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Influence of process factors on shape memory effect of CuZnAl alloys

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Abstract: Thermal cycle training of CuZnAl shape memory alloys with different transformation temperatures was carried out. The influence of different pre-strains, heat treatments and media on the shape memory effect(SME) of CuZnAl alloys with different transformation temperatures was studied by means of scanning electron microscopy(SEM) and X-ray diffractometry(XRD). Experimental results show that despite respective variation in heat treatment, medium and cycling number, the recovery rate always decreases as pre-strain increases. The decline is obvious when pre-strain is less than 2.6% but not so sharp when pre-strain exceeds 2.6%. Larger pre-strain results in more than one slip system and causes intercutting of the martensite strips among martensitic variants, then leads to the decline of SME. The SME of alloys with transformation temperatures below 347 K is larger than that of alloys beyond 361 K by 20%−40%. The recovery rate of two-step aged alloy is higher than that of step-quenched alloy by 20%−25%. During thermal cycling, the recovery rate in oil is better than that in water.

Key words: CuZnAl shape memory alloys; pre-strain; transformation temperature; shape memory effect; thermal cycling; heat treatment

1 Introduction

CuZnAl shape memory alloy(SMA), characterized by low cost and high processing performance, has been studied comprehensively and has developed rapidly in recent years. Since the fundamental problems of large grain and martensitic stabilization were resolved[1−4], CuZnAl SMA has been applied in practice gradually. For example, the devices of fire-preventing system in underground pit for fire monitoring and overheat protector are made of CuZnAl SMA for its dual functions of temperature sensing and driving[5−7]. The damper for reducing vibration is made of CuZnAl SMA for its superelastic damping property[8]. For its repeated shape memory effect or its superelasticity, CuZnAl alloys must endure the periodic action of temperature and stress. PERKINS and MUSEING[9], LI and ANSELL[10] and TADAKI et al[11] studied the effect of thermal cycling on CuZnAl alloys. DVORAK and HAWBOLT[12], SAKAMOTO and SHIMIZU[13], YANG et al[14] and THUMANN and HORNBOGEN[15] investigated the variation of Cu-based shape memory alloys in thermal cycling. But only the effect of stress cycling under invariable temperature and the effect of thermal cycling without external stress on shape memory alloy have been studied. SMA must withstand complex action of force and temperature, so it is necessary to investigate the change of shape memory effect(SME) in thermal cycling, especially for those alloys with different transformation temperatures. In this study, the influence of different pre-strains, heat treatments and media on the SME of CuZnAl SMAs with different transformation temperatures is investigated. The results are advantageous to more extensive applications of CuZnAl SMAs.

2 Experimental

The sample preparation method has been explained in detail in Ref.[1]. The composition (mass fraction, %) of the alloy used in this study included 26%Zn, 4%Al, 1%Ni, 0.01%−0.10% compound RE (La+Ce) and balance Cu. Several transformation temperatures M_s were obtained by adjusting chemical components. Those temperatures were 315, 326, 339, 347, 361 and 398 K(Table 1). M_s was obtained by the resistance-temperature curve measuring apparatus. The samples have the dimension of 1.5 mm×4 mm×100 mm. In order

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to carry out thermal cycling, we stretched the samples with the dimension of 0.3 mm×4 mm×100 mm by WDW-200 electronic universal material tester controlled by a computer. The pre-strain was set to 1.3%, 1.7%, 2.6%, 3.9% and 8.5%, respectively. Media used in the cycling were water of room temperature and 373 K respectively, oil of room temperature and 423 K respectively. Thermal cycling was carried out by keeping constant strain and the maintaining time in medium was 5 s. Martensitic interface morphology was observed by MM6 optical microscope and JXA-840 SEM with sample dimension of *d*15 mm×10 mm. Phase components of alloy were tested by D-5000 X-ray diffractometer with sample dimension of *d*15 mm×1 mm. Heat treatments were described as follows. 1) After being held at 1 123 K for 15 min, the samples were quenched into oil of room temperature, aged for 15 min at 423 K and held in water of 323 K for 10 min (two-step ageing). 2) After being held at 1 123 K for 15 min, the samples were quenched into oil of 423 K and held for 15 min (step quenching). Transformation temperature in this paper is M_s temperature.

