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## Shape memory materials<sup>①</sup>

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**[Abstract]** Compared with piezoelectric ceramics and magnetostrictive materials, the shape memory materials possess larger recoverable strain and recovery stress but slower response to external field. It is expected that the magneto-shape memory materials may develop considerable strain as well as rapid and precise shape control. Pseudoelasticity and shape memory effect (SME) resulted from martensitic transformation and its reverse transformation in shape memory materials were generally described. The requirements of appearing the shape memory effect in materials and the criteria for thermoelastic martensitic transformation were given. Some aspects concerning characteristics of martensitic transformation, and factors affecting SME in NiTi, CuZrAl and FeMnSi based alloys as well as ZrO<sub>2</sub> containing ceramics were briefly reviewed. Thermodynamic calculation of  $M_s$  temperature as function of grain size and parent ordering in CuZrAl was presented. The works on prediction of  $M_s$  in FeMnSi based alloys and in ZrO<sub>2</sub>-CeO<sub>2</sub> were mentioned. Magnetic shape memory materials were briefly introduced.

**[Key words]** shape memory materials; NiTi; CuZrAl; FeMnSi; martensitic transformation; thermoelastic transformation; magnetic shape memory materials

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### 1 INTRODUCTION

Shape memory materials are recognized as quite fascinating materials and are now being practically used as functional materials for pipe couplings, antennae for cellular phones, various actuators and medical implants and guide wires. They possess potentiality for application as smart materials, since they function as sensors as well as actuators. A book entitled "Shape Memory Materials" edited by Otsuka and Wayman was published in 1998<sup>[1]</sup>. Ullakko compared four kinds of actuator materials, namely piezoelectric ceramics, magnetostrictive materials, conventional shape memory materials and magnetically controlled shape memory materials<sup>[2]</sup>. Piezoelectric ceramics deform when subjected to an electrical field. Frequency response of piezoelectric ceramics is fast, but strain amplitudes are very small which limits their application only in micro-machinery. Under a magnetic field, magnetostrictive materials are strained by the rotation of magnetic domains. The strain of Fe-Dy-Tb alloy (Terfenol) is up to 0.17%, which is one order of magnitude higher than that of the current piezoceramics. The stress induced by Terfenol is about 20 times higher than that of piezoceramics and the energy density of Terfenol actuators is 10 times higher than that attained in with hydraulic machines. In conventional memory shape alloys or ceramics, strain of several per cent can be completely recovered and the recovery stress of over 900 MPa have been attained, however, the response in these materials is

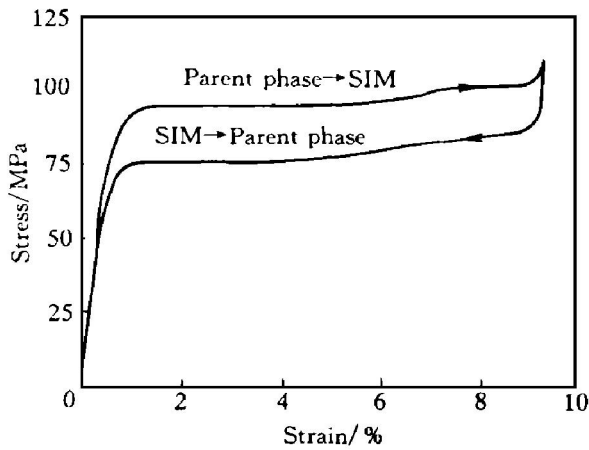
rather slow due to the thermal mechanical control and the energy conversion is also low, only a few per cent. In the magneto-shape memory (MSM) materials, ascribed as a new kind of actuator materials, the shape change is driven by the applied magnetic field, which causes the motion of twin boundaries in martensite or the interfaces between the martensite and the parent phase. It is expected that the MSM materials may develop considerable strains of several percent as well as rapid and precise shape control and will be commercially exploited in the near future. In present paper, the author attempts to present some aspects of characteristics of martensitic transformation and shape memory effect in NiTi, CuZrAl, FeMnSi based shape memory alloys and ZrO<sub>2</sub> containing shape memory ceramics revealed by the present author and his colleagues and to briefly introduce the magnetically controlled shape memory materials. The most of the content in this paper are excluded in the book mentioned above.

### 2 PSEUDOELASTICITY AND SHAPE MEMORY EFFECT RESULTED FROM MARTENSITIC TRANSFORMATION AND ITS REVERSE TRANSFORMATION

When the stress is released in some shape memory alloys after the formation of stress-induced martensite (SIM), the strain recovers as the SIM revert to the parent phase. This phenomenon is called pseudoelasticity. As the stress is released, the strain fully re-

