Vol. 8 № 4 **Trans. Nonferrous Met. Soc. China** Dec. 1998

STABILIZATION OF MARTENSITE IN Cu-Zn-Al ALLOY AND ITS REVERSE SHAPE MEMORY EFFECT①

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ABSTRACT The stabilization of martensite in Cu-14.5%Zn-7.1Al% (mass fraction) alloy was studied by SME measurement, optical microscope observation, X-ray diffraction and TEM. In the stabilization process, the alloy exhibited reverse shape memory effect while reordering state almost didn't change, and the density of stacking faults decreased. It is concluded that the stabilization of martensite is the process of $M18R \rightarrow N18R$ which is a diffusion shear. The similarity of the crystal transformation between $M18R \rightarrow N18R$ and $\beta_1 \rightarrow M$ is the origin of the reverse SME in our experiment.

Key words SMA stabilization of martensite reverse shape memory effect

1 INTRODUCTION

The stabilization of martensite refers to the phenomenon that the reverse transformation start and finish temperatures (A_s and A_f) increase during aging in the martensite phase, which hinders the application in Cu-based SMA by lowering its thermal stability and SME. There are two main categories so far about its mechanism: (1) martensite boundary pinning by vacancies or precipitation[1]; (2) atoms reordering in martensites[2, 4, 7]. Nakata and Yamamoto[3, 5] have recently proved that this reordering is caused by the interchange between Cu and Zn atoms in the martensite of Cu-Zn-Al alloy. In this paper, some new experimental phenomena, such as reverse shape memory effect and re-relief of martensite were observed in the martensite stabilization process. These phenomena have been explained by the phenomenological crystallographic theory and analyzing the structure change of this alloy.

2 EXPERIMENTAL

Cu-14.5Zn-7.1Al% alloy was prepared by induction melting the component metals in an intermediate frequency induction furnace, and the ingot obtained was homogenized at 850 ℃ for 24 h, then hot-rolled into sheets of 1 mm thickness after the surface defects of the ingots were cut off. All of the experimental specimens were cut from the sheets and air-quenched after solution-treated at 750 ℃ for 5 min. X-ray diffraction experiment was performed on D-5000 diffractometer, using Co-K_α radiation. The martensitic transformation temperature M_s of the alloy is about 200 ℃.

3 RESULTS

3.1 Shape memory effect measurement

The air-quenched specimen was bent to "U" shape, 45 mm × 5 mm × 1 mm in size and its chord was measured after heated to different temperatures at a rate of 10 ℃ per minute, respectively. The results are shown in Fig. 1. The specimen was observed to exhibit reverse SME within 300 ℃.

3.2 X-ray diffraction

Fig. 2 shows the X-ray diffraction spec-

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① Project 59671024 supported by the National Nature Science Foundation of China and project (1995) 252 supported by the Natural Science Foundation of Hunan province Received Apr. 3, 1998; accepted Jul. 2, 1998

trums at different temperatures by heating the air-quenched specimen at a rate of 10 ℃/min. The results show as follows: (1) the alloy was in martensite phase within 280 ℃ and didn't show reverse transformation almost; (2) (12L), (20$\bar{L}$) and (04L), (32$\bar{L}$) diffraction-pairs tended to get closer during heating; (3) the intensity of the diffraction indicated that the ordering state of "nn" and "nnn" changed little; (4) the 2θ value of (0018) diffraction decreased.

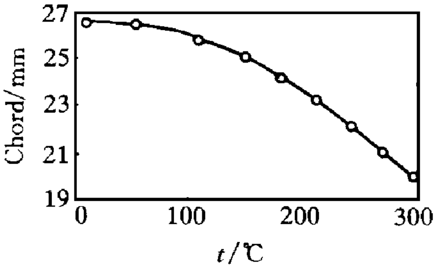

Fig. 1 Reverse shape memory effect

From the X-ray diffraction results, the relation between heating temperature and variation of the lattice parameters a, b, c, β was obtained. As shown in Fig. 3, during the stabilization of martensite, the a and c increased while b decreased, $a/b \to 0.866$, $\beta \to 90$ ℃.