Table 1 Transformation temperatures of samples

Sample No.	A_s/K	A_f/K	M_s/K	M_f/K
1	313	321	315	307
2	323	331	326	318
3	334	343	339	330
4	339	352	347	335
5	361	366	361	346
6	390	403	398	385

3 Results and discussion

3.1 Influence of pre-strain and transformation temperature on SME

For investigating the influence of pre-strain on SME, the pre-strain was defined by 1.3%, 1.7%, 2.6% and 3.9%, respectively. Alloys with different transformation temperatures were treated by different heat treatments and then cycled in different media, and their shape recovery rates were measured simultaneously. The first 50 cycles were restricted training, while the others were free cycles.

The recovery rates of alloys with different transformation temperatures which are carried out by two-step ageing and step quenching respectively are depicted in Fig.1, where water of 373 K and oil of 423 K serve as cycling media. Several conclusions can be obtained.

1) Both in restricted training (Figs.1(a), (c), (e) and (g)) and in free cycling (Figs.1(b), (d), (f), and (h)), when pre-strain is less than 2.6%, the recovery rate decreases rapidly as pre-strain increases, then decreases slowly as pre-strain exceeds 2.6%. And the above phenomenon becomes more obvious after 50 cycles.

2) For all alloys with different transformation temperatures adopted in our experiment, the recovery rates of alloys with transformation temperatures below 347 K are larger than those of alloys with M_s beyond 361 K by 20%−40%. The trend still exists as thermal cycling number increases.

3) The recovery rates of two-step aged alloys are 10%−30% higher than those of step-quenched alloys.

4) The recovery rates of alloys cycled in oil of 423 K are 10%−30% higher than those of alloys cycled in water of 373 K. This trend remains in two-step aged alloy and step quenched alloy as well.

Some common characteristics can be seen from Fig.1 that although heat treatment and medium vary dramatically, SME of alloys with transformation temperatures below 347 K is satisfied, while that beyond 361 K is not so well. Scanning electron micrographs of some two-step aged alloys are shown in Fig.2 after 50 cycles. It can be found from Figs.2(a)−(d) that in alloys with transformation temperatures ranging from 315 K to 347 K, arranging directions of martensitic pin-like structures are consistent. While in Fig.2(e) and Fig.2(f), after thermal cycling, in alloys with transformation temperatures ranging from 361 K to 398 K, arranging directions become inconsistent. Experimental results show that the pin-like structures emerge in all alloys with increasing cycling number. But much more pin-like structures different from the original martensitic structures can be found in those alloys with higher transformation temperatures. The appearance of pin-like structures will conduce to bad reversibility and regeneration of structure transformation in subsequent thermal cycling, then the decline of SME.

Comparing the eight images in Fig.1, we can deduce that recovery rate decreases invariably as pre-strain increases although heat treatment, medium and cycling number vary respectively. Recovery rate decreases rapidly when pre-strain is less than 2.6%, then decreases slowly when pre-strain is more than 2.6%. Ref.[16] shows that there exists a critical pre-strain, ε_L. When pre-strain ε is less than ε_L, linear relation lies between shape recovery rate and ε. On the contrary, the shape recovery rate decreases. It is indicated in Ref.[17] that little pre-strain contributes to the forming of crystal nucleus and their growing up in stress-induced martensite. It also helps to the moving and retaking direction of variants and best martensite orientation. It also contributes to two-way shape memory property of