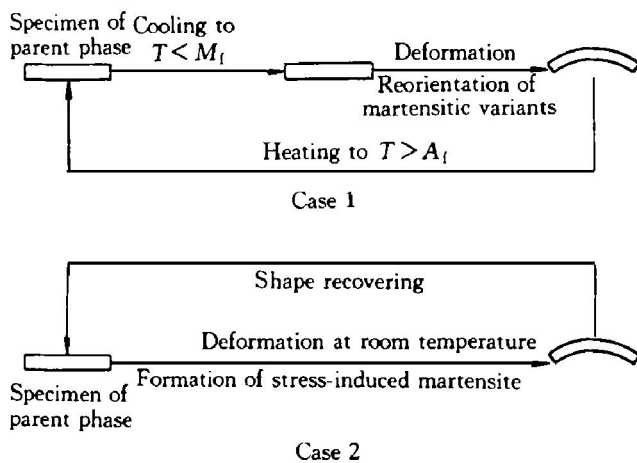
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covers to zero, superelasticity is often termed. Fig. 1 shows the stress-strain curve for a single crystal of a Cu-39.8%Zn (mass fraction) shape memory alloy tensilely deformed at about 50 °C above its  $M_s$  temperature<sup>[3]</sup>, demonstrating superelasticity through stress-induced martensitic formation and its reverse transformation. This behavior corresponds to a mechanical shape memory. Thermal-induced martensite in shape memory materials may be reorientated under stressing and may also show certain extent of pseudoelasticity.



**Fig. 1** Superelastic stress-strain loop for Cu-39.8%Zn single crystal deformed at about -77 °C

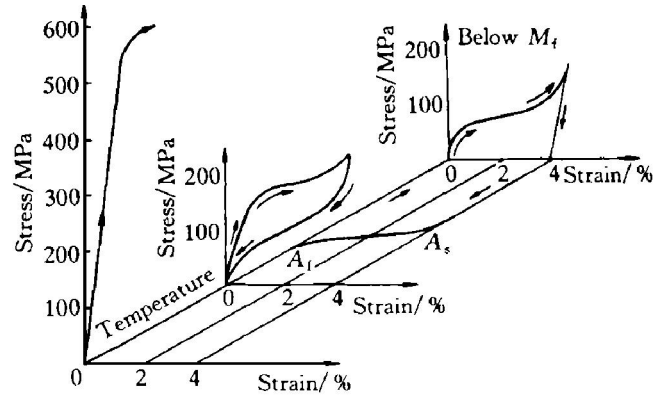
Some shape memory alloys, i. e. Au-Cd and Ir-Tl, show rubber-like behavior. Shape memory effect can be schematically illustrated in Fig. 2. Ni-Ti and Cu-based alloys act as case 1 and Fe-Mn-Si based alloys act as case 2.



**Fig. 2** Schematic illustration of shape memory effect

Fig. 3 is a stress-strain-temperature diagram for a Ni-Ti shape memory alloy, showing shape memory effect after straining and heating to above  $A_f$ , superelastic characteristics after stress releasing and the deformation behavior of the parent phase above the  $M_d$  temperature (left side)<sup>[4]</sup>.

Shape recovery to parent phase as heating to



**Fig. 3** Stress-strain-temperature diagram for Ni-Ti shape memory alloy

( $A_s - A_f$ ) is named as one-way shape memory effect. Two-way SME represents that the shape recovery can be brought to the original shape of the parent phase as well as the deformation shape of martensite. In 1951, Chang and Read<sup>[5]</sup> found the reverse motion of the parent/martensite interface with the variation of temperature and discovered the shape memory effect. In 1963, Buehler et al<sup>[6]</sup> first used the term, shape memory, to describe the strain recovery of Ni-Ti. After then researchers paid due attention to this subject.

### 3 REQUIREMENTS FOR SHAPE MEMORY EFFECT AND CRITERIA FOR THERMOELASTIC MARTENSITIC TRANSFORMATION

In 1972, Wayman and Shimizu<sup>[7]</sup> suggested that the requirements for the appearance of SME in alloys which may undergo the martensitic transformation are: 1) the martensitic transformation might be thermoelastic; 2) parent phase possesses atomic ordering; 3) the lattice invariant displacement should be twinning. It is well known that the substructure of martensite in Cu-Zn-Al alloys possessing complete SME is stacking fault. In Fe-Mn-Si, there exhibits SME through a semi-thermoelastic martensitic transformation from disordered parent phase. Later, Wayman emphasized the crystallographic reversibility and the self-accommodation of martensite to be the required condition for the appearance of SME<sup>[4]</sup>.

The self-accommodation is a general phenomenon in martensitic structure for minimizing the strain energy during the martensite formation, but in different extent in various materials. With the interference of the slip displacement in transformation, in many iron-based alloys, there often appears a very limited self-accommodation between martensite variants. Under deformation, a well-accommodated martensite can easily undergo reorientation to become a nearly single martensite which is a main condition for appearing the crystallographic reversibility.

Suggested by the present author<sup>[8,9]</sup>, a martensitic transformation can be defined as a first-order

nucleation-growth transformation with shape change and surface-relief, and characterized by an invariant planar strain resulted from the diffusionless shear displacement of substitutional atoms. From the characteristics of the martensitic transformation given above, the shape memory effect behavior is basically a natural consequence of a martensitic transformation and its reverse reaction from a single or nearly single variant of martensite, provided that the resistance of SME, or the factors interfering the SME, must be prevented during the transformation. It has been found by Kajiwara that the austenite orientation can fully recover after a reverse transformation in iron-based alloys<sup>[10]</sup>. Incomplete SME appears even in high Ni content Fe-Ni alloy associated with a lenticular martensite formation<sup>[11]</sup>. Thus, it may be suggested that the only requirement for the appearance of SME in materials undergoing a martensitic transformation and its reverse reaction in absence of the resistance against SME is the formation of single or nearly single variant of martensite.

