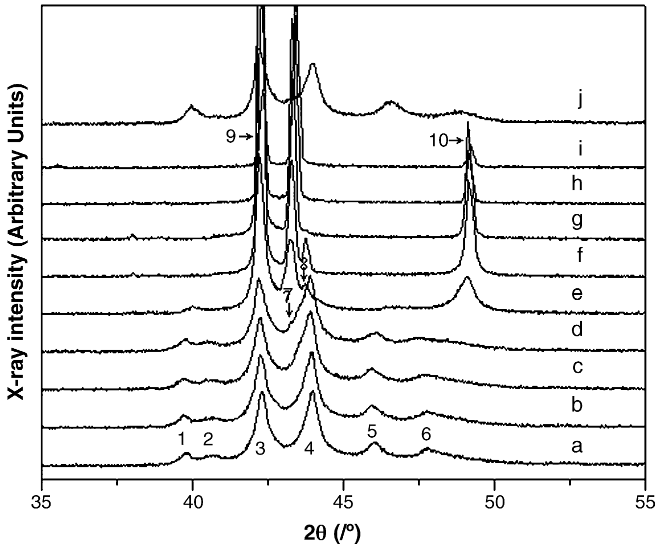

Fig. 3. X-ray diffraction spectrums of Cu-13Zn-15Al alloy heated to different temperature at a rate of 5 °C/min. (a) as-quenched, (b) heated to 180 °C, (c) 280 °C, (d) 320 °C, (e) 380 °C, (f) 400 °C, (g) 430 °C, (h) 450 °C, (i) 470 °C (j) heated to 500 °C and then air-cooling to room temperature. (1) $1\ 2\ \bar{2}_M$, (2) $2\,0\,2_M$, (3) $0\,0\,1\,8_M$, (4) $1\ 2\ \bar{8}_M$ ($2\,0\,8_M$), (5) $1\,2\,1\,0_M$, (6) $2\ 0\ \bar{1}\ \bar{0}_M$, (7) $2\,2\,0_\beta$, (8) $4\,1\,1_\gamma$, (9) $1\,1\,1_\alpha$, (10) $2\,0\,0_\alpha$.

3.3. *X-ray diffraction*

The in situ X-ray profiles of the alloy are taken at various temperatures during heating at a heating rate of 5 °C/min and shown in Fig. 3. As the heating temperature is lower than 380 °C, the distance between $(1\,2\,2)_M$ and $(2\;0\;\bar{2})_M$, as well as the distance between $(1\,2\,1\,0)_M$ and $(2\;0\;\overline{10})_M$, decreases with the increasing temperature, subsequently air-cooling to room temperature, the X-ray profile of the sample maintains the same as that in the heating-state. The martensite structure transforms from M18R (monoclinic 18R) into N18R (normal 18R) according to the formula as: $1/d^2 = h^2/a^2 \sin^2\beta + k^2/b^2 + l^2/c^2 \sin^2\beta - 2hl\cos\beta/ac\sin^2\beta$. The reverse transformation occurs near 320 °C (martensite transformed into β_1-phase), but a large fraction of martensite is still retained up to higher temperature. It is concluded that the peak at 320 °C on the resistivity curve of the quenched sample shown in Fig. 1 is related to the transformation of the martensite to parent β_1-phase. This retained martensite disappears at the temperature between 380 °C and 400 °C as shown in Fig. 3.