3.3 Optical microscope observation

Fig. 4 shows the changes of morphology when the air-quenched specimen was heated to different temperatures. The four optical micrographs were taken from the same field of the specimen. Figs. 4(a, b) show air-quenched morphology by using polarized light and incandescent light respectively, while Figs. 4(c, d) show the morphology in 160 ℃ and 200 ℃ respectively by using incandescent light alone.

We can observe the re-relief of martensites from polished surface on the basis of martensites shown in Fig. 4(a). During heating, the re-relief increased. It is known that, in $\beta_1 \to M$ transformation, the lattice shear can lead to relief in martensites. In our experiment, relief appeared in the stabilization process, so it is called re-relief.

4 DISCUSSION

4.1 The stabilization of martensite

As we know, the "nnn" superlattice diffraction characterizes the 18R structure martensite, such as (111) and (019) diffraction[6]. So, through the appearance of (111) and (019) diffraction spectra in the stabilization process as shown in Fig. 2, we can determine this alloy is 18R structure martensite. Meanwhile, the (12L), (20$\bar{L}$) and (04L), (32$\bar{L}$) diffraction-pairs are in splitting state, which is the characteristic of diffraction spectrum of modified martensite structure[6]. Therefore, the alloy is modified 1 8 R structure, i. e. M 1 8 R as

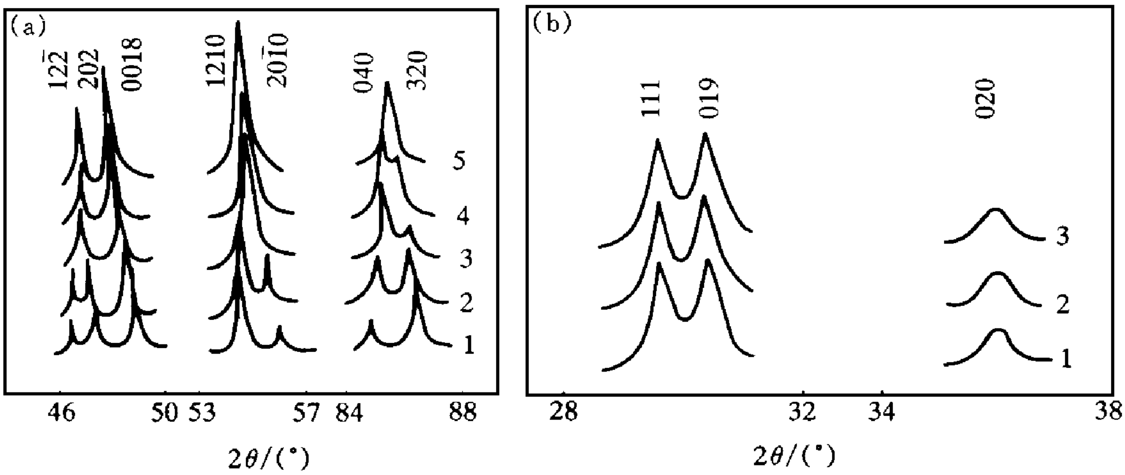

Fig. 2 X-ray diffraction spectrums at different temperature
(a) 1—RT, 2—200 ℃, 3—240 ℃, 4—280 ℃, 5—300 ℃;
(b) 1—RT, 2—200 ℃, 3—280 ℃