The above description may be expressed mathematically from the application of group theory to martensitic transformation<sup>[12]</sup>. Let the symmetry group of the parent phase be  $G_0$ , that of the external medium be  $G_1$  which reflects anisotropy of the solicitation applied to the crystal. When  $G_1$  reaches a critical value of temperature or stress, a transformation would be induced. At the transformation temperature, all thermodynamic properties of the transformation are invariant through any symmetry elements belonging simultaneously to both groups  $G_0$  and  $G_1$ .

Assume the symmetry group to be  $H$  which is an intersection group of  $G_0$  and  $G_1$

$$H_0 = G_0 \cap G_1$$

where  $H_0$  is called the group of isoprobability of nucleation of the transformation product, i. e. a symmetry group for the nucleation of martensite.

Let  $G$  stand for the symmetry group of martensite,  $N_{01}$  be the set of the common symmetry element  $H_0$  and  $G$ , and  $n_{01}$  be the number of variant of martensite, we have

$$N_{01} = H_0 \cap G, \quad n_{01} = \text{index}(H_0 / N_{01})$$

For the reverse transformation

$$H_1 = G \cap G_1, \quad N_{01} = H_1 \cap G_0$$

The required condition for the crystallographic reversibility is then

$$n_{01} = 1$$

The single or nearly single variant of martensite may be obtained through stress inducing or reorientation by deformation.

Generally, the thermoelastic or non-thermoelastic transformation is only differentiated by the amount of the thermal hysteresis, i. e.  $(A_s - M_s)$  or  $(A_f - M_s)$ , and it seems an incomplete criterion. Referring to the points of view given by Wayman<sup>[4]</sup> and the

present author<sup>[12~14]</sup>, the criteria suggested for the thermoelastic transformation are: 1) a small critical driving force for transformation and a small hysteresis; 2) reversibility of the motion of the interface between martensite and the parent phase; 3) the strain is accommodated elastically and the storing elastic energy in martensite may contribute part of the driving force for the reverse transformation. A martensitic transformation which fulfills the above criteria may be termed as a thermoelastic transformation; a transformation which is contrary of the above three conditions may be classified as a non-thermoelastic one; and a transformation which incompletely fulfill the above criteria may be called a semi-thermoelastic one<sup>[13,14]</sup>.

Martensitic transformation in Ni-Ti based alloys, Cu-based alloys (i. e. Cu-Al-Ni and Cu-Zn-Al), Au-Cd, Ir-Tl alloys are thermoelastic.

In Fe-Mn-Si based alloys, it is found that the interface of  $\gamma/\epsilon$ , or the Shockley partial dislocation  $a/6\langle 112 \rangle$ , can move reversely but the thermal hysteresis  $(A_s - M_s)$  is as high as 100 K, implying that no storing elastic energy can be contributed as part of the driving force for the reverse transformation. Accordingly, the  $\gamma \rightarrow \epsilon$  transformation in alloys with low stacking fault energy may be classified as a semi-thermoelastic martensitic transformation<sup>[15]</sup>.

It is uncertain whether the martensitic transformation  $t \rightarrow m$  in  $ZrO_2$  containing ceramics is thermoelastic or not. This problem needs to be further clarified.

## 4 Ni-Ti ALLOYS

Ni-Ti based alloys are currently being widely used in instrument industry and especially as prosthesis or biomaterials in medicine and dentistry because of their excellent mechanical stability, corrosion resistance, bioactivity and biocompatibility.

In binary Ni-Ti alloy,  $B2 \rightarrow$  incommensurate phase  $\rightarrow R$  phase  $\rightarrow B19'$  martensite and  $[\bar{1}\bar{1}0]_{B19'} \parallel [1\bar{1}0]_{B2}$  and  $(001)_{B19'}$  deviates from  $(110)_{B2}$  by  $6^\circ$  were found by TEM and electrical resistivity measurements<sup>[16]</sup>. The orientation relationship between  $B2$  and  $R$  phases, as well as the  $B19'$  martensite were also determined and it is found that upon heating, only the  $B19' \rightarrow B2$  transformation occurs and the substructure of martensite changes from twins to finer twins to stacking faults with increasing cooling rate<sup>[17]</sup>. Effect of various processes of heat treatment (solution treatment and aging) on shape memory effect in Ni-Ti was studied in detail<sup>[18]</sup>. It was found that various processes of heat treatment change the sequence of phase transformation. Aging at 400~600 °C brings about the ordering of the  $B2$  and precipitation of  $Ti_3Ni_4$ . Ordering of  $B2$  is beneficial to the formation of  $R$  phase which will contribute the one

third of the shape memory effect. Fig. 4<sup>[18]</sup> shows the effect of various phase states on SME in a 49.43% NiTi (mole fraction) alloy. Fig. 5<sup>[18]</sup> indicates that the volume change during  $R \rightarrow B19'$  (linear expansion of 0.055%) is much greater than that during  $B2 \rightarrow R$  (linear contraction of 0.03%) and may create stress to induce the shape memory effect. The linear expansion during  $B2 \rightarrow$  martensite is 0.025%<sup>[18]</sup>. The stress field induced by precipitation may also be beneficial to SME<sup>[19]</sup>.

