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Twice reverse shape memory effect in CuZnAl shape memory alloy ①

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Abstract: The variations of the shape memory effects in the Cu-13Zn-15Al(mole fraction, %) alloy upon successive heating (the rate of heating is 5 ℃/min) have been studied by means of $\rho-T$ curve, shape memory effect measurement, optical metallographical observation and X-ray diffraction. The first abnormal reverse shape memory effect occurs when the tested alloy is heated to the temperature below 320 ℃; when it is heated to the temperature between 320 ℃ and 450 ℃, the forward shape memory effect occurs; in the two stages, the shape of the sample remains the same as that in the furnace when it is taken out from the furnace and air-cooled; when the tested alloy is heated to the temperature above 450 ℃, the shape of the sample remains unchanged during heating, but the second reverse shape memory effect occurs after it is air-quenched.

Key words: CuZnAl alloy; shape memory alloy; martensite; reverse shape memory effect
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1 INTRODUCTION

Cu-based shape memory alloys are commercially attractive systems for the practical exploitation of the shape memory effect because of their lower cost and relative ease of processing[1, 2]. However the Cu-based shape memory alloys are less stable than the Ni-Ti-based alloys above the room temperature. In fact, reverse transformation starting temperature (A_s) increases during holding in the martensite phase in the Cu-based shape memory alloy[3-9]. This phenomenon is called stabilization of martensite. It is shown that the martensite stabilization is accompanied by a relief of the martensite, an increase of resistance and a reverse shape memory effect (RSME)[10-15]. In this study, the second reverse memory effect presents when the air-quenched Cu-13Zn-15Al(mole fraction, %) shape memory alloy is heated to 500 ℃ at a rate of 5 ℃/min and then air-cooled, which may be used to design high-temperature thermal sensor (> 400 ℃). The purpose of this study is to reveal these two reverse shape memory effects.

2 EXPERIMENTAL

The tested alloy Cu-13Zn-15Al was induction-heating melted, cast into flat ingots and then homogenized at 850 ℃ for 24 h. The ingots were then hot-rolled into sheets of 1 mm in thickness after its surface was renewed. The sheets were solution-treated at 850 ℃ for 10 min and then air-quenched. M_s is 200 ℃ and A_s is 190 ℃ when the air-quenched sample was heated at a rate of 100 ℃/min and measured by $\rho-T$ curve(voltage-temperature curve). The specimen was bent to "U" shape, and its chord width was measured as the flag of the shape memory effect after heated to different temperatures at a rate of 5 ℃/min. The specimens of voltage-temperature curve measurement, the optical metallographical observation, and shape memory effect measurement were cut from the sheet. The metallographical specimen was mechanically polished and then electro-polished in a solution of CH_3CH_2OH and H_3PO_4 with a volume ratio of 1∶1. Incandescent light and polarized light were used in turn. The former could display the surface state of sample, such as martensite relief and flat surface. The latter could distinguish the different variants of the martensite even the surface was electropolished into flat, because the variants grow in different crystal directions. X-ray diffraction (XRD) experiment and data processing were performed on a D-5000 diffractometer with powder specimens with particle size of less than 75 μm. The powder specimens were solution-treated at 850 ℃ for 10 min in a sealed quartz tube filled with argon, followed by air-quenching.

3 EXPERIMENTAL RESULTS

3.1 Voltage-temperature characterization

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Fig. 1 shows the change of voltage as a function of temperature by heating the air-quenched specimen at a rate of 5 ℃/min. The reverse transformation of martensite does not occur when the temperature is below 320 ℃. With the increasing of the temperature, the voltage increases, and it deviates from linear relation and increases sharply at the temperature above 130 ℃, reaches the maximum at 320 ℃ and then decreases, the reverse transformation of martensite occurs; the voltage increases again at the temperature above 380 ℃. After cooling, the reverse transformation does not occur. In this process, the heating rate is very slow, the martensite as-quenched in the tested alloy undergoes a significant aging effect, and the martensite stabilization occurs, which results in the increasing of A_s(A_s is 190 ℃ as the heating rate is 100 ℃/min).

