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Thermal cycling effect in Cu 11. 9Al 2. 5Mn shape memory alloy with high M_s temperature^①

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[Abstract] The effects of thermal cycling on martensite transformation in Cu 11. 9Al 2. 5Mn (mass fraction, %) shape memory alloy (SMA) with high M_s temperature were studied by means of electrical tension vs temperature ($U-T$) measurement, optical microscopy observation and X-ray diffractometry. It shows that with increasing thermal cycles, the transformation temperatures decreased, which are accompanied by changes of martensite structure such as the decline of NNN ordering degree and monoclinic angle $\beta \rightarrow 90^\circ$. Compared with traditional Cu-base SMA, the alloy has rather high thermostability and can work at 200~300 °C. Its excellent thermostability comes from two factors: 1) its β_1 parent structure is stable and difficult to decompose at work temperature; 2) its martensite structure is close to N18R ($\beta = 89.6^\circ$), which restrains the process of M18R \rightarrow N18R and the tendency of martensite stabilization and decomposition.

[Key words] shape memory alloy; Cu-Al-Mn alloy; martensite; thermal cycling; thermostability

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1 INTRODUCTION

Problems of thermal stability, including martensite stabilization, parent phase decomposition and cycling property degradation, have hindered the application of Cu-base shape memory alloy (SMA) for a long time. Martensite stabilization is regarded as the results of its structure destabilization ($M18R \rightarrow N18R$)^[1~5]. Parent phase decomposition leads to the changes of transformation temperature and decreases of reversible martensite, which are concerned with variation of ordering degree, transformation of parent phase to bainite and decomposition of parent phase^[1]. Thermal cycling usually makes transformation temperature change and shape memory effect (SME) decline due to the formation of vacancy clusters, accumulation of dislocation and destruction of ordering degree^[6~8]. In general, structure stability of martensite and parent phase plays a key role on Cu-base SMA's thermal stability and that of parent phase is particularly significant considering that martensite is transformed from parent phase while parent phase is a metastable one obtained by quenching. Research work in Cu alloy shows that there are two methods to stabilize the structure of parent phase: 1) increasing Al content to restrain $\beta \rightarrow \alpha$ transformation; 2) adding other component (such as Mn) to check $\beta \rightarrow \gamma_2$ transformation caused by higher Al concentration. Therefore, the present study is conducted to clarify the changes of martensite transformation properties of Cu-11. 9Al-2. 5Mn (mass fraction, %) SMA de-

signed by the methods mentioned above in thermal cycling.

2 EXPERIMENTAL

Cu-11. 9Al-2. 5Mn (mass fraction, %) was prepared by melting the component metals in an intermediate frequency induction furnace and the ingot obtained was homogenized at 850 °C for 24 h after its surface defects were cut off, then hot-rolled into sheets of 1 mm in thickness. All of the experimental specimens were cut from the sheets and measured (or observed) after different heat treatments.

Martensite transformation temperature is determined by $\rho-T$ curve^[4]. X-ray diffraction experiment was performed on D-5000 diffractometer using powder samples (120~152 μ m) and its data were analyzed by SIMENS diffraction software. Optical microscopy observation was taken on NEOPHOT 21 instrument.

3 RESULTS

3.1 Change in transformation temperature

Fig. 1 shows $U-T$ curves in first two cycles. We find that when being heated immediately after quenching the tested alloy exhibits certain tendency of martensite stabilization but the martensite doesn't decompose and proceed thermoelastic inversion at about 400 °C. After that, the parent phase doesn't decompose obviously and can transform to martensite again at about 230 °C. As reported, similar studies were

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carried on Cu-Zn-Al SMA^[2], which led to the results that thermoelastic reversion of as-quenched martensite couldn't happen in normal transformation temperature because of martensite stabilization and decomposition. Moreover, if martensite decomposes, the alloy will never continue thermoelastic transformation when it is cooled down. In addition, in Cu-Zn-Al SMA, the β_1 parent phase obtained by martensite inversion will decompose to the equilibrium phase ($\beta_1 + \alpha + \gamma_2$) as soon as it is heated above 200 °C. Therefore, compared with traditional Cu-base (Cu-Zn-Al) SMA, the tested alloy has rather high thermostability both in martensite and parent phase states.