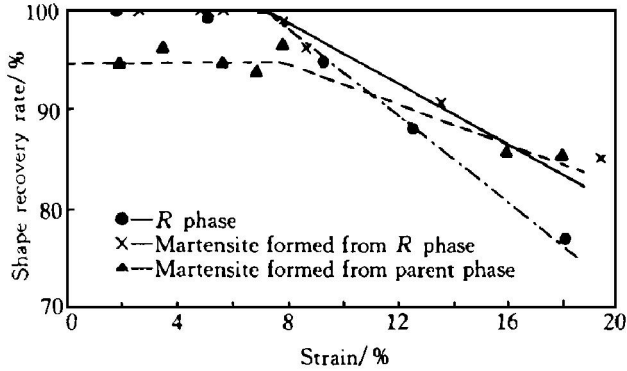


Fig. 4 Effect of various phase states on shape recovery rate in 49.43% NiTi (mole fraction) alloys

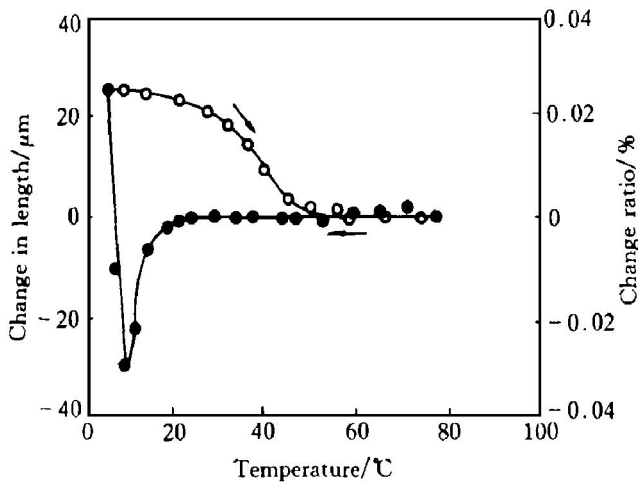


Fig. 5 Changes in length upon cooling and heating for specimen of 49.43% NiTi (mole fraction) alloy (Solution treated at 800 °C for 20 min, furnace cooled and aged at 500 °C for 2 h)

### 5 Cu-Zr-Al ALLOYS

Owing to easy fabrication and low cost, Cu-Zr-Al shape memory alloys have been paid much attention by researchers and industrial employers. A mathematical expression of the influence of grain size and ordering degree of the parent phase on the  $M_s$  temperature of Cu-Zr-Al alloys was derived as<sup>[20]</sup>

$$M_s = M_s^s + Kd^{-1/2} \quad (1)$$

$$M_s^s = \left[ 1 + \frac{\tau_0 \epsilon_p + \Delta \epsilon_c^V}{\Delta H(\beta \rightarrow M)} \right] T_0,$$

$$K = \frac{k \epsilon_p T_0}{\Delta H(\beta \rightarrow M)}$$

where  $M_s^s$  is the  $M_s$  of a single crystal ( $d \rightarrow \infty$ );  $T_0$  is the temperature at which  $\Delta G_c(\beta \rightarrow M)$ , the change in chemical free energy at  $\beta \rightarrow M$ , equals to zero;  $\Delta \epsilon_c^V$  is the strain energy difference caused by volume change for transformation,  $\Delta H(\beta \rightarrow M)$  is the change in enthalpy for  $\beta \rightarrow M$ ;  $\tau_0$  is the critical shear stress of a single crystal ( $d \rightarrow \infty$ );  $\epsilon_p$  is the shear strain and  $k (> 0)$  is a constant depending on material. Eqn. (1) is consistent quite well with experimental result. For Cu-25.62Zr-3.96Al alloy, it gives

$$M_s (\text{°C}) = 168.2 - 94.5d^{-1/2} \quad (2)$$

$\beta$  phase in Cu-Zr-Al alloy possesses a disordered structure of A2 at high temperature. Upon quenching  $\beta$  phase will be changed to ordered B2, while with certain temperature range, the stable ordered phase is of DO<sub>3</sub>, or L2<sub>1</sub>. Under further cooling to a temperature below  $M_s$ , B2 or DO<sub>3</sub> changes to 9R or 18R martensite respectively. Applying the Landau's theory to analysis the dependence of  $M_s$  on ordering degree gives<sup>[20]</sup>

$$M_s = \frac{M_s^d + \gamma T_c' \zeta^2}{1 + \gamma \zeta^2} \quad (3)$$

where  $M_s^d$  is the  $M_s$  at disordered states ( $\zeta = 0$ ) or a constant concerned with material;  $T_c'$  is a constant characterizing the temperature of ordering transition and  $\zeta$  is the order parameter. For Cu-25.62Zr-3.97Al,

$$M_s (\text{K}) = \frac{323.9 + 560.42 \gamma \zeta^2}{1 + \gamma \zeta^2} \quad (4)$$

$$\gamma \zeta^2 = \exp\left(-\frac{22078}{RT} + 18.91\right) \cdot (t - t_0) \quad (5)$$

where  $t$  is the holding time at every step quenching temperature and  $\zeta = 0$  at  $t = t_0$ . Eqn. (4) is supported by experimental results.