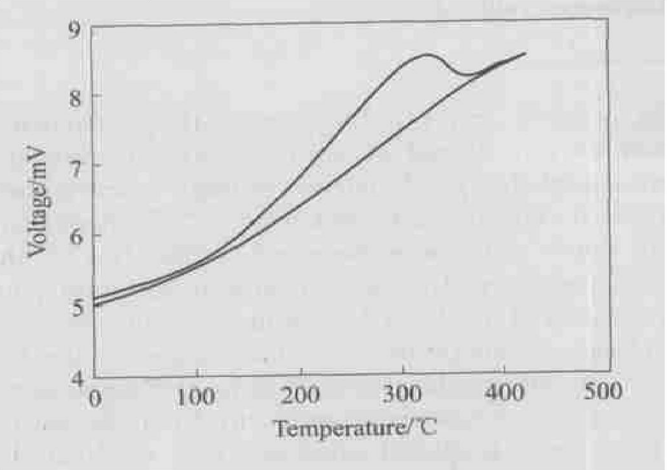

Fig. 1 Voltage—temperature relation of as-quenched Cu-13Zn-15Al alloy($M_s \approx 200$ ℃)

3.2 Shape memory effect

"U"-shape sample as air-quenched is heated to 300 ℃ at the heating rate of 100 ℃/min, and it stretches and remains the stretching state after air-cooling.

Fig. 2 shows the relation between the chord width (CM) of the "U"-shape sample and temperature when the "U"-shape sample is heated at a rate of 5 ℃/min. A curious three-step shape memory effect is found. The first step, $t <$ 320 ℃, the CW decreases as the temperature increases, which is called the first reverse shape memory effect (RSME) (1-stage); the second step, 320 ℃ $< t <$ 450 ℃, the CW increases as t increases, giving a forward shape memory effect (2-stage); in the two stages, the CW remains the same as that in the furnace after air-cooling, and at the three step, 450 ℃ $< t <$ 550 ℃, the CW remains unchanged during heating (broken line in 3-stage), but when the sample is taken out from the heating furnace and air-cooled, the CW decreases again, which is called the second RSME (real-line in 3-stage).

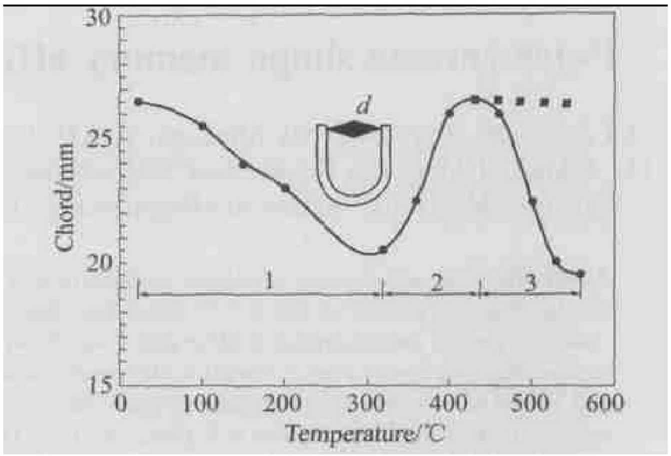

Fig. 2 Relation between chord width and temperature

3.3 Optical metallographical observation

Fig. 3 shows the change of metallography for the alloy air-quenched during the process of heating at 5 ℃/min. Figs. 3(a) and (b) show the same field of view of sample as-quenched. Fig. 3(a) is taken by incandescent light. The flat surface of the sample electropolished is shown. Fig. 3(b) is taken by polarized light, and self-accommodation configuration of martensite as quenched is displayed. Heated to 280 ℃ (before reverse transformation according to Fig. 1), the sample surface in the same field of view as that in Fig. 3(a) presents the abnormal re-relief phenomenon (Fig. 3(c), the incandescent light). Compared with Fig. 3(b), it can be seen that the pattern of relief is the same as that of primary martensite (Fig. 3(c)). It is suggested that the abnormal re-relief forms on the base of primary martensite. For the tested alloy, only does martensite stabilization occur, the reverse transformation does not occur as the temperature is below 320 ℃ (Fig. 1), therefore the re-relief phenomenon is caused by the martensite stabilization.

Fig. 3(d) shows the change of metallography after the sample air-quenched is heated to 380 ℃. The interface among primary martensite plate becomes coarse. White and black stripes like the pattern of twin presents in every single primary martensite plate. Its structure is determined by XRD as a mixture of α and β phases (Fig. 4). For the alloy, M_S is 200 ℃, and the structure of the quenched sample is completely composed of martensite, therefore, α and β phases here obviously transform from the stabilized martensite, which suggests that the decrease of voltage—temperature and the forward shape memory effect above 320 ℃ as shown in Fig. 1 and Fig. 2 respectively are generated by the reverse transformation of stabilized martensite. According to the erosion resistance of β phase and α phase, we know that the