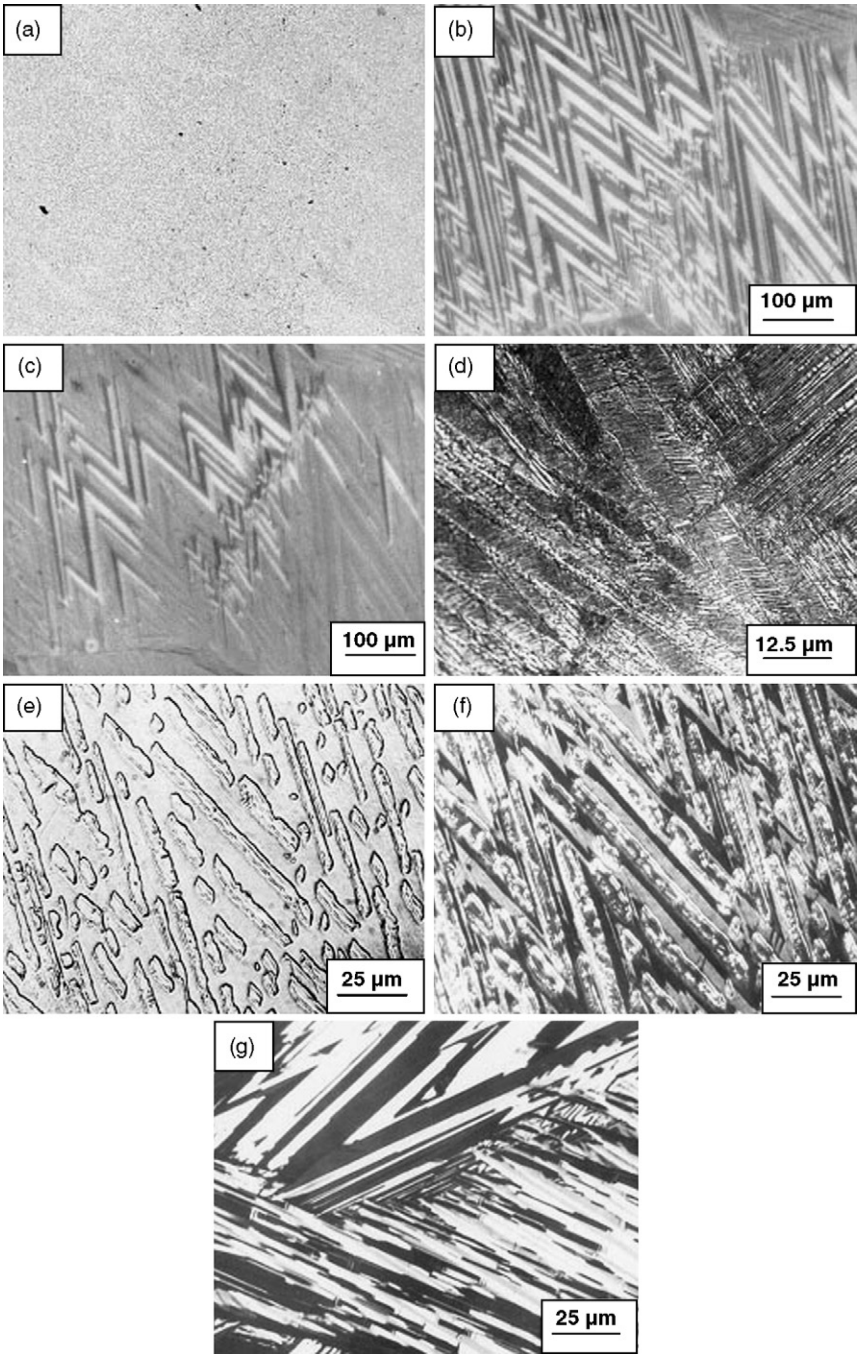

Fig. 4. The optical micrographs of Cu-13Zn-15Al alloy heated to different temperature at a rate of 5 °C/min: (a) as-quenched, (b) as-quenched (polarized light), (c) heated to 240 °C, (d) 430 °C, (e) heated to 500 °C and then air-cooling, (f) the same field of view (e) (polarized light), (g) putting into 500 °C oil bath followed by air-quenching (incandescent light).

Furthermore, it can also be seen that the precipitation of α- and γ_2 phase occurs as the sample is heated up to 400 °C, the rapid increase in resistivity starting from 400 °C is due to the precipitation of α- and γ_2 phase. With the temperature above 400 °C, the relative intensity of α- and γ_2 phase diffraction peaks decreases and that of β_1-phase diffraction peaks increases with the temperature, the amount of the β_1-phase increases and that of the α- and γ_2 phase decreases as well(shown in Fig. 3 (g,h,i)).

When the sample is heated to 500 °C and then air-cooling to room temperature, the martensite phase appears again and the α phase still exists (shown in Fig. 3 (j)).

3.4. Optical micrograph observation

The change of optical micrograph of the alloy is taken at various temperatures during heating at a heating rate of 5 °C/min and shown in Fig. 4. Fig. 4(a) and (b) represent the quenched sample in the same field. Fig. 4(a) is taken by incandescent light, where the flat surface of the sample electro-polished is displayed. Fig. 4(b) is taken by polarized light, and typical martensite morphology can be found. As the sample is heated to 240 °C, the abnormal surface re-relief phenomenon presents (shown in Fig. 4(c)), which is in the same field as that in Fig. 4 (a) and by the incandescent light. When subsequently air-cooling to room temperature, the abnormal surface re-relief phenomenon remains unchanged. Compared with Fig. 4 (b) and Fig. 4(c), the orientation relationship of the abnormal surface re-relief shown in Fig. 4(c) is completely coincidence with that of the as quenched martensite shown in Fig. 4 (b). As the sample is heated to 430 °C, white and black stripes present in every single primary martensite variant plate(shown in Fig. 4(d)). The white and black stripes are the precipitation of α- and γ_2 phase according to X-ray diffraction results shown in Fig. 3. When the sample is heated to 500 °C and then air-cooling to room temperature, the α phase precipitates along the boundary of the martensite variant (Fig. 4 (e), (f) (polarized light)).