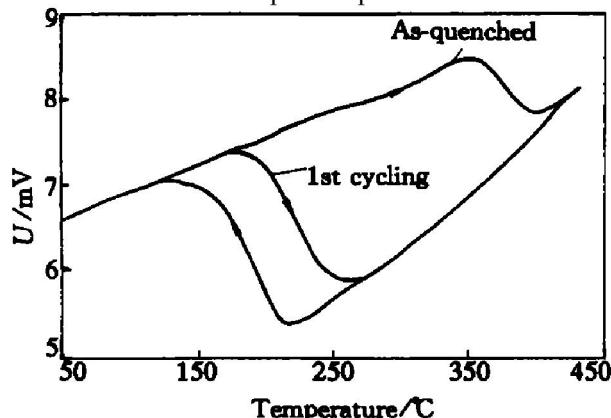


Fig. 1 $\rho-T$ curves after immediate quenching

Fig. 2 shows transformation temperatures as a function of the number of thermal cycles. It's noticed that with increasing thermal cycle the martensite characteristic temperatures, such as M_s , M_f , A_s , A_f decrease, which is consistent with the result in a Cu-Al-Ni alloy reported by Nakata and Tadaki et al^[6, 7]. Such similarity may be contributed by the fact that their parent phases are both of a DO_3 type ordered structure. As to variations in transformation temperature, we can see most of that happen before 10th cycling, and the ΔM_s , ΔM_f , ΔA_s , ΔA_f , are respectively 15 °C, 12 °C, 6 °C and 13 °C. After that apparent changes cannot be seen with increasing cycles, which implies that the alloy has high thermostability in cycling. Notably, the experiments are taken at the upper temperature as high as 300 °C, far above that of many reported Cu-base SMA (usually no higher than 120 °C)^[1~7]. This means the Cu-11.9Al-2.5Mn SMA is promising in practical use as high temperature SMA.

3.2 Change in martensite morphology

Fig. 3 shows the changes of martensite morphology of an identical region for the tested alloy during thermal cycling. It can be seen that: 1) In quenching state martensite morphologies are mostly spear-like and orderly arrayed (as shown in Fig. 3(a)); 2) Upon 1st cycling the spear-like parts largely become finer while some martensite grow a little (marked “ \rightarrow ” as shown in Fig. 3(b)). Martensite with other orienta-

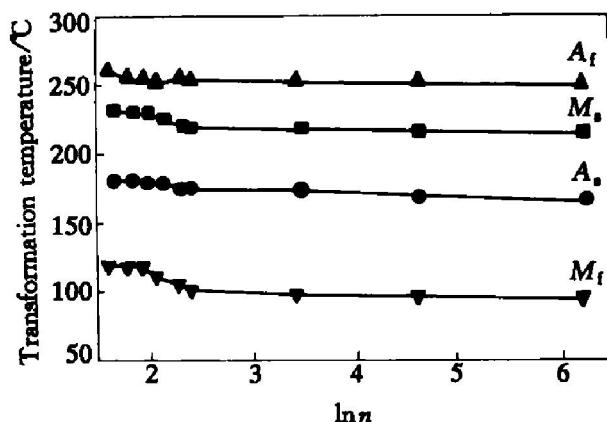


Fig. 2 Changes in transformation temperature with thermal cycling (n)

tion is found to insert into spear-like parts (marked “ \rightarrow ” as shown in Fig. 3(b)). The changes mentioned above may be caused by defects (such as dislocations) which are produced in thermal cycling and have effects on the nucleation and growth of martensite; 3) Upon 100th cycling, spear-like martensite is already finer and denser. Some bright stripes, which may be caused by stabilization, appear along the direction where martensite previously grew (as shown in Fig. 3(c)); 4) Upon 500th cycling, the former spear-like martensite is hardly recognized and martensite morphologies are far away from ordered arrangement. Bright ones increase, which indicates that thermal cycling deepens the stabilization degree in some orientation (as shown in Fig. 3(d)).

3.3 X-ray diffraction

Fig. 4 shows X-ray diffraction patterns of martensite in cycling. It appears that the intensity of 111, 019 diffraction reduces, which results from the destruction of NNN ordering degree with increasing cycles. As we know, 111, 019 diffractions characterize the NNN ordering in the 18R martensite structure^[5]. Meanwhile, 320 and 040 diffraction pairs with a large $\Delta 2\theta$ are hardly separated even in quenching state ($\Delta 2\theta$: angle difference between one diffraction pair). Since $\Delta 2\theta$ is a measurement of monoclinic angle β ^[3], the smaller the $\Delta 2\theta$ is, the bigger the angle β of martensite is. When $\Delta 2\theta = 0$, $\beta = 90^\circ$. So the phenomenon above implies that thermal cycling can make monoclinic angle β of martensite towards 90° .

