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## Superelastic behavior and stabilization of stress-induced martensite in Cu-13.4Al-4.0Ni single crystals<sup>①</sup>

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**[Abstract]** By applying tensile stress along  $\langle 100 \rangle$  of  $\beta$  phase, the superelastic behavior and stabilization of stress-induced martensite (SIM) of Cu-13.4Al-4.0Ni (mass fraction, %) single crystals were studied. The results show that the pseudo yield stress decreases with the increase of cycling number, and keeping load isothermally has an effect on stabilization of SIM. Previous thermal cycling between ( $M_s - 20$  °C) and ( $A_f + 20$  °C) promotes the superelasticity and the stabilization of SIM as well; the prethermal cycling also reduces the pseudo yield stress. However, once the stabilization of SIM is produced, it can be destabilized by either the afterwards thermal cooling-heating cycling or load and immediately unload cycling in ( $A_f \sim M_d$ ). Isothermal treatment in ( $A_f \sim M_d$ ) brings restabilization of SIM. The maximum superelastic value from  $\beta \rightarrow \beta_1(18R)$  is 9% for the studied single crystal. When test temperature is in  $A_f \sim (A_f + 50$  °C) and stress is in 0~350 MPa, the superelastic behavior exist.

**[Key words]** Superelasticity; Stabilization; Stress-induced martensite; CuAlNi single crystal; Destabilization

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### 1 INTRODUCTION

Most of shape memory alloys (SMAs) are thermoelastic, i. e. the growth or shrinking of martensite variants varies with decreasing or increasing temperature. Because of the self-accommodation feature under free load, the overall macroscopic deformation upon transformation is zero. However, when such shape memory alloy is deformed, thus a preferential martensite is formed and a macro-strain is obtained, further heating will make the preferential martensite transform back to parent phase, resulting in a shape memory effect. The thermoelastic SMAs also display superelasticity, i. e. when the parent phase is deformed above  $M_s$ , the martensitic transformation occurs prematurely because the applied stress substitutes for the thermodynamic driving force usually obtained by cooling<sup>[1]</sup>. Since the applied stress is basically uniaxial, only one orientation of martensite is selectively formed, and this imparts an overall deformation to the specimen. This deformation disappears when the stress is released and the original specimen shape is restored, leading to a mechanical shape memory. Both the one way memory effect (OWME) and the superelasticity above  $A_s$  are properties inherent to the thermoelastic martensite transformation. However, the two-way memory effect (TWME) is not an inherent behaviour. From three dimensional stress—

strain—temperature diagrams<sup>[2]</sup>, it can be found that the temperature range difference between exhibiting fully superelasticity and training for TWME is that for superelasticity, the temperature is in ( $M_d - A_s$ )<sup>[1-5]</sup>, while training for TWME,  $t_{\min} = M_f - 20$  °C and  $t_{\max} = A_f + 20$  °C. Due to many interrelations between superelasticity and TWME, the study of superelasticity for CuAlNi single crystal is of great importance for the training of TWME as well as superelastic applications. The present paper describes the experimental superelasticity results based on the uniaxial tension test on CuAlNi single crystals by changing temperature and applied stress as well as isothermal treatment.

### 2 EXPERIMENTAL

The alloy used was single crystal with a nominal composition of Cu-13.4Al-4.0Ni (mass fraction, %). The dimensions of the specimen were  $d3\text{ mm} \times 200\text{ mm}$ . The axial direction of the sample was close to  $\langle 001 \rangle$  of parent phase at high temperature. After heat-treated at 850 °C for 20 min and then quenched into water at room temperature, the transformation temperatures of the specimen measured by DSC were:  $M_s = 96$  °C,  $M_f = 71$  °C,  $A_s = 71$  °C and  $A_f = 105$  °C.

Superelasticity tests were carried out with the

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apparatus described in Ref. [5]. The gauge length was 100 mm. The loading-unloading speed was about 73 MPa/min.