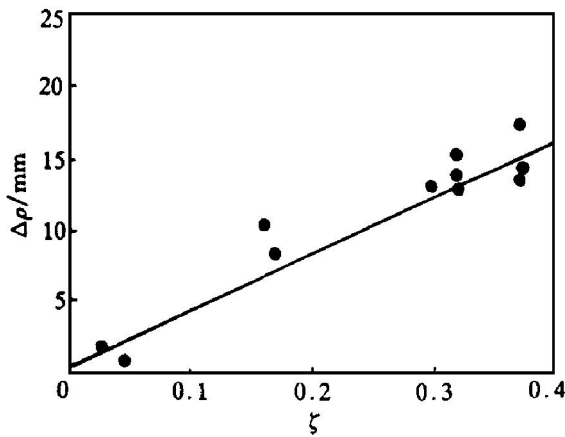
Internal friction study on martensitic transformation in Cu-25.59Zr-3.93Al (mass fraction, %) shape memory alloy revealed<sup>[21]</sup>: 1) in fully aged martensite, there is only a precipitation of  $\alpha$  phase process upon heating to above 120 °C; 2) B2  $\leftrightarrow$  9R and DO<sub>3</sub>  $\leftrightarrow$  18R martensitic transformations may coexist in alloys treated by step quenching and short time holding in parent state. After a prolonged holding, only a single DO<sub>3</sub>  $\leftrightarrow$  18R transformation exists; 3) for the specimen immediately up quenching to 100 °C or 150 °C after quenching, there is a pair of sharp internal friction peak, corresponding to B2  $\leftrightarrow$  9R transformation with a smaller hysteresis than that of DO<sub>3</sub>  $\leftrightarrow$  8R; 4) a rapid quenching from the parent phase region can not suppress the ordering transformation A2  $\rightarrow$  B2, but may suppress B2  $\rightarrow$  DO<sub>3</sub>. An enough vacancy concentration seems to be a necessary condition for the occurrence of B2  $\rightarrow$  DO<sub>3</sub> transformation. Theoretical  $T_0$  temperature or the equilibrium temperature between disordered  $\beta$  phase and martensite,  $M_s$  temperature

of ordered  $B2$ , ordered  $DO_3$  and  $L2_1$ , can all be thermodynamically calculated and the calculated  $M_s$  from  $L2_1$  are consistent with the experimental (step quenching) values<sup>[22]</sup>.

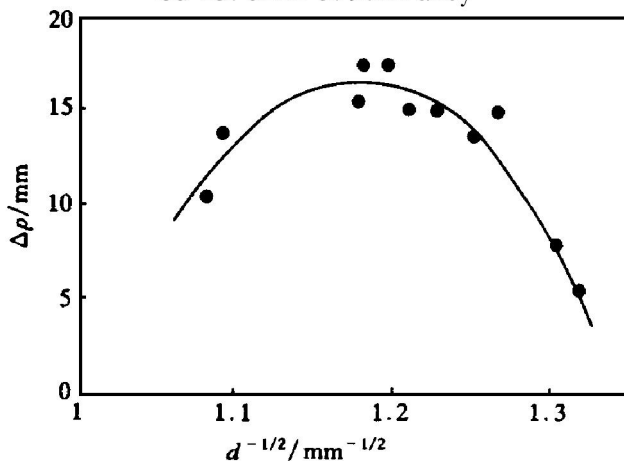
Main factors affecting the shape memory effect which is usually expressed as recovery rate in CuZrAl alloys are the ordering degree of  $B2$  phase<sup>[23,24]</sup>, the grain size of the parent phase<sup>[24,25]</sup> and the pre-deformation amount in the martensitic state<sup>[26,27]</sup>. Figs. 6, 7<sup>[24]</sup> and 8<sup>[27]</sup> show the effect of parent ordering degree (with ordering parameters  $\zeta$ ), grain size of the parent phase,  $d$ , and the pre-deformation amount,  $\epsilon$ , on SEM in CuZrAl alloy respectively. A mathematical expression including all three factors affect the shape recovery rate  $\eta$  is deduced as<sup>[28]</sup>

$$\eta = \begin{cases} K_1 \zeta (1 - 2\lambda/d)(E\epsilon - A), & (\epsilon < \epsilon_L) \\ \frac{K_2 \zeta (1 - 2\lambda/d) \arcsin 2(\tau_0 + kd^{-1/2})}{E\epsilon}, & (\epsilon \geq \epsilon_L) \end{cases}, \quad (6)$$

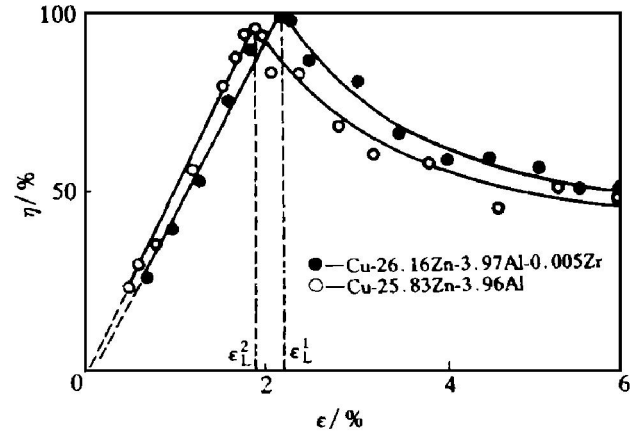
where  $K_1$  and  $K_2$  are proportional constants,  $\epsilon_L$  is the critical pre-strain (corresponding to the maximum  $\eta$ ),  $E$  and  $A$  are constants,  $\lambda$  is the width of grain