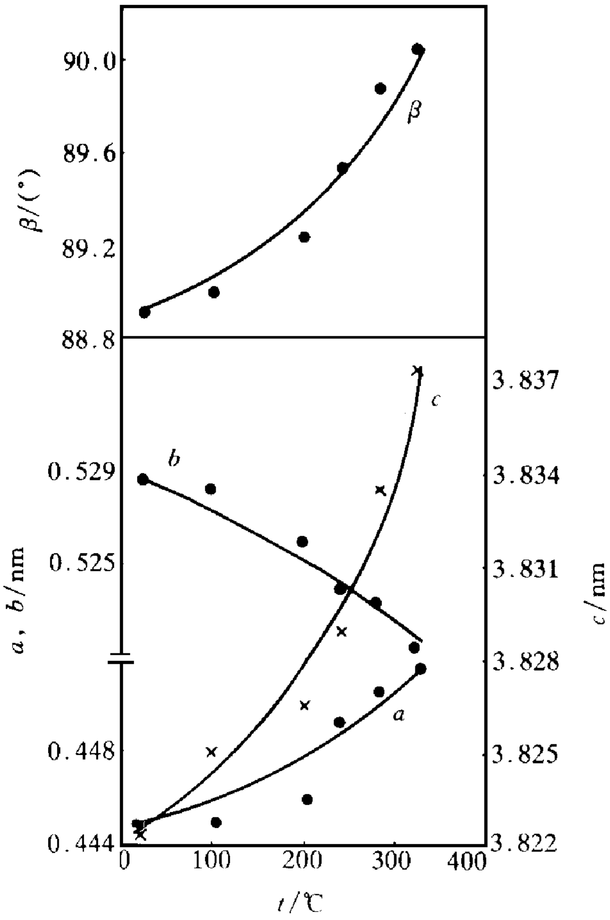

Fig. 3 Variation of martensitic lattice parameters as a function of temperature t/ ℃

shown in Fig. 5. It is attributed to the different size of the atoms in the basal plane of martensite, which makes the basal plane distorted from the exact hexagon structure and consequently the stacking positions of the 1st and 2nd layers are shifted from the $a/3$ and $2a/3$ position.

(12L), (20$\overline{L}$) and (04L), (32$\overline{L}$) diffraction-pairs were drawing closer during the stabilization process (Fig. 2). According to the X-ray diffraction results, the variation of the lattice parameters can be obtained: a, c increased, b decreased, $a/b \to 0.866$, $\beta \to 90$ ℃(Fig. 3). It is obvious that the atom arrangement in basal plane was approaching to an exact hexagon, which resulted in the angle β between a and c axes approaching the rectangular. It is obvious that during stabilization process, modified 18R structure was transforming into normal 18 R structure, i. e. $M18R \to N18R$.

According to the above experiment results, we conclude that there were atom rearrangement in the stabilization process. Nakata and Yamamoto[3] have detected the atomic distribution in the basal plane in Cu-Zn-Al alloy by ALCHEMI as shown in Fig. 5(b): Ⅰ-Al+ Cu, Ⅱ-Cu, Ⅲ-Zn+ Cu. We have obtained the same result by analyzing the X-ray diffraction spectra[6]. The atom rearrangement means there were interchange between atom-pairs or disordering in the specimen. But in Fig. 2(b), the intensity of "nn" and "nnn" ordering diffraction, i. e. (020) and (111), (019) diffraction didn't change almost. So, the atom rearrangement must be the interchange between Cu-Zn "nn" atom pair. Because of the little difference of scattering factors between Cu and Zn atoms, the interchange between them can hardly affect the "nn" ordering diffraction, such as (020) diffraction. Although the interchange between "nnn" atom-pairs can change the intensity of "nnn" ordering diffraction[9], we had not observed their change, either. Therefore, we can conclude that "nnn" ordering state didn't change in our experiment.

Fig. 4 Optical micrographs showing the surface re-relief of martensites upon heating
(a) —RT(polarized light); (b) —RT; (c) —150 ℃; (d) —280 ℃

And the interchange between "nn" atom-pairs means there was atom diffusion in the stabilization process.

4.2 The reverse shape memory effect in the stabilization process

The reverse SME has been observed in the stabilization process (Fig. 1). We know, in TWME, $\beta_1 \to M$ transformation can lead to reverse shape memory effect. This is because the martensite variants grow preferentially as a function of the applied stress, which can lead to deformation of the whole specimen. When being heated to A_s, SME begins to remove the deformation. But there is still residual stress in the specimen which can lead to re-deformation, i.e. reverse SME when $\beta_1 \to M$ transformation happens again.

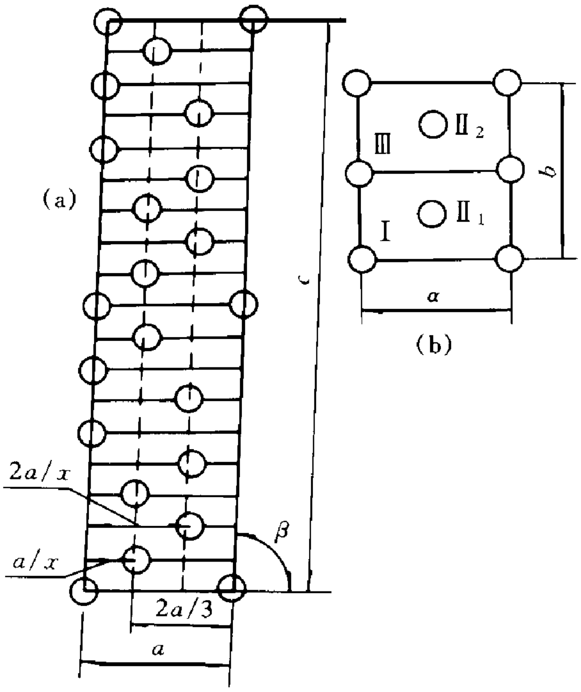

Fig. 5 Crystal structure model of $M18R$ martensite

(a) —viewed from [010] direction;

