

QUENCH IN STABILIZATION OF Cu-Zr-Al ALLOY^①

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ABSTRACT The effects of quenchant temperature on the stabilization and property of Cu-Zr-Al alloy were investigated by means of X-ray diffraction and electrical resistivity measurement. Experimental results show that, when the quenchant temperature is higher than A_f , thermoelastic martensite will be obtained; when the quenchant temperature is between M_s and M_f , martensite will exhibit partial stabilization and when the quenchant temperature is lower than M_f , martensite will be stabilized. The stabilization may be in close relation with the suppression of $B_2 \rightarrow DO_3$ transformation.

Key words shape memory alloy stabilization quenchant

1 INTRODUCTION

Since the stabilization was discovered in CuZnAl alloy in 1981^[1], the stabilization effect of the martensite phase in Cu based shape memory alloy has been extensively studied by many researchers^[2-5]. Cu based shape memory alloy will be stabilized after direct quenching, but the stabilization may be avoided by step quenching and its property can be improved. Some mechanisms have been proposed for the martensite stabilization: a) the pinning mechanism of supersaturated vacancies, b) the pinning mechanism of precipitates, c) the reordering mechanism in the martensite phase and d) the mechanism of atom rearrangement. The change of martensite crystal structure destroyed the crystallographic relationship between martensite phase and parent phase, thus suppressing the transformation.

The importance of the configurational changes in the atomic structure as the cause of the stabilization has become more and more evident^[6-9]. Although it was found that the quenchant temperature has a significant effect on the Cu based alloy^[9], a systematic study on the effects of the quenchant temperature on the stabili-

zation and its order is absent. In this paper, the results obtained under different quenchant temperatures are reported, the relationship between its property and its ordering are obtained, and the mechanisms of stabilization are discussed.

2 EXPERIMENTAL

The nominal composition of the alloy used is Cu-20.8% Zr-5.8% Al-0.05% Ce. The master ingots was prepared by melting pure Cu, Zn, Al and Al-Ce alloy in an induction furnace. Thin sheet specimens were obtained from the ingots by hot rolling and cold rolling. They were then cut into samples used for electrical resistivity-temperature measurements (160 mm × 30 mm × 0.7 mm) and X-ray diffraction sample (20 mm × 20 mm × 0.7 mm) after polishing. They were homogenized at 800 °C for 5 min and quenched into 100, 80, 70, 60, 40 °C and room temperature water and held at these temperatures for 30 min, then cooled to room temperature with the water. The electrical resistivity-temperature curves were obtained by X-Y recorder. X-ray diffraction analyses were conducted on

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SIEMENS D-500 diffractometer using $\text{CuK}\alpha$ radiation (35 kV, 30 mA). The step scanning step length was 0.02° , time 20 s, and continuous scanning rate was $0.5^\circ/\text{min}$.

3 RESULTS

3.1 Electrical resistivity-temperature curves

In order to study the effect of quenching rate on properties, we measured the electrical resistivity-temperature curves of the specimens after quenched into different temperature water, the results are shown in Fig. 1 and its relative transformation temperatures are listed in Table 1. With decreasing quenchant temperature, the curves become shorter and wider, the amount of martensite transformation decreases, the hysteresis loop widens, and the reverse transformation temperature increases. However, M_s and M_f do not show significant changes, which is in accordance with the results in Ref. [11].

Table 1 Influence of quenchant temperature on transformation temperature

Quenchant temp / $^\circ\text{C}$	A_s / $^\circ\text{C}$	A_f / $^\circ\text{C}$	M_s / $^\circ\text{C}$	M_f / $^\circ\text{C}$
100	64	74	63	52
80	65	75	64	52
70	67	76	65	53
60	72	84	65	52

3.2 X-ray diffraction

The test samples were solution annealed for 5 min at 800°C , then quenched into 100°C water (step quenching) and room temperature water (direct quenching) separately. Their X-ray diffraction patterns were shown in Fig. 2. The lower angle diffraction peak is the long range order superstructure diffraction peak of M_{18R} martensite, so the long range order can be analysed by the relative intensity changes of (019) diffraction peak.