According to geometrical status of the testing specimen and the direction of stress applied, for the transformation from the parent disordered bcc structure to ordered  $\beta_1$  (18R) through  $\beta \rightarrow \{110\} \langle 110 \rangle$  martensite, both the Schmid factor of the crystal and the critical stress needed for the formation of a favourite martensite variant can be obtained. Therefore the preferential formation of this martensite variant will contribute to the corresponding macro-strain change. The fully recovered superelasticity of 9% was obtained by Dios-Jara<sup>[6]</sup> and Wayman<sup>[1]</sup> through calculation and experiments on Cu-14.4Zn-17.7Al (mole fraction, %) and Cu-39.8Zn (mass fraction, %) single crystals respectively, which can be viewed as the maximum superelasticity, the upper limit of OWME as well as the upper limit of STWME during constant load thermomechanical cycling for single crystal at a given orientation. Beyond this limit, there will exist some plastic deformation after unloading because the relatively high stress is applied, which should be avoided as far as possible during thermomechanical cycling tests. Our experiments are based on such consideration. The specimen was heated to 0~50 °C above  $A_f$ , then the stress was applied at different level according to the experimental need.

### 3 RESULTS AND DISCUSSION

#### 3.1 Effect of superelastic cycling and isothermal loading on superelastic behavior

The procedure in this test is programmed as follows: heat from room temperature to 122 °C  $\rightarrow$  load ( $\sigma = 200$  MPa) and unload immediately (curve marked Cycle 1 in Fig. 1)  $\rightarrow$  load again (curve marked Cycle 2 (load) in Fig. 1) and load isothermally for 1 h before unload (curve marked Cycle 2 (unload) in Fig. 1)  $\rightarrow$  load and unload immediately (curve marked Cycle 3 in Fig. 1). According to the stress-strain curve, the stability of SIM can be evaluated. For up-loading process, the lower the stress at which the superelastic deformation starts and finishes, the easier the  $\beta \rightarrow$  SIM transformation; for unloading process, the lower the stress at which the superelastic recovery starts and finishes, the stabler the SIM. Physically, the area covered by the superelastic stress-strain loop can be regarded as the work done by the external applied stress. This area is a reflection of the energy absorbed by the specimen with respect to engineering shape memory and/or superelastic devices. Since the changing magnitude in the part of curve of uploading is generally smaller than that of unloading, a judgement on the degree of stabilization of SIM can be given by evaluating this area's value. The larger the area, the bigger the tendency of stabilization.

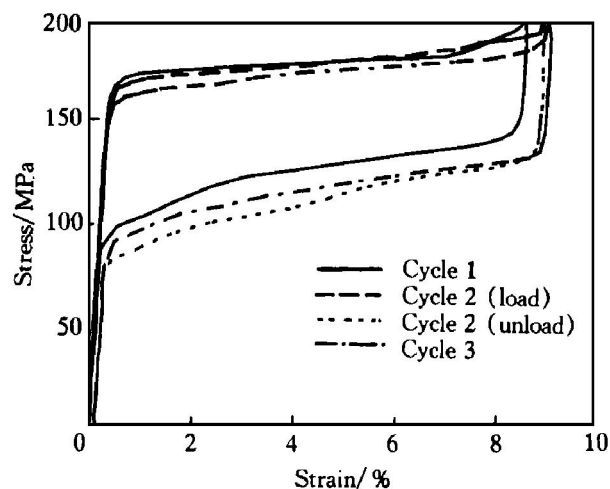
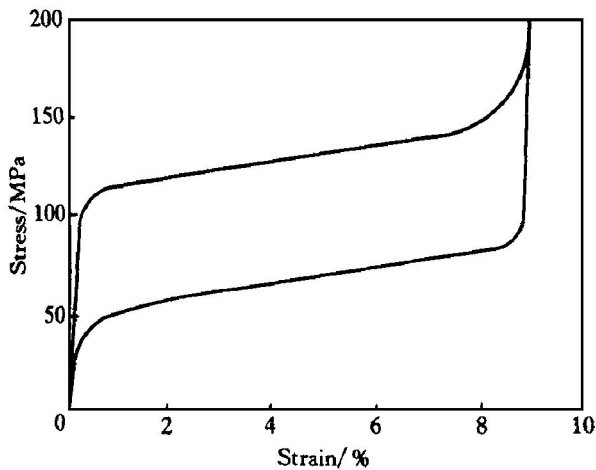