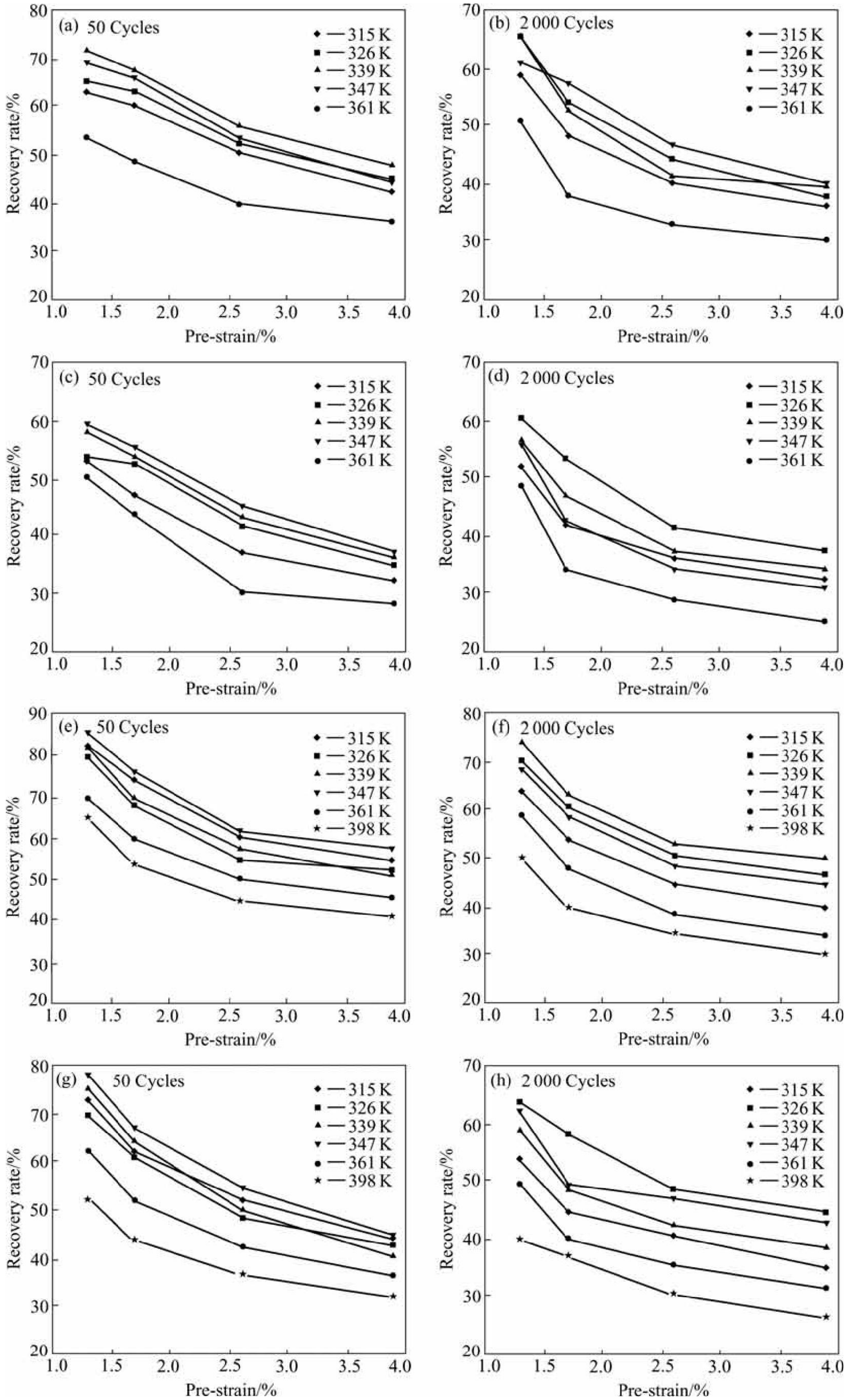

Fig.1 Recovery rate versus pre-strain for alloys with different transformation temperatures: (a) Two-step aged in water; (b) Two-step aged in water; (c) Step quenched in water; (d) Step quenched in water; (e) Two-step aged in oil; (f) Two-step aged in oil; (g) Step quenched in oil; (h) Step quenched in oil