Fig. 3 shows that the intensity changes of (111) and (019) diffractions. It can be concluded that, with the decrease of the quenchant temperature, the intensity of (019) diffraction peak decreases, and the distance between the (111)_M

and (111) _{β_1} peaks decreases gradually.

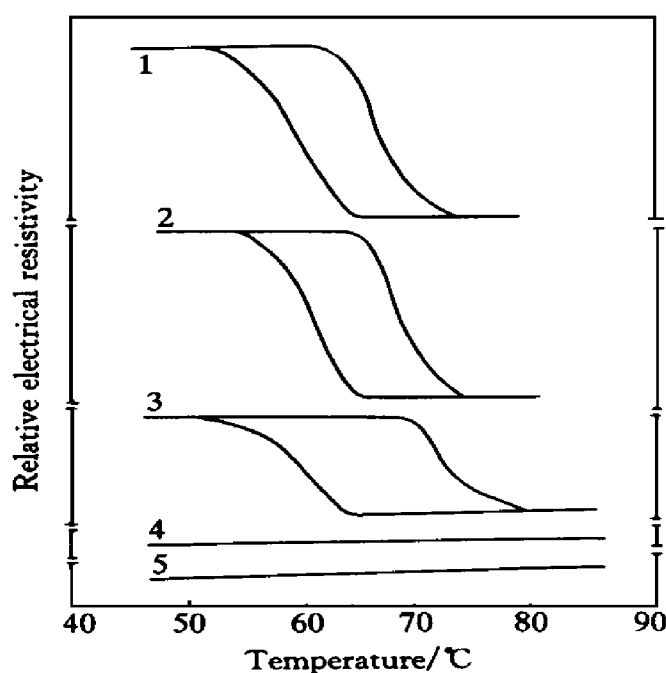


Fig. 1 Influence of quenchant temperature on resistivity-temperature curves

- 1—Quenched into 100°C water;
- 2—Quenched into 80°C water;
- 3—Quenched into 60°C water;
- 4—Quenched into 40°C water;
- 5—Quenched into RT water

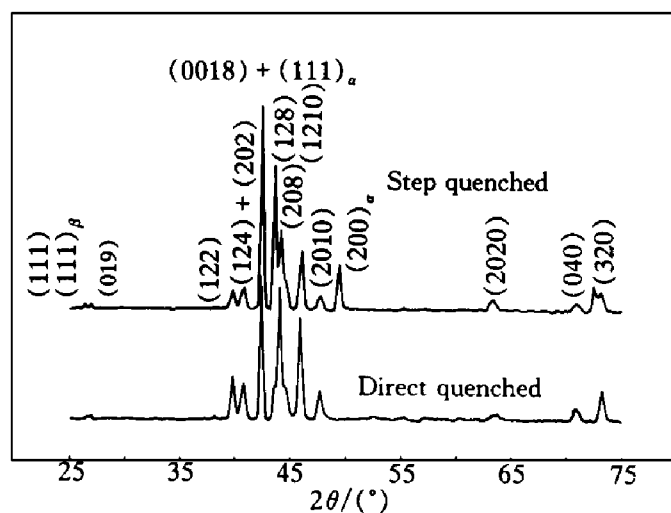


Fig. 2 X-ray diffraction patterns of step and direct quenching

We also measured the splitting parameter Φ of the diffraction line pair (122) and (202), the splitting parameter means the order of martensite^[9, 12]. The parameter Φ is defined as

$$\Phi = |\sin^2 \theta(112) - \sin^2 \theta(202)|$$

where $\theta(hkl)$ is the Bragg angle of (hkl) diffraction peak. For $M18R$ martensite, when its DO_3 order, Φ reaches the maximum values, with the decrease of the long range order the values of Φ decrease. The results are shown in Table 2.