Fig. 1 Influence of isothermal loading at temperature above  $A_f$  on superelastic behavior

In the first cycle, the superelastic deformation in the uploading procedure starts at about 165 MPa and finally reaches 8.65% at 200 MPa; upon unloading the reverse transition of this deformation starts at about 150 MPa and finishes at about 90 MPa, however during the second loading, the superelastic deformation starts at about 160 MPa and finally reaches 9.0%. Here, it is necessary to define the “pseudo-yield stress”. It means that in ( $A_s \sim M_d$ ), the stress at which the deformation deviates the linear elastic relation and a large number of superelastic deformation is produced. Because this deformation is not really yielded by plastic deformation, it can be recovered elastically upon unloading. The experimental results show that the pseudo-yield stress decreases with the increase of cycles. However, as Ono<sup>[3]</sup> pointed out that according to the experiments at ( $M_s + 38$  °C) on Cu-Zn-Al polycrystals by straining at a given value  $\rightarrow$  unloading  $\rightarrow$  thermal cycling procedure, this kind of pseudo-yield stress decreases with the increase of cycles until Cycle 8, the superelastic behavior is considered to be nearly stable because the remaining dependence of the pseudo-yield stress on cycling number is negligible small. In the second cycle, after the load is kept isothermally for 1 h then unload, the superelastic recovery starts at stress below 140 MPa and finishes at 75 MPa, which means that the stabilization of SIM occurs during isothermal treatment under the load. At the next load+ immediately unload cycle, the superelastic deformation starts at about 150 MPa and finally reaches 9.18% at 200 MPa, 0.18% greater than the calculated superelastic strain; at the unloading procedure, the superelastic recovery starts at 140 MPa and finishes at 80 MPa, finally this 0.18% plastic deformation is retained.

The thermomechanical cycling history of the specimen has a strong influence on the superelastic behavior. For example, the as-quenched specimen is subjected to heat from room temperature to 158 °C for

1 min  $\rightarrow$  cool to 122 °C for 60 min  $\rightarrow$  cool to room temperature, repeat 2 times, and then heat from room temperature to 122 °C  $\rightarrow$  load and unload immediately for superelastic tests Fig. 2. Although the testing parameters for superelasticity are the same as that of cycle 1 in Fig. 1, for the thermal cycled specimen the superelastic deformation starts only at 89 MPa, which is 76 MPa lower than that of as-quenched, and the final deformation reaches 9%. It suggests that the martensitic transformation is promoted by the previous thermal cycling (heat from room temperature to 158 °C for 1 min  $\rightarrow$  cool to 122 °C for 60 min  $\rightarrow$  cool to room temperature). In other words, the thermal cycling at temperature above  $A_f$  has a promoting effect on the formation of martensite. This might be the softening effect by thermal or thermomechanical cycling, which is shown in a separate paper. Also Uno<sup>[2]</sup> reported in the effect of load-cycling on the pseudoelastic behavior in a polycrystalline Cu-Zr-Al SMA that the yield stress decreases with training cycle. Perkins<sup>[7]</sup> reviewed that with the training going on, the stress decreases significantly in the initial cycling because of the formation of martensite.