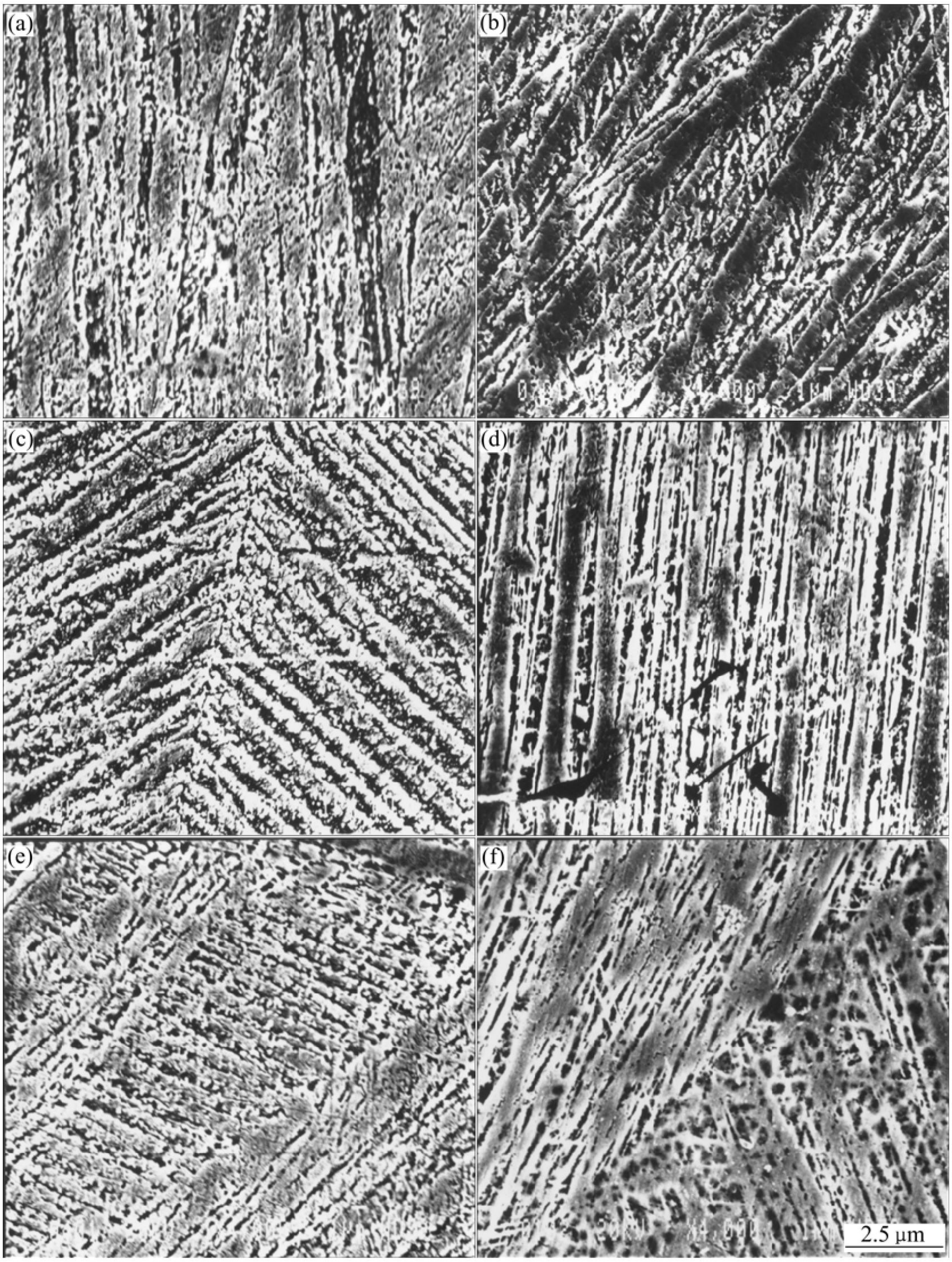

Fig.2 Scanning electron micrographs of samples with different transformation temperatures: (a) M_s=315 K; (b) M_s=326 K; (c) M_s=339 K; (d) M_s=347 K; (e) M_s=361 K; (f) M_s=398 K