4 DISCUSSION

As mentioned above, Cu-11.9Al-2.5Mn alloy has better thermostability than traditional Cu-base SMA in the way that both its martensite at 400 °C and the parent phase at 230 °C are thermoelastic as well as its transformation temperature is little affected by thermal cycling except the 1st one. All these can be explained by the stability of its structure.

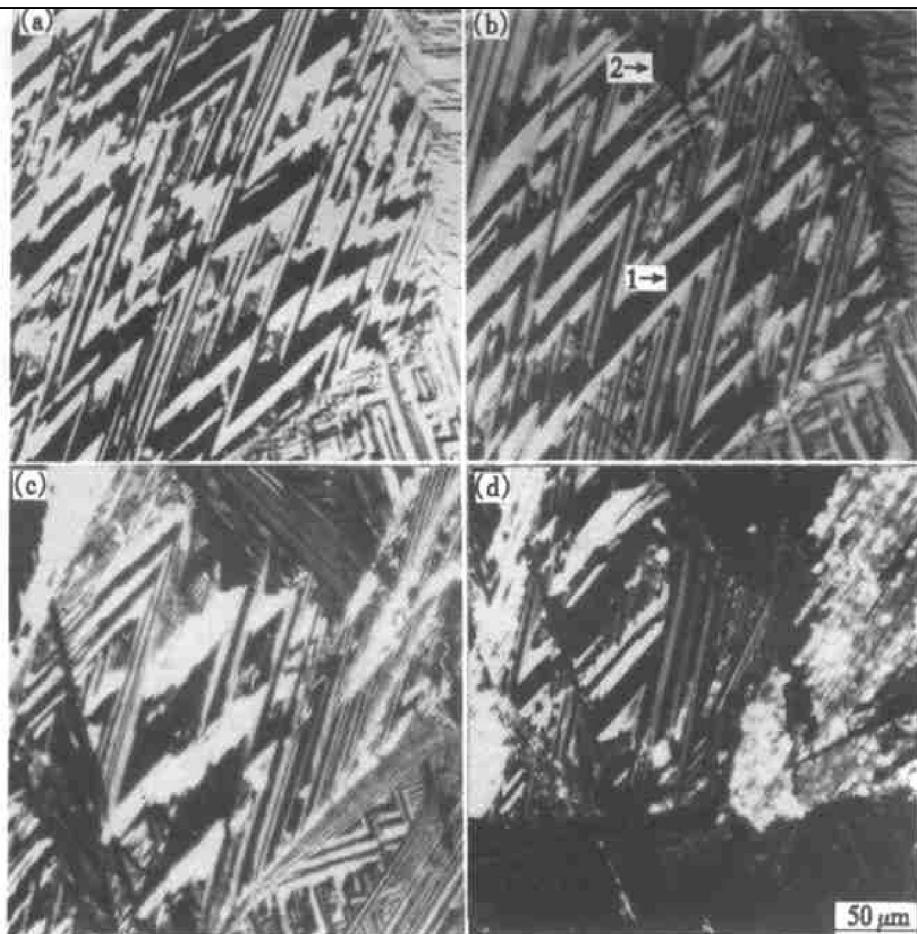


Fig. 3 Optical micrographs of alloy in thermal cycling
(a) —As quenched; (b) —1st cycling; (c) —100th cycling; (d) —500th cycling