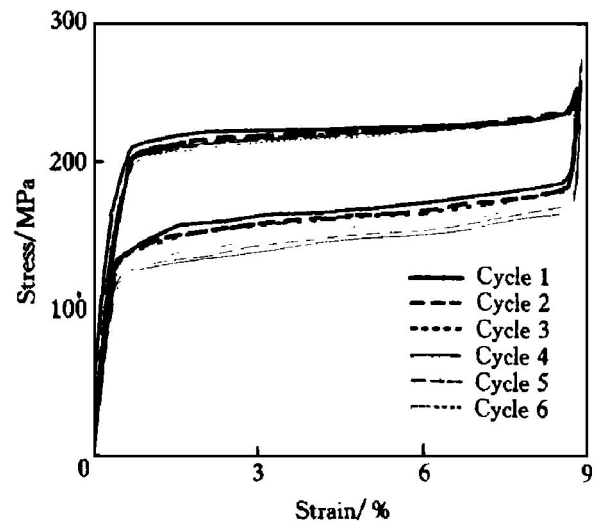


**Fig. 2** Stress—strain curves at 122 °C of as-quenched sample with thermal treatment

### 3.2 Effect of thermal cycling and isothermal treatment on superelastic behavior

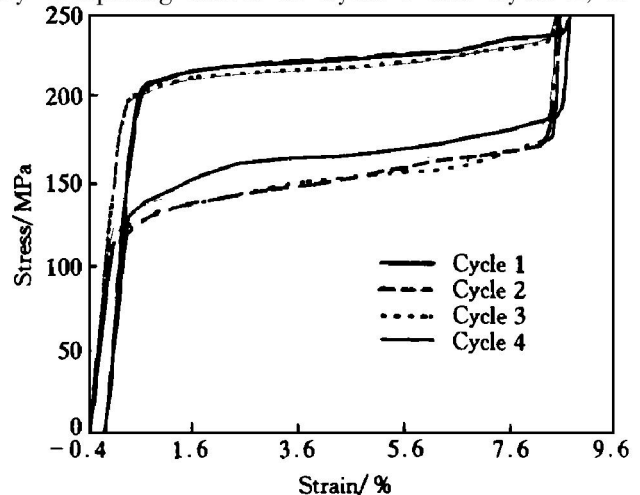
In this test, the procedure is programmed as following: heat from room temperature to 168 °C  $\rightarrow$  cool to 132 °C  $\rightarrow$  load and unload. The stress—strain curves are shown in Fig. 3. At different cycles the parameters of test are changed. For Cycles 1~3, the tests are carried out by load and immediately unload at 132 °C. It is seen from Fig. 3 that there is a stabilization effect with cycling. However, in Cycle 4 the load is isothermally kept at 132 °C for 2 h before unload. It can be easily seen that the procedure of keeping load isothermally causes stabilization of SIM. This means thermal treatment can lower the pseudo-yield stress as well as spring-back during unloading<sup>[8-10]</sup>. Then in the 5th cycle the specimen is

cooled down to 50 °C and reheated to 132 °C, then is loaded isothermally again for another 1 h before unloading. It is seen that there is a destabilization effect in Cycle 5 compared with that in Cycle 4. This destabilization may be caused by the cooling and heating after Cycle 4. For Cycle 6, the test is carried out after Cycle 5 through load and immediately unload, which shows further destabilization effect. This implies that the stabilization effect caused by isothermally loading can be reduced by both the cycling of load + unload immediately and thermal cycling between ( $M_f \sim A_f$ ).



**Fig. 3** Superelastic behavior with cycling and different loading methods

An additional test is made on the above cycled specimen. The procedure is programmed as: heat from room temperature to 158 °C  $\rightarrow$  cool to 132 °C  $\rightarrow$  load and immediately unload (Cycle 1)  $\rightarrow$  load isothermally for 2 h  $\rightarrow$  unload (Cycle 2)  $\rightarrow$  load isothermally for 1 h  $\rightarrow$  unload (Cycle 3)  $\rightarrow$  load and unload immediately (Cycle 4), and the results are shown in Fig. 4. By comparing curves of Cycle 1 and Cycle 2, it is



**Fig. 4** Stabilization caused by loading isothermally and destabilization caused by load+ unload immediately

clearly shown that the isothermal loading at 132 °C for 2 h has an effect of stabilization, and at the same time, it also causes the creep like permanent deformation which is in the reverse direction of the applied load. The curve of Cycle 3 also proves this result. From the curve of Cycle 4, it can be seen that the stabilization caused during isothermally loading can be reduced through the cycling of load and immediately unload procedure.