the alloy. As pre-strain increases, the positive and reverse martensitic transformations occur during thermal cycling. The phase boundary between martensite and parent phase reciprocates with the variation of outside temperature. Dislocations on the phase boundary increase during reciprocation. Dislocation density reaches saturation quickly. So the martensitic transformation extent is influenced, which decreases the shape memory property. With the increase of pre-strain, the permanent irrecoverable deformation resulted from full dislocations increases. These full dislocations are the moving barriers of the interface between martensite and parent phase. The transformation quantity of the positive and reverse thermoelastic martensite is affected and SME declines. Simultaneously, large pre-strain causes more than one slip system, which leads to the intercutting of martensites. With small deformation, there is one orientation for martensite in each grain. As the deformation increases, the quantity of martensite in one grain increases, which makes the martensitic variants intercut. Then SME declines. The influence of pre-strain on the microstructure is shown in Fig.3. In Fig.3(a) there is one martensitic orientation in each grain. But in Fig.3(b) the martensitic variants intercut as the pre-strain increases, which reduces SME.

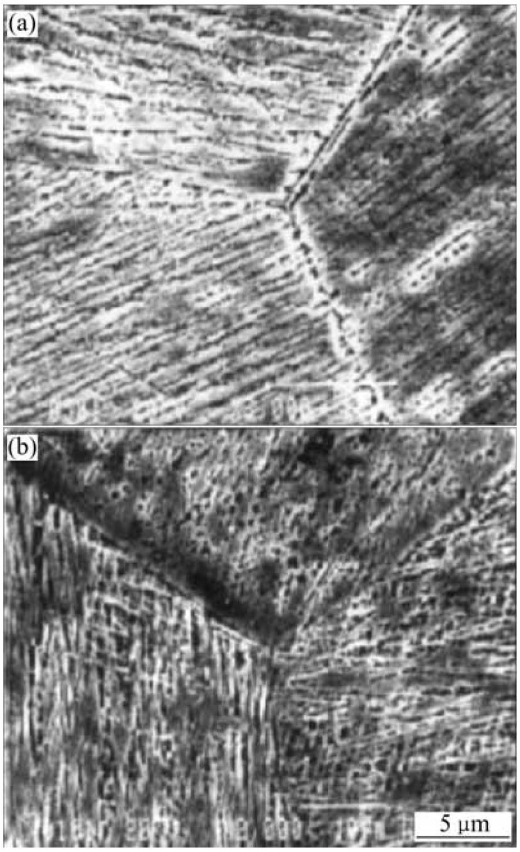

Fig.3 Influence of pre-strain on microstructures with different pre-strains (M_s=347 K): (a) 2.6%; (b) 8.5%

No detailed investigation has been reported regarding the phenomenon that in thermal cycling SME of alloys with high transformation temperatures (above 361 K) gets worse. The phenomenon appears all along in our repeated experiments. In the experiments, the martensitic variants change, the dislocations increase and the ordering degree declines. The reason has not been reported in previous literatures. It is well known that between 173 K and 413 K, CuZnAl SMA has SME. Approaching the two extreme temperatures, the martensitic variants change easily, and the quantity of dislocations in martensite increases largely. Meanwhile, the martensitic interface is prone to be pinned, which causes the ordering degree of martensite and SME declines.

3.2 Influence of different heat treatments on SME

Different heat treatments have different effects on SME. Meanwhile SME declines as pre-strain and cycling number increase. Under different heat treatments, the relationship between recovery rate and cycling number with pre-strain of 2.6% is described in Fig.4.

Some common characteristics can be seen in Fig.4. 1) With increasing cycling number, the shape recovery rates of all alloys increase firstly and then decrease gradually. 2) After thermal cycling, with either high or low transformation temperatures, the recovery rates of aged alloys are higher than those of step-quenched alloys by 20%−25%. 3) When the cycling number approaches 4 000, the two recovery rates almost reach the same value.

Some conclusions can also be obtained from Fig.4. 1) For the alloys with low transformation temperatures (such as 315 K and 326 K), when the cycling number is less than 50, the shape recovery rates of step-quenched alloys are much larger (see Figs.4(a) and 4(b)). 2) For the alloys with high transformation temperatures, as thermal cycling number increases, the shape recovery rates decline rapidly. After 4 000 cycles, their recovery rates are only about 20%, while the recovery rates of other alloys are about 40%.