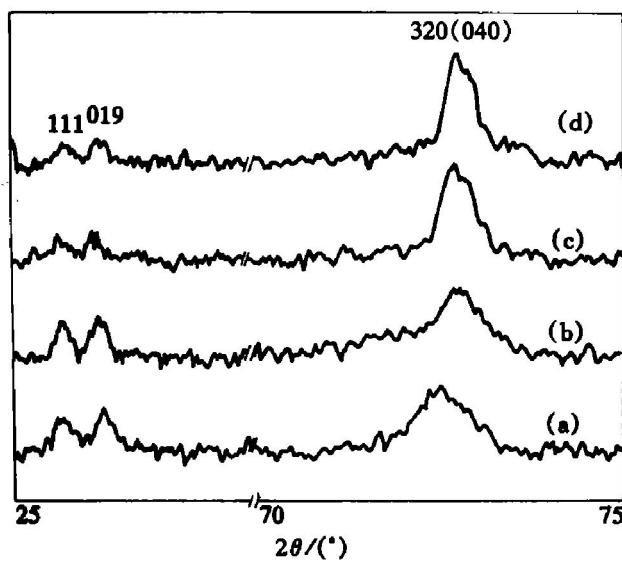


Fig. 4 X-ray diffraction patterns of alloy in thermal cycling
(a) —As quenched; (b) —1st cycling;
(c) —100th cycling; (d) —500th cycling

It is reported that in most traditional Cu-base SMA, such as Cu-18Zn-14Al (mole fraction, %) ($\beta = 88.6^\circ$)^[5], Cu-14.5Zn-7.1Al (mass fraction, %) ($\beta = 88.9^\circ$)^[9], the martensite structure is M18R with the value of monoclinic angle β less than 89° . In these alloys, some diffraction pairs of the as-quenched martensite, such as 12L and 20L, 32L and 04L, are separated and these martensite will be stabilized easily

in aging. Martensite stabilization is accompanied by the merger of 12L and 20L, 32L and 04L (including 320 and 040) and the change of monoclinic angle β approaching 90° with its martensite structure transforming from M18R to N18R. In our experiment it is hard to differentiate the martensite diffraction pairs mentioned above (here only 320 and 040 be given in Fig. 4) in Cu-11.9Al-2.5Mn alloy, which attributes to the results that the martensite structure of the tested alloy is close to N18R. In fact its monoclinic angle β of martensite in quenching has been calculated to be 89.6° ^[10, 11], which means that in the process of martensite stabilization, the largest potential change of β (i.e. $\Delta\beta$) is 0.4° , far less than that of the traditional SMA ($\Delta\beta > 1^\circ$). Therefore it is concluded that the martensite structure of the tested alloy is more stable than that of traditional Cu-Zn-Al alloys. Besides, the tendency of its martensite stabilization or decomposition is largely restrained though the process of martensite stabilization is inevitable. The transformation of martensite to parent phase proceeds at about 400°C , which exhibits high thermostability.

As to parent phase, its thermostability can be explained in its structure stability as well. The eutectoid reaction $\beta_1 \rightarrow \alpha + \gamma_2$ happens in parent aging of traditional Cu-base SMA, which will restrain the transformation of parent to martensite. As mentioned above, the alloy's component approximates that of

eutectoid phase to restrain the possibility of $\beta_1 \xrightarrow{\text{ }} \alpha + \gamma_2$ so that the structure of β_1 parent phase is stable and even be heated over 300 °C in thermal cycling the parent phase can still perform normal martensite transformation.

Moreover, many researchers reported dislocation accumulation in thermal cycling. Nakata et al^[6] suggested that the dislocations moving in the parent phase with DO_3 ordering structure of $a/4$ [111] type, which destroy the ordering structure in parent phase to make M_s decrease; Tadaki^[7] further made the explanation as that dislocations mentioned above are in correspond to those with Burgers vector of $\pm 1/2[1, 1/2, 0]$ in martensite of 18R, which demand a reaction of two kinds of partials $\pm 1/3[100]$ and $\pm 1/2[1/3, 1/2, 0]$ as a prerequisite for the formation of $\pm 1/2[1, 1/2, 0]$ type. When the latter partials move both the NNN order and NN order are inevitably destroyed among which the destruction of NNN order makes M_s decrease. Such opinion is in consistent with our X-ray diffraction results.

5 CONCLUSIONS

1) With increasing thermal cycle, M_s temperature of the Cu 11.9Al 2.5Mn alloy decreases due to destruction of NNN ordering in martensite; but small amount of the change means good stability at high temperature.

2) With increasing thermal cycle, most martensite morphologies become finer and shorter with poor orderly arrangement. Some are found to have tendency of stabilization.

3) During thermal cycling, the parent phase of Cu 11.9Al 2.5Mn alloy is stable and it is difficult to decompose at work temperature, which means its parent phase has high thermostability.

4) The structure of as-quenched martensite in Cu 11.9Al 2.5Mn alloy is near to N18R and restrains the process of martensite transformation from M18R to N18R, which implies the process of martensite sta-

bilization is restrained as well.

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