### 3.3 Stabilization, destabilization and restabilization of SIM

In this group of experiments, the procedure is programmed as: heat from room temperature to 144 °C → load and unload immediately (Cycle 1) → load isothermally for 2 h → unload (Cycle 2) → load and unload immediately (Cycle 3) → isothermal for 30 min → load and unload immediately (Cycle 4), as indicated in Fig. 5. Although the applied stress is 250 MPa, a nearly full super-elastic strain of 9% can be obtained at 132 °C, but with the corresponding same stress level at 144 °C for the first load and immediately unload cycle, the obtained superelasticity is only about 2.5% which is far from the saturated superelasticity of 9% just because of the lack of driving force for the formation of martensite at this relatively high temperature and insufficient stress applied. However, during the next load isothermally for 2 h then unload, the superelasticity is increased up to 8.83% and there is a strong stabilization effect on the SIM through keeping load isothermally. The curve of Cycle 3 shows the destabilization effect on the superelastic loop through the afterwards load and unload immediately procedure. It is interesting to notice that after Cycle 3 by isothermal treatment at 144 °C for 30 min then load and immediately unload, the stabilization effect occurs again, and here it is called “restabilization”. From these results, it can be concluded that both isothermal loading and isothermal treatment (without

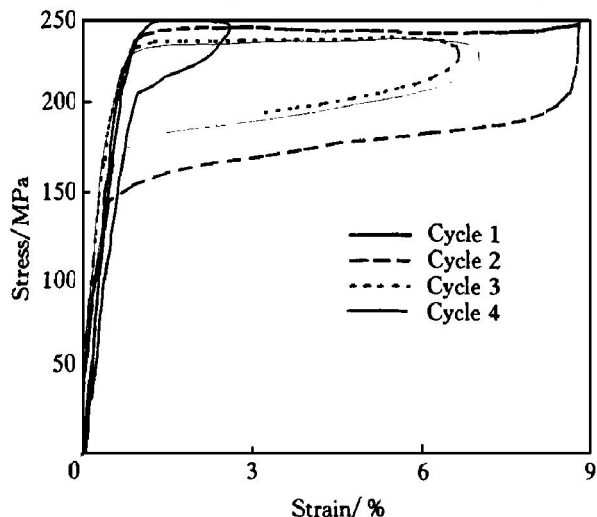


Fig. 5 Stabilization, destabilization and restabilization of SIM at 250 MPa

macro-stress applied) have the effect of stabilization on SIM; once the stabilization effect is produced, it can be reduced by the load and immediately unload cycling procedure.

With the same program as above, another series of experiments are made, in which the only difference with the above experiments is the stress applied, as illustrated in Fig. 6. From Fig. 6 the significant effect of isothermal loading on the stabilization of SIM, the destabilization effect through load and immediately unload procedure as well as the restabilization effect through isothermal treatment can be easily found. Under given stress level ( $\sigma = 280$  MPa), the super-elastic strain reaches about 9%.

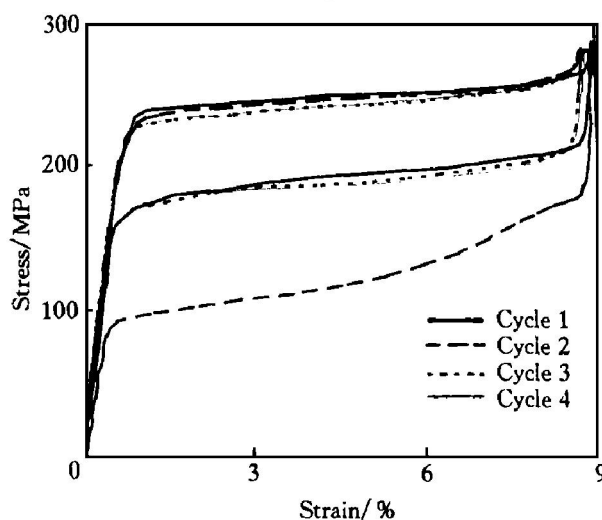


Fig. 6 Stabilization, destabilization and restabilization of SIM at 280 MPa

### 3.4 Effect of temperature on pseudo-yield stress

Fig. 7 shows the stress-strain curves at different temperatures and loading levels. All the curves are taken in the first cycle for the as-quenched specimens. It can be seen from Fig. 7 that the pseudo-yield