After thermal cycling the recovery rate of aged alloy is higher than that of step-quenched alloy. The reason lies in that for the samples treated by two-step ageing, both 9R and 18R martensite emerging after quenching change into 18R martensite during two ageing stages. At the same time, the stress in the alloy declines. So it is hard for the martensite to stabilize[2]. Thereby the SME is satisfied. In step quenching, B2 and DO_3 coexist. So the transformation from B2 to 9R and the transformation from DO_3 to 18R coexist, which destroys the coherence of 9R martensite and B2 parent phase, and makes 9R martensite stabilize for lack of thermal elasticity. Thus the SME of step-quenched alloy is bad. It can be seen in Fig.5 that at room temperature the microstructure of aged alloy is M18R while the microstructure of step-quenched alloy consists of M18R mainly and a small quantity of β phase. It is the difference between the two kinds of microstructures that result in different SME.

3.3 Influence of different cycling media on SME

According to the experimental data, we find out the influence of different media on SME from the example of alloy with transformation temperature of 347 K. Some conclusions can be obtained from Fig.6. 1) Whether the medium is oil or water, the recovery rate increases firstly and then decreases as cycling proceeds. The recovery

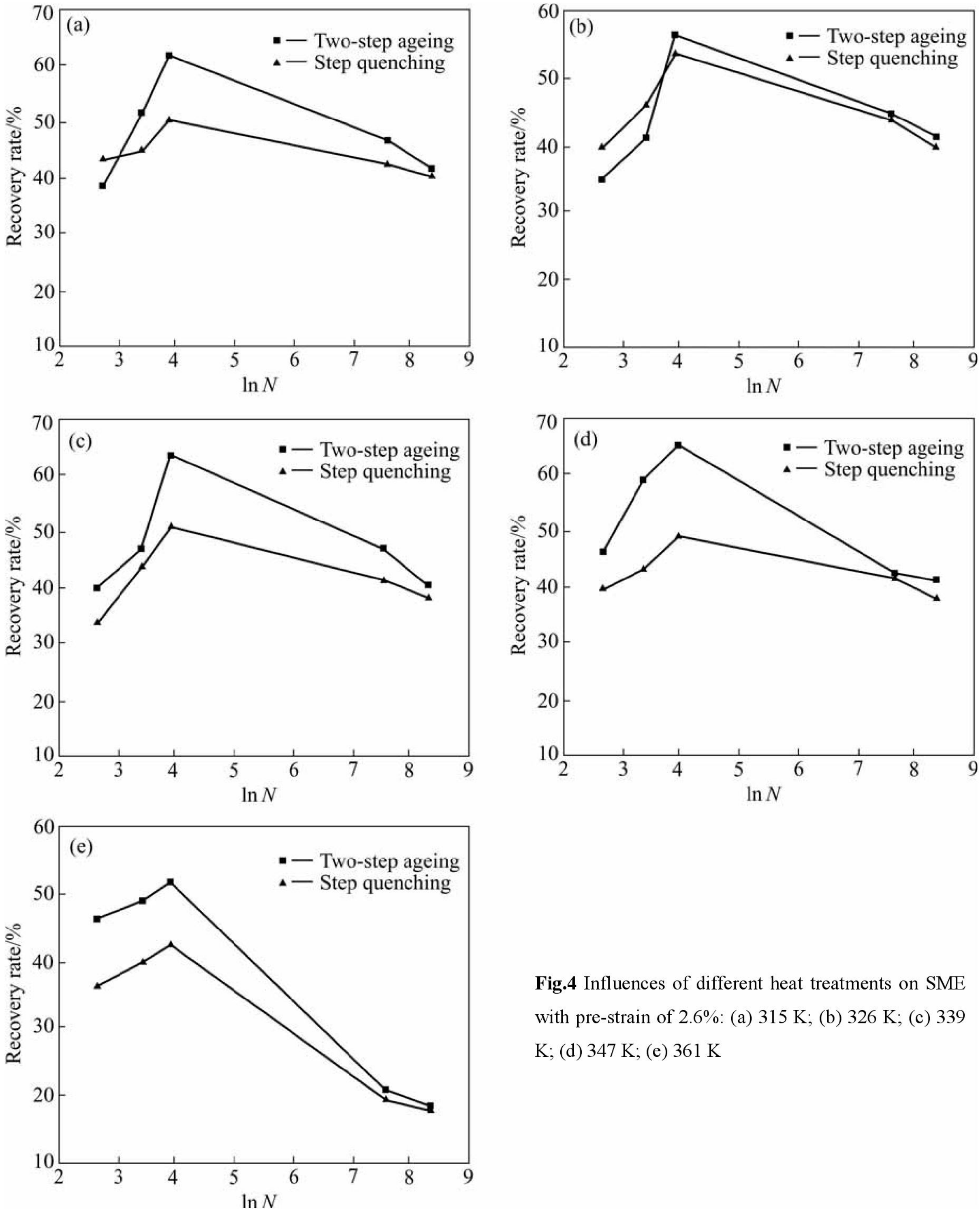

Fig.4 Influences of different heat treatments on SME with pre-strain of 2.6%: (a) 315 K; (b) 326 K; (c) 339 K; (d) 347 K; (e) 361 K

rate in oil is higher than that in water. 2) The maximum recovery rate is 91.3% in oil of 423 K and 65% in water of 373 K. 3) In different media the shape recovery rate of aged alloy is always higher than that of step-quenched alloy. 4) When pre-strain becomes larger, the maximum recovery rate is 81.8% in oil of 423K and 52.7% in water of 373 K. 5) After 4 000 cycles, the difference of recovery rates in the two media can be neglected.

The attenuation quantity of SME in oil of 423 K is less than that in water of 373 K. The reason lies in that during cycling in oil of 423 K, the transformation between martensite and parent phase is comparably completed, while in water of 373 K, the transformation is not so sufficient. This results in the appearance of remained martensite in alloys, especially nearby the crystal boundaries, then leads to the decrease of rever-

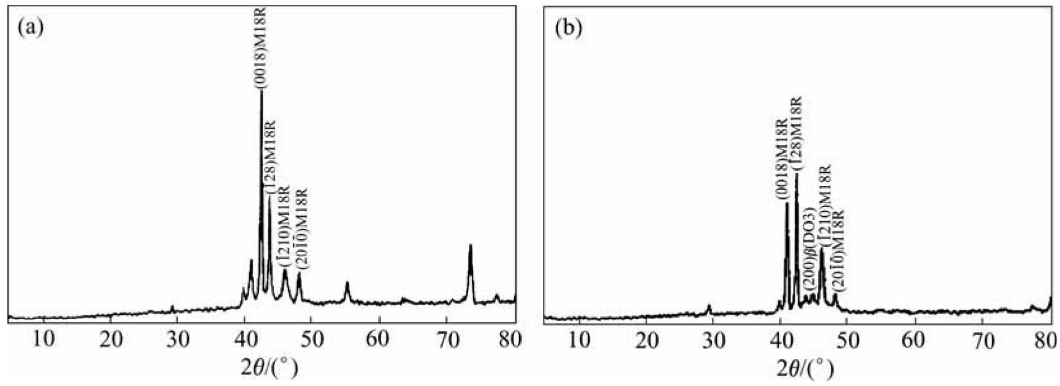

Fig.5 X-ray diffraction patterns of alloy with transformation temperature of 347 K after different heat treatments: (a) Two-step ageing (b) Step quenching