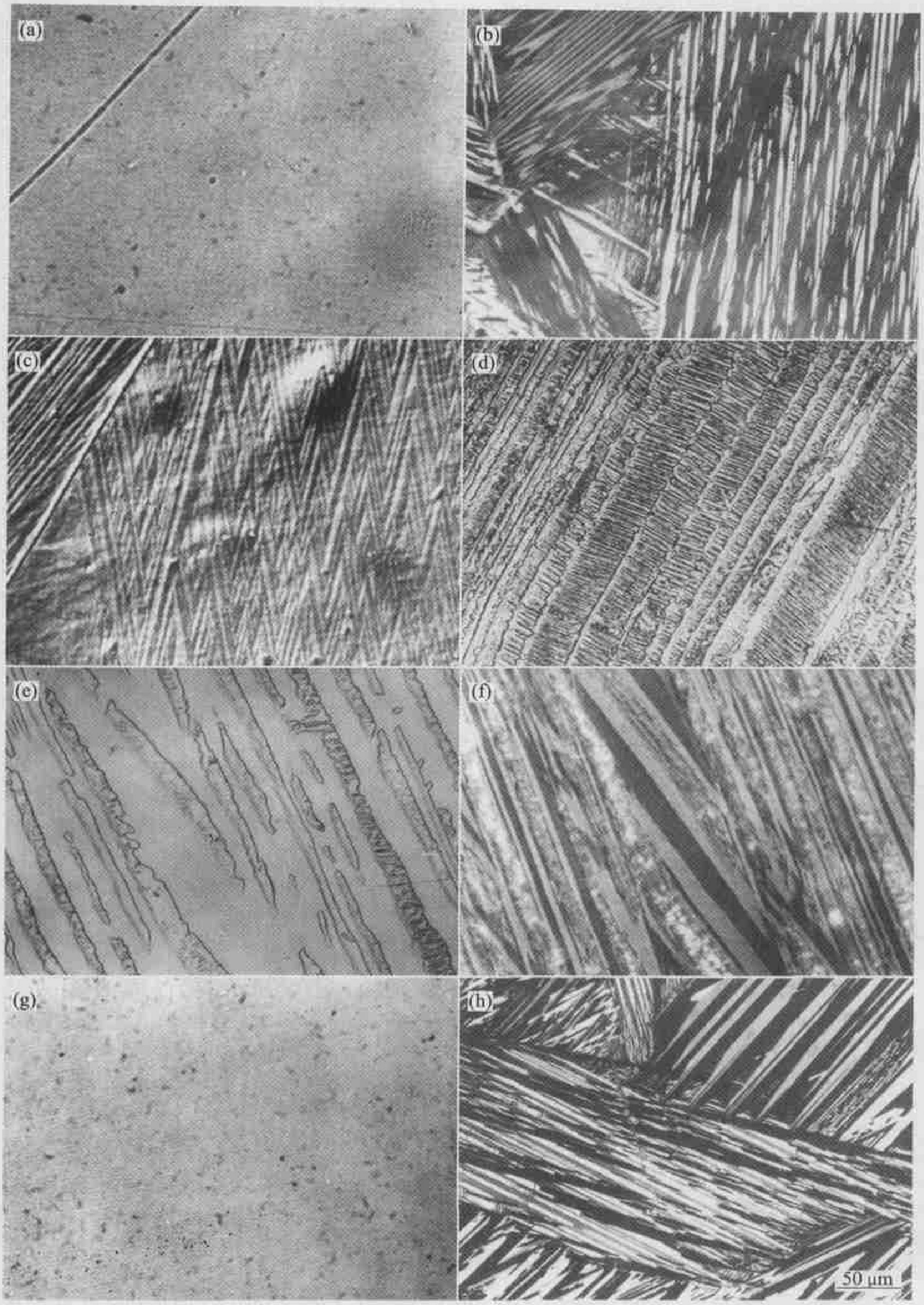

Fig. 3 Optical micrographs of air-quenched samples with various heating temperatures
(a) —RT; (b) —RT (polarized light); (c) —280 ℃(same view as that of (b)); (d) —380 ℃; (e) —500 ℃(incandescent light); (f) —500 ℃(polarized light, same view as that of (e)); (g) —300 ℃(incandescent light, quick heating to 300 ℃); (h) —300 ℃(polarized light, same view as that of (g))

erosion resistance of β phase is worse than that of α phase, therefore black stripes should be the β phase and the white one should be the α phase inside the primary martensite plate, and the white line in the boundary of primary martensite plate should be the α phase. When heated to 500 ℃, the pattern of the field of view likes "sandwich", and the α phase holds the martensite(Figs. 3(e) and (f).

The metallography for the air-quenched sample heated to 300 ℃ at a heating rate of 100 ℃/min and then air-quenched is shown in Figs. 3(g) and (h). The structure of it is completely composed of martensite.