(b) —the atomic configuration on the basic plane

In our experiment, reverse SME appeared in the stabilization process, in which the $\beta_1 \to M$ transformation had completed, thus the reverse SME may not be related to $\beta_1 \to M$, but $M18R \to N18R$. In addition, the re-relief of martensites can be observed in the optical micrographs during $M18R \to N18R$ transformation. This phenomena is also quite coincident with that in $\beta_1 \to M$ transformation. It is obvious that $M18R \to N18R$ transformation and $\beta_1 \to M$ transformation have similarity in microscopic.

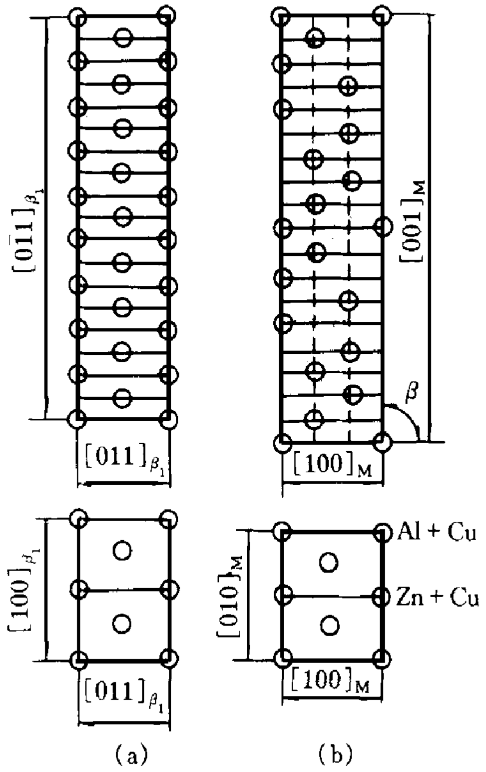

Fig. 6 Crystal structure model of $\beta_1 \to M$ transformation

(a) —parent phase β_1;

(b) —normal $18R$ type martensite

The baintic transformation in $\beta_1 \to M$ is as follows[8]: the $[100]_{\beta_1}$ direction in $(1\bar{1}0)_{\beta_1}$ plane contracts, $[011]_{\beta_1}$ direction expands; $[100]_{\beta_1} \to [0\bar{1}0]_M$, $[011]_{\beta_1} \to [100]_M$; $[0\bar{1}0]_{\beta_1}$ direction expands while the shears take place along $[011]_{\beta_1}$ direction in $(0\bar{1}1)_{\beta_1}$ plane (Fig. 6). In $M18R \to N18R$ transformation the lattice parameters a, c increased, b decreased, $a/b \to 0.866$, which have the same tendency of lattice structure change as $\beta_1 \to M$ transformation. Similar to $\beta_1 \to M$ transformation, the stabilization process must be accompanied with lattice shear which results in re-relief of martensite and reverse SME.

Therefore, we can conclude that $M18R \rightarrow N18R$ transformation is a shear transformation controlled by diffusion which is similar to $\beta_1 \rightarrow M$ transformation in microscopic and phenomenological crystallography. That is the reason of reverse SME and re-relief of martensite in the stabilization process.

5 CONCLUSIONS

(1) The stabilization process is considered as the process of $M18R \rightarrow N18R$ transformation, which is related to the interchange between Cu-Zn atoms.

(2) During $M18R \rightarrow N18R$ transformation, there are phenomena such as: reverse SME, re-relief of martensite and the lattice parameters changes. All of these should be result from similarity in the microscopic and phenomenological crystallography between $M18R \rightarrow N18R$ and $\beta_1 \rightarrow M$ transformation.

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(Edited by Zhu Zhongguo)