**Fig. 6** Effect of ordering parameter of parent phase ( $\zeta$ ) on shape recovery amount ( $\Delta\rho$ ) in Cu-25.6Zr-3.97Al alloy



**Fig. 7** Effect of parent grain size ( $d$ ) on shape recovery amount ( $\Delta\rho$ ) in Cu-25.6Zr-3.97Al alloy



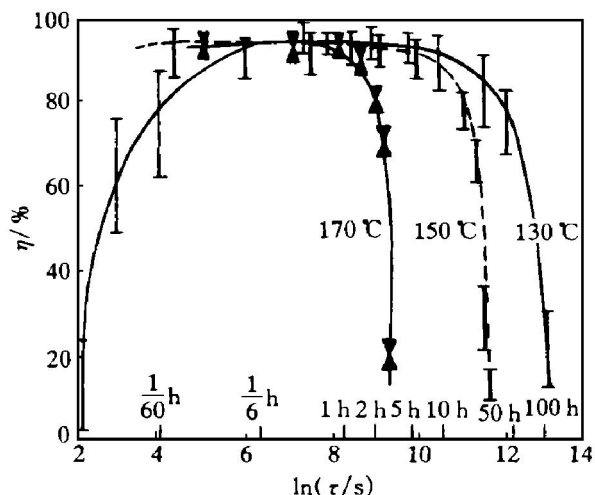
**Fig. 8** Effect of predeformation amount in martensitic state ( $\epsilon$ ) on shape recovery rate  $\eta$

boundary-affected zone being incapable of recovery,  $\tau_0$  is the critical shear stress of a single crystal and  $k$  is a constant characterizing the resistance of grain boundaries to the motion of dislocations. The experimental phenomena can be well interpreted by Eqn. (6).

The deficiencies of CuZrAl shape memory alloys are: 1) appearance of the stabilization of martensite, 2) degradation of shape memory effect in prolonged application and 3) rather low fatigue life.

The stabilization of martensite is characterized by the inhibition of the normal reversible martensitic transformation after the alloys have undergone a post-quench aging in the martensitic state at a relatively low temperature. Vacancy behavior in Cu-26Zr-4Al alloy during aging was investigated by means of positron annihilation and electrical resistivity measurements and revealed that the clustering of quenched-in vacancies is responsible for the stabilization of martensite at the early stage in CuZrAl alloys, i. e., the  $S$  parameter of CuZrAl specimens measured at liquid nitrogen temperature increases at first and then decreases, while that of CuAlNi specimens remains unchanged<sup>[29]</sup>. HRTEM observation<sup>[23]</sup> also confirms that the clustering of vacancies leading the disordering of martensite deteriorates the SME. Internal friction study<sup>[21]</sup> also shows that the supersaturated vacancies may play an important role in the stabilization of martensite. Immediate up-quenching for the quenched CuZrAl alloys is an effective process to suppress the stabilization of martensite and to make the reverse transformation complete.

Bainite formation in CuZrAl alloys lowers the SEM<sup>[30]</sup>. Fig. 9 shows the effect of aging duration at 130 °C, 150 °C and 170 °C on shape recovery rate in a quenched Cu-25.5Zr-3.92Al (mass fraction, %) alloy. The recovery rate remarkably increases at the early stage of aging due to the annihilation of the quenched-in vacancies and lowers considerably at prolonged aging due to bainite formation<sup>[31]</sup>. Thermodynamics consideration indicates that the bainite forma-



**Fig. 9** Effect of aging duration ( $\tau$ ) at 130 °C, 150 °C and 170 °C on shape recovery rate ( $\eta$ ) in quenched Cu-25.5Zr-2.92Al alloy

tion in Cu-Zr-Al alloys is a diffusional process and X-ray analysis also confirms that the bainite in Cu-Zr-Al alloys does not inherit the ordering of the parent phase<sup>[32]</sup>. Consequently, bainitic transformation in Cu-Zr-Al alloys does not show the shape memory effect, but shows a reverse one<sup>[33]</sup>. Experimental result of internal friction studies on Cu-Zr-Al alloy and steels<sup>[34]</sup> as well as Ag-Cd alloy<sup>[35]</sup> indicates that the structural change within the incubation period of bainite formation may be a nucleation process accompanying lattice instability of the parent phase. Accordingly, in the course of a long time application of Cu-Zr-Al shape memory alloys, the nucleation and/or the formation of bainite in materials may accrue and degrade the shape memory effect. Addition of alloying element which will prolong the incubation period of the bainite transformation may improve the life duration of Cu-Zr-Al shape memory alloys.

The low fatigue life of Cu-based shape memory alloys may be related to the intrinsic grain boundary embrittlement in these alloys. Grain refining of the alloys may be an effective way to improve the fatigue property.

## 6 Fe-Mn-Si BASED ALLOYS

In 1982, Sato et al<sup>[36]</sup> found a nearly complete SEM in a Fe-30Mn-1Si single crystal in which a single variant of  $\epsilon$  martensite was induced by the application of a tensile stress along a  $\langle 414 \rangle$  direction and the recoverable strain is as high as 9%. Based on the recent studies<sup>[12, 15, 37-46]</sup>, the characteristics of the fcc( $\gamma$ )  $\rightarrow$  hcp( $\epsilon$ ) martensitic transformation in Fe-Mn-Si based alloys are as follows.