The optical micrograph of the sample at 500 °C salt bath for 60 s and followed by air-cooling to room temperature is shown in Fig. 4(g) (by polarized light)). Its structure is completely martensite phase.

4. Discussions

A particular shape change of the "U" -form ribbon on successive heating and cooling shown in Fig. 2 indicates that the shape change is associated with the formation of various phases.

When a particular stress is retained in or a small amount of stress is applied to the matrix crystals, bainitic transformation occurs and it is often accompanied by a macroscopic shape change. This shape change is thought to be caused by the martensitic nature involved in the bainitic transformation [9]. For the tested alloy, only does martensite stabilization occur, the reversible transformation (martensite transform into β_1- phase) does not occur before heated to 320 °C (shown in Figs. 1 and 3), therefore the abnormal surface re-relief on the basis of as-quenched martensite is caused only by the martensite stabilization. The orientation relationship of the abnormal surface re-relief is completely coincidence with that of the martensite as-quenched, and its typical optical micrographs is obviously different from that of bainite in the Cu-Zn-Al alloy [9,11,12]. The abnormal surface re-relief phenomenon and the FRSME are two of the most important evidences, which support the martensite stabilization process to take place with a shear process. Namely the FRSME is caused by the martensitic nature involved in the martensite stabilization.

On the other hand, the following experimental results clearly suggest that the martensite stabilization process proceeds by a diffusion-controlled process. The distance between $(1\,2\,2)_M$ and $(2\ 0\ \bar{2})_M$, as well as the distance between $(1\,2\,1\,0)_M$ and $(2\ 0\ \overline{10})_M$, decreases during martensite stabilization process, a transformation from M 18R to N l 8R occurs. Such a transformation is a consequence of the order-disorder atomic diffusion process [13–15]. The basal plane of the ordered thermoelastic martensite cannot be closely packed into a regular hexagon as the ordered Cu, Zn and Al atoms have different radii. Therefore, the adjacent layer cannot fit exactly in the 1/3 position. This results in a monoclinic structure. In the alloy, the monoclinic angle β tends to 90° during the course of heating, which indicates that order-disorder atomic diffusion process occurs. Nakata Y [13] has revealed that this diffusion process of the CuZnAl alloy during ageing in the martensite phase is the interchange between Zn atom on the β-plane and Cu on the α- plane by the ALCHEMI method.

Suzuki et al. [14] reported that the stabilized martensite in CuZnAl alloy could transform to the β_1 parent phase, but this reverse transformation was incomplete. We obtain the same experimental results (shown in Figs. 1 and 3). Therefore the FSME is attributed to this transformation. Only does a fraction of stabilized martensite transform into β_1 parent phase, the shape memory capacity is reduced, the FSME is little.

From the Figs. 3 and 4, we can suggest that as heating temperature between 450 °C and 500 °C, the precipitated α- and γ phase inside the primary martensite variant as-quenched have re-dissolved into the β_1-phase, the α phase distributing along boundary of the primary martensite variant has not re-dissolved (the asymmetric and oriented displaying of α-precipitates) with the temperature. subsequently air-cooling to room temperature, the β_1- phase transforms into martensite, an asymmetric martensite phase growth can be obtained due to the constraining of the α-precipitates displaying along the boundary of the new-formed martensite variants. When the tested alloy is air-cooled without constraining factor, possible 24 variants of the martensite will be formed with an equal probability (shown in Fig. 4(g)), and no shape change can be observed. Therefore, the growth of an asymmetric martensite phase due to the constraining of the α-phases distributed along the boundary of the new-formed martensite variants is thought to be the origin of the SRSME.

5. Conclusions

The shape change and the transformation process of the Cu-13Zn-15Al (at%) alloy on successive heating and cooling has been investigated by electrical resistivity measurement, optical metallographic observation and X-ray diffraction measurement. The following results have been obtained.

(1) The martensite stabilization process in Cu-13Zn-15Al alloy not only possesses a martensitic nature but also possesses diffusion-control nature. The martensite stabilization is accompanied by (1) A_s increasing; (2) the abnormal surface re-relief phenomenon emerging; (3) the reverse shape memory effect occurring; (4) the monoclinic angle β of the martensite tending to 90°.

(2) As the heating temperature is below 320 °C, the FRSME in the Cu-13Zn-15Al alloy occurs due to the martensitic nature transformation in the martensite stabilization process; between 320 and 400 °C, the FSME in the Cu-13Zn-15Al alloy exists due to the reverse transformation of the stabilized martensite.

(3) As the heating-temperature is higher than 450 °C and then air-cooling, the SRSME in the Cu-13Zn-15Al alloy occurs, which attributes to the growth of an asymmetric martensite phase due to the restraint of the α-phases distributed along the boundary of the new-formed martensite variants.

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