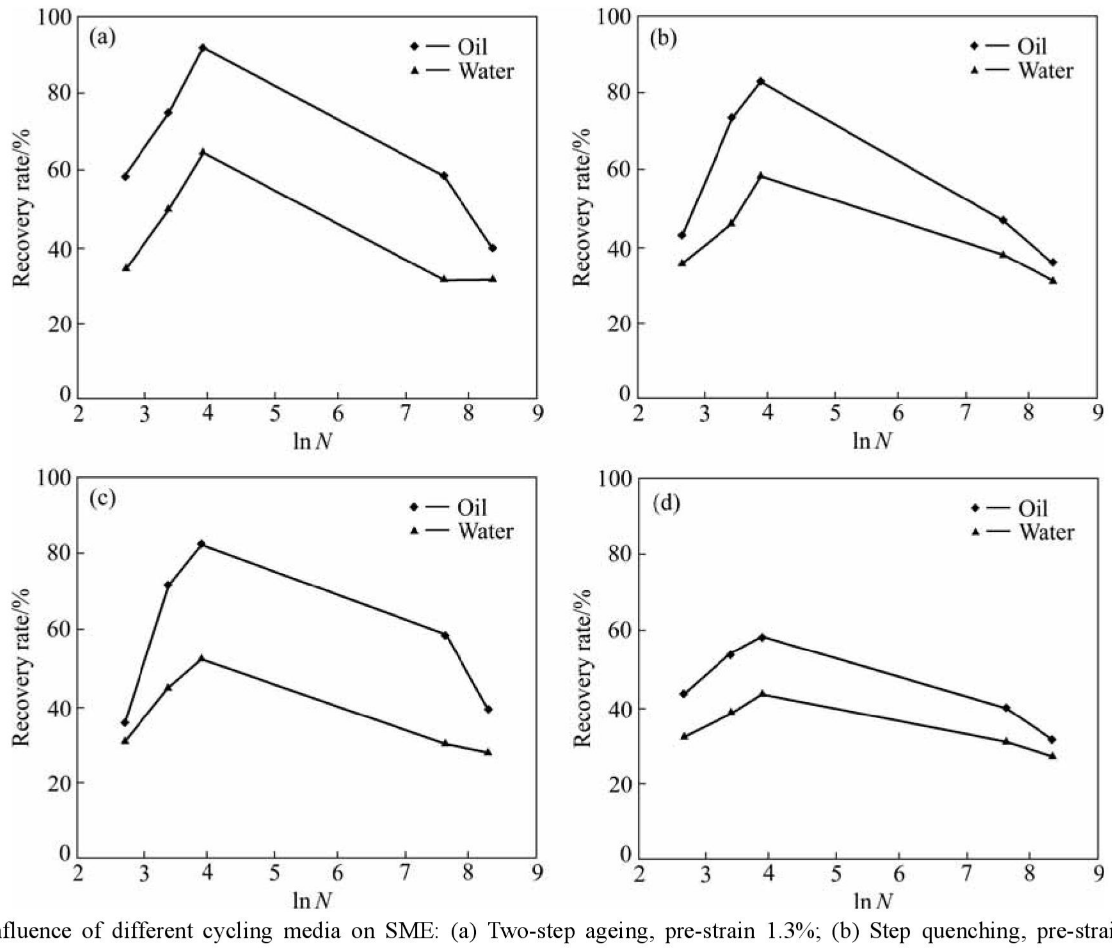

Fig.6 Influence of different cycling media on SME: (a) Two-step ageing, pre-strain 1.3%; (b) Step quenching, pre-strain 1.3%; (c) Two-step ageing, pre-strain 3.9%; (d) Step quenching, pre-strain 3.9%

sible martensite.

4 Conclusions

1) Despite the respective variation in heat treatment process, cycling medium and cycling number, the recovery rate decreases as pre-strain increases. When the pre-strain is less than 2.6% the decline trend is obvious, and when the pre-strain exceeds 2.6% the trend abates. Increase of pre-strain results in more than one slip system, then causes intercutting of the martensite strips between martensitic variants. All these help to the decline of SME.

2) SME of alloys with transformation temperatures below 347 K is larger than that of alloys beyond 361 K by 20%−40%. After thermal cycling, the recovery rate of aged alloys is higher than that of step-quenched alloys by 20%−25%. The trend still exists with increasing cycling

number.

3) During thermal cycling, both in two-step aged alloy and step-quenched alloy, the recovery rate in oil of 423 K is higher than that in water of 373 K.

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