1) It may be classified as a semi-thermoelastic transformation.

2)  $M_s$  does not markedly vary with the grain size of the parent phase and there does not show a consid-

erable decrease of the elastic modulus during the transformation. It is thought that nucleation of  $\epsilon$  martensite is not related to soft modes. The nucleation of  $\epsilon$  martensite may occur directly through an overlapping of stacking faults and would not dominantly operated by pole mechanism.

3) The stacking fault energy is an important factor acting as barrier for the transformation and

$$\Delta G(\gamma \rightarrow \epsilon) = A\gamma + B$$

where  $A$  and  $B$  are constants;  $\gamma$  is stacking fault energy of material.

4) Antiferromagnetic transformation depresses the transformation in such a way that it decreases the amount of  $\epsilon$  martensite formed and delays the completion of the transformation.

5) In the reverse transformation, two processes may coexist, i. e. the reverse movement of Shockley partial dislocation and the nucleation of fcc( $\gamma$ ) phase in  $\epsilon$  matrix occurring through the stacking faults.

6) On crystallographic feature, when  $d_{111} \neq d_{0002}$ , a shuffle on  $(111)_\gamma$  plane is required to make the habit plane be the invariant plane, and the surface relief and the strain energy after thermal induced transformation are mainly dependent on the degree of self-accommodation.

The main factors controlling the SME are austenite strengthening, stacking fault energy or stacking fault probability and antiferromagnetic temperature. In Fe-Mn-Si, addition of nitrogen will powerfully strengthen austenite and rare earth elements will increase considerably the strength of austenite. Silicon lowers the stacking fault energy (SFE). Replacement a part of Mn with Cr and addition of rare earth elements also reduce the SFE and lower the Néel temperature. A complete SME can be attained in Fe-Mn-Si based alloys by the application of an appropriate thermomechanical training, i. e. several cycles of 2% deformation at room temperature and heating to 600 °C. The improvement of SME by training may be mainly attributed to the formation of nearly single variant of  $\epsilon$  martensite and to enhance the reversible transformation.

Néel temperature in Fe-Mn-Si alloys with various alloying contents are evaluated<sup>[47]</sup> and  $M_s$  temperature of ternary Fe-Mn-Si with various contents of alloy element can be thermodynamically predicted<sup>[48, 49]</sup>. The SME of Fe-Mn-Si alloys can be interpreted through an analysis of the stress-strain curve of the alloy<sup>[50]</sup>. Two novel shape memory alloys Fe-Mn-Si-RE and Fe-Mn-Si-Cr-N are recommended as shape memory materials with nice SME<sup>[37, 50]</sup>, i. e. with a recoverable strain of 4%<sup>[36, 51]</sup>.

## 7 SHAPE MEMORY CERAMICS

ZrO<sub>2</sub> containing ceramics possess  $t$  (tetragonal

phase)  $\rightarrow$   $m$  (monoclinic phase) martensitic transformation and its reverse transformation. The shape recovery has been observed in Mg-PSZ (9.2% MgO-ZrO<sub>2</sub>)<sup>[52]</sup> and Ce-TZP (12% CeO<sub>2</sub>-ZrO<sub>2</sub><sup>[53]</sup> and 10% CeO<sub>2</sub>-ZrO<sub>2</sub><sup>[54]</sup>) (mole fraction). The effects of strain on shape recovery in Ce-TZP (10% CeO<sub>2</sub>-ZrO<sub>2</sub>, and Ce-Y-TZP (8% CeO<sub>2</sub>-0.5% Y<sub>2</sub>O<sub>3</sub>-ZrO<sub>2</sub>) (mole fraction) are shown in Figs. 10 and 11<sup>[55]</sup>. Fig. 10 shows the pseudoelasticity and shape memory effect in ZrO<sub>2</sub> containing ceramics with the recoverable strain of 1.5%. More than 1% pre-strain lowers the shape recovery rate, as shown in Fig. 11 and this may be attributed to the creation of micro-cracks in materials.

Based on the thermodynamic calculation of the equilibrium temperature between the tetragonal and monoclinic phases in CeO<sub>2</sub>-ZrO<sub>2</sub><sup>[56]</sup>,  $M_s$  temperature can be calculated in a 8% CeO<sub>2</sub>-ZrO<sub>2</sub> (mole fraction)<sup>[57]</sup>. The size effect in  $t \rightarrow m$  transformation is reasonably deduced as strengthening of parent phase resulted from grain refining causing the reduction of  $M_s$ <sup>[58]</sup>.

### 8 MAGNETIC SHAPE MEMORY MATERIALS (MAGNETICALLY CONTROLLED SHAPE MEMORY MATERIALS — MSM MATERIALS)

In crystalline ferromagnetic materials, magnetization vectors lie along certain definite crystallographic axes called direction of easy magnetization. Crystal anisotropy energy is an energy that directs the magnetization along these directions. When an external magnetic field is applied, the magnetization tends to turn from the easy direction of the unit cell to the direction of the external magnetic field, as shown for a magnetostrictive materials in Fig. 12(a)<sup>[2]</sup>. The motion of the twin boundaries or austenite/martensite interface is controlled by magnetic field in an analogous way as they are controlled thermo-mechanically in conventional shape memory alloys. Figs. 12(b) and

(c)<sup>[2]</sup> show a two-dimensional illustration of the motion of martensite twin boundaries by stress in conventional shape memory alloys and by the magnetic field in the magnetically driven shape memory alloys.