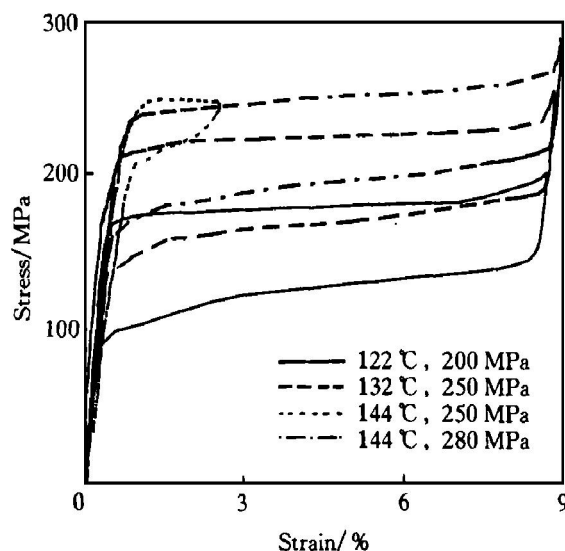


Fig. 7 Superelastic curves at different temperatures and stress levels

stress increases with the testing temperature.

Fig. 8 shows the evolution of stresses (for both loading and unloading) with temperature when the strain is 4.5%. Because the characteristics of superelastic deformation in stress-strain curve is like a plateau, the stresses at strain of 4.5% (which is half of the strain from  $\beta \rightarrow \beta_1$  (18R)) can be used to express the superelastic deformation behavior. During both loading and unloading procedure, the stress corresponding to 4.5% strain increases with testing temperature, well in accordance with modified Clausius-Crapeyron formula. The  $\Delta\sigma/\Delta t$  is about 3.5 MPa/°C.

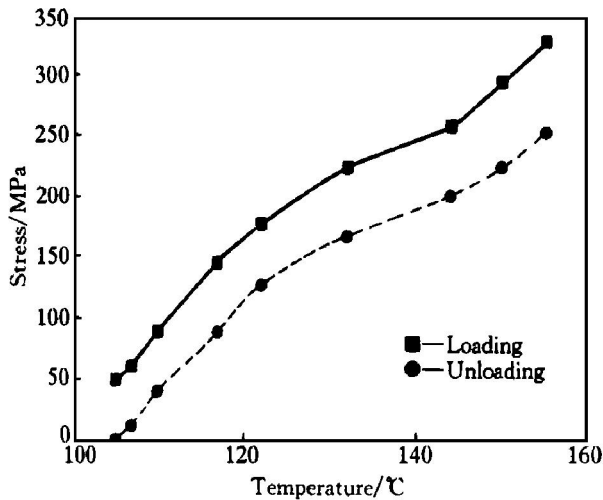


Fig. 8 Plateau stress at strain of 4.5% with temperature

#### 4 CONCLUSIONS

1) For Cu-13.4Al-4.0Ni (mass fraction, %) single crystals, the pseudo-yield stress decreases with the increase of cycling, and keeping load isothermally has an effect on stabilization of SIM.

2) Previous thermal cycling between ( $M_s - 20$  °C) and ( $A_f + 20$  °C) promotes the occurrence of superelasticity and the stabilization of SIM as well; the pre-thermal cycling also reduces the pseudo-yield stress. However, once the stabilization of SIM is produced, it can be destabilized either by thermal cool-

ing-heating cycling or load and immediately unload cycling in ( $A_f \sim M_d$ ). Isothermal treatment in ( $A_f \sim M_d$ ) brings restabilization of SIM.

3) The maximum superelastic value from  $\beta \rightarrow \beta_1$  (18R) is 9% for CuAlNi single crystal. The superelastic behavior exists when temperature is  $A_f \sim (A_f + 50$  °C) and stress is 0~ 350 MPa.

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