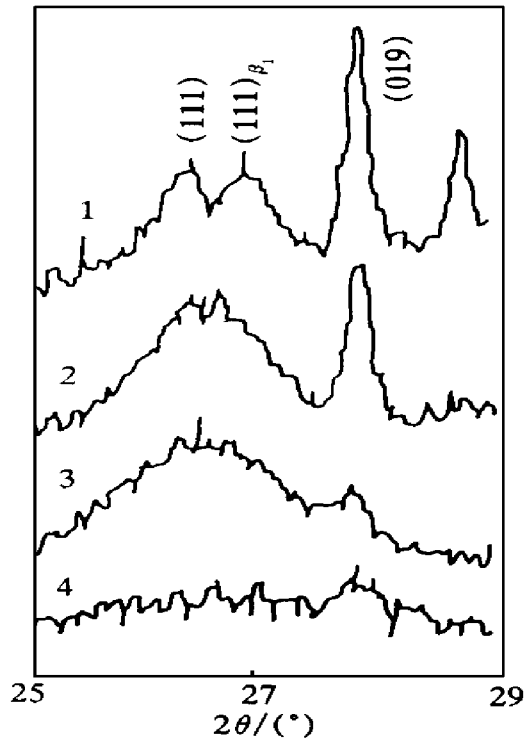


Fig. 3 X-ray diffraction patterns of different temperature quenching

- 1—Quenched into 100 °C water;
- 2—Quenched into 80 °C water;
- 3—Quenched into 60 °C water;
- 4—Quenched into RT water

Table 2 Influence of quenchant temperature on Φ

Quenchant temp / °C	$2\theta(122)$ / (°)	$2\theta(202)$ / (°)	Φ / 10^{-3}
100	39.872	40.884	5.721
80	39.870	40.878	5.700
60	39.960	40.848	4.966
40	40.000	40.820	4.638

4 DISCUSSION

During the quenching process, rapid cooling leads to the stabilization of martensite. Rapid

cooling can not suppress the $A_2 \rightarrow B_2$ ordering transformation, but it can suppress the $B_2 \rightarrow DO_3$ ordering transformation. The values of the long range order can be indicated by the intensity of superlattice diffraction peak in X-ray diffraction patterns, the splitting parameter Φ between a certain pair of peaks^[3, 12, 13].

In Fig. 3, it can be seen that with the decrease of quenchant temperature, the quenching cooling rate increases, the intensity of (019) superlattice diffraction peak, and the distance between the $(111)_M$ and $(111)_\beta$ peak decrease.

Table 2 lists the values of the splitting parameter Φ . It can be seen that, with the decrease of the quenchant temperature, the values of Φ decrease, i.e. the ordering decreases. These results are in accordance with the intensity change of superlattice diffraction peak. These all indicate that the long range order in martensite decreases with the decrease of the quenchant temperature.

In Fig. 1, the samples were quenched into 60 °C water, the height of its transformation curve decreases obviously, reverse transformation temperature and hysteresis increase. This is because 60 °C is between M_s and M_f , the samples were directly quenched into the double phases state, in which the martensite stabilized during the isothermal process, only those kept in parent phase state during the isothermal process retain memory property after quenching. It can be seen from Fig. 1 and Table 2 that the partial stabilization in the samples is in relation with the partial were suppressed of $B_2 \rightarrow DO_3$ ordering change during the quenching and the long range order decreases.

When samples were quenched into 40 °C water and room temperature water they are completely stabilized. This indicates that samples quenched into the water whose temperature is lower than M_f directly. Due to the rapid cooling rate, the $B_2 \rightarrow DO_3$ ordering change was seriously suppressed, the order can not attain the values to produce reversible transformation, so the sample shows complete stabilization. Comparing Fig. 1 with Fig. 3, it can be seen that, as the quenchant temperature decreases, the long range order in martensite decreases, memory property

worsens, and when the quenchant temperature is lower than M_f , the sample will show complete stabilization.

It is well known that $M18R$ martensite is inherited from the atom ordering arrangement of $D0_3$ parent phase. Because of the higher order of the parent phase, the order of $M18R$ martensite transformed from the $D0_3$ parent phase is high, which is profitable for the martensite transformation to parent phase along a certain crystallographic path during the heating process.

Thus, the $B_2 \rightarrow D0_3$ ordering change during quenching may be an important cause of the stabilization in CuZnAl alloys.

5 CONCLUSIONS

(1) When samples are quenched into the quenchant at temperature higher than M_s and isothermally aged for 30 min, thermoelastic martensite will be obtained.

(2) When the quenchant temperature is between M_s and M_f , the quenched martensite will be partially stabilized.

(3) When samples are quenched into the quenchant at temperature lower than M_f , martensite will show complete stabilization.

(4) Martensite stabilization is in close relation with the long range order.

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