3.4 X-ray diffraction

Fig. 4 shows the X-ray diffraction patterns of air-quenched samples at various temperatures(the heating rate is 5 ℃/min). From the patterns one finds the following results: ① the reverse transformation of martensite in the tested alloy does not occur below 320 ℃. The structure of the tested alloy is α+ β phase when heated to 380 ℃. When heated to 500 ℃ and then air-cooled to room temperature, the structure is martensite+ α phase; ②within 320 ℃, the $(12l)_M$ and $(20\bar{l})_M$, $(04l)_M$ and $(32\bar{l})_M$ diffraction pairs tend to get closer during heating, and merge into one diffraction peak respectively at last ; ③the 2θ value of $(0018)_M$ diffraction peak decreases, and the monoclinic angle approaches 90 ℃.

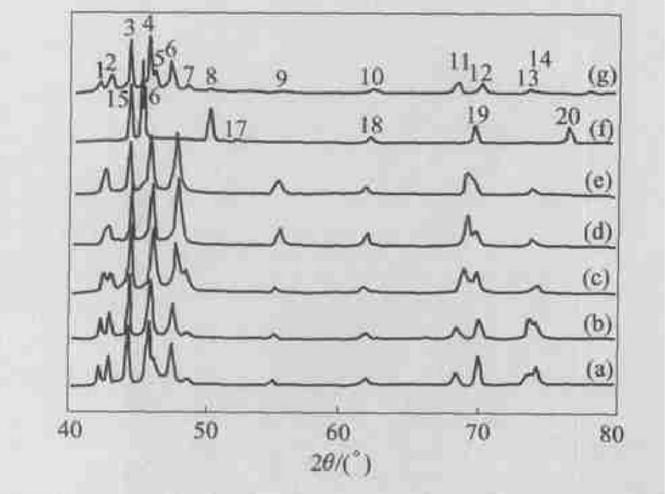

Fig. 4 X-ray diffraction patterns at different temperatures

(a) —As-quenched; (b) —180 ℃; (c) —240 ℃; (d) —280 ℃; (e) —320 ℃; (f) —380 ℃; (g) —500 ℃
1 —$12\bar{2}_M$; 2 —202_M; 3 —$0018_M(111_\alpha)$; 4 —$12\bar{8}_M$; 5 —208_M; 6 —$1\,210_M$; 7 —$20\,\overline{10}_M$; 8 —200_α; 9 —$2\,016_M(20\,\overline{16}_M)$; 10 —$2\,020_M(12\,\overline{20}_M)$; 11 —$040_M$; 12 —$320_M$; 13 —$2026_M$; 14 —$12\,\overline{26}_M$; 15 —$111_\alpha$; 16 —$220_{\beta_1}$; 17 —$311_{\beta_1}$; 18 —$400_\beta$; 19 —$220_\alpha$; 20 —$422_\beta$

4 DISCUSSION

The tested alloy is heated up to 380 ℃ at a rate of 5 ℃/min, the martensite phase decomposes into β + α phases. As heated up to 450 ℃, the inner structure (α+ β phases) of the primary martensite has re-dissolved into the β phase, the α phase distributing along boundary of it has not re-dissolved yet; the β phase transforms into the β_1 phase, β_1 phase transforms into martensite and α phase remains unchanged after cooling, the re-formed martensite grows preferentially along with the orientation of the primary martensite because of the holding of the orientated arranging α phase along the boundary of the primary martensite, which produces the macro-accumulation of the shearing effect, results in the second reverse memory effect.

The martensite stabilization does not occur when the air-quenched sample is heated to 300 ℃ at a heating rate of 100 ℃/min because of the short aging time in the martensite state. The thermoelastic martensite transforms to the β phase, the complete shape memory effect occurs, and β phase transforms into martensite after air-cooling, here, the orientation of the re-formed martensite is random, which unnecessarily coincides with that of primary martensite, and the second reverse memory effect does not occur.

5 CONCLUSIONS

1) For the Cu-13Zn-15Al alloy, the martensite stabilization is easy to occur. The martensite stabilization is accompanied by ① A_S increasing; ② the electrical resistance of martensite abnormally increasing; ③the abnormal re-relief phenomenon emerging; ④the reverse shape memory effect occurring; ⑤ $12l_M$, $20\bar{l}_M$ and $04l_M$, $32\bar{l}_M$ diffraction pairs of the martensite tending to get closer, the d-value of 0018 M diffraction increasing, the martensite parameter a and c increasing, b decreasing, a/b → 0.866, the monoclinic angle β→90°.

2) For Cu-13Zn-15Al alloy, it is heated up to 450 ℃ at a heating rate of 5 ℃/min, the second reverse shape memory effect presents after air-cooling.

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