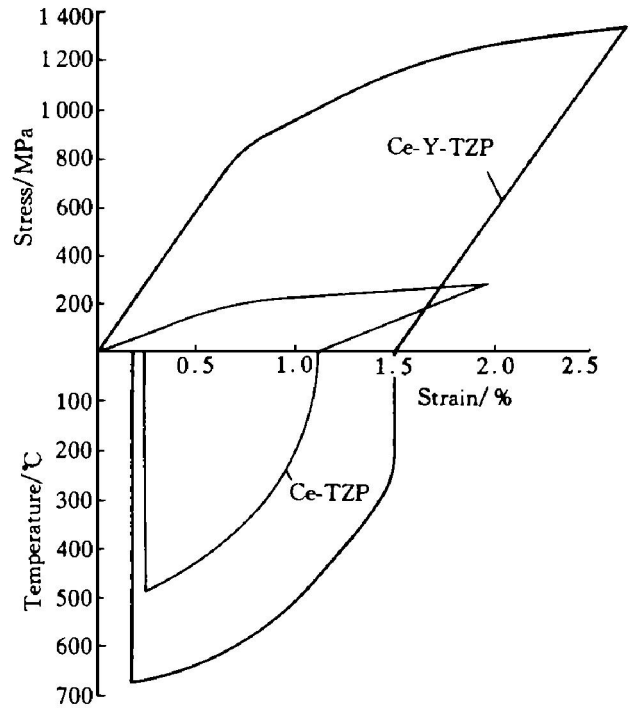


Fig. 10 Stress—strain—temperature diagram for Ce-TZP and Ce-Y-TZP

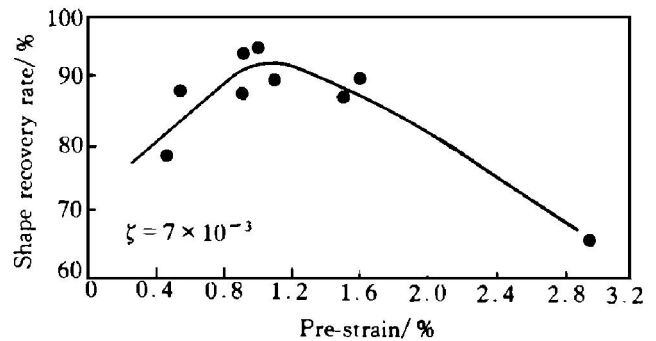


Fig. 11 Effect of strain amount on shape recovery rate in Ce-Y-TZP

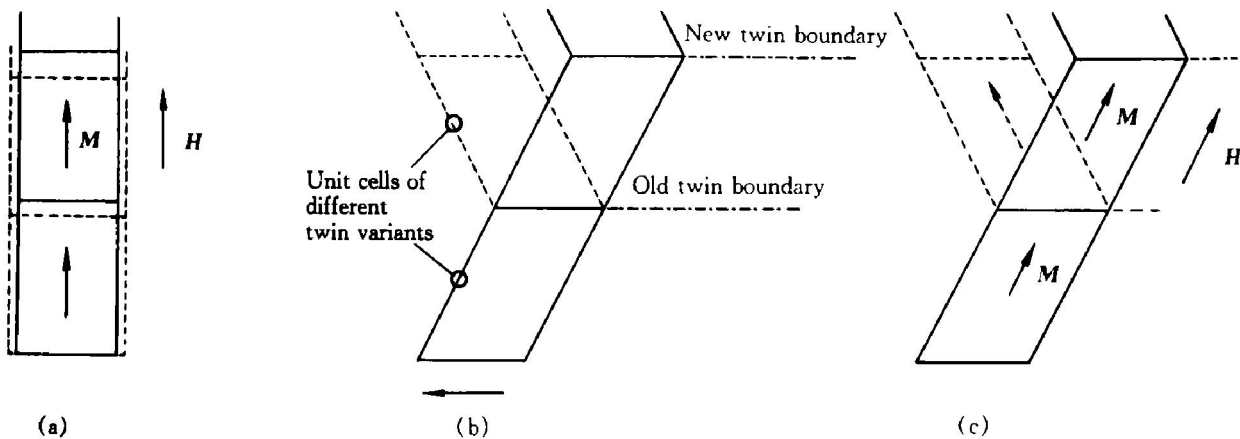


Fig. 12 Schematic presentations of shape changes that cause strokes in magnetostrictive (a), conventional shape memory materials (b) and magnetically driven shape memory materials (c)

Fig. 12(c) illustrates how the unit cells of one variant are turned into another by external magnetic field. As a result, twins in favorable orientation to magnetic field grow at the expense of other twins. Applied magnetic field can cause strokes of a few percent in MSM materials. When the magnetic field and stress are alternatively applied, the recoverable strain called "magneto-supereasticity" can be performed.

Studies on Heusler alloys  $\text{Ni}_2\text{MnGa}$  and other ferromagnetic shape memory materials are in progress<sup>[51]</sup>. Single crystal  $\text{Ni}_2\text{MnGa}$  shows a nearly 0.2% strain under a magnetic field of 636.62 kA/m at 8 °C<sup>[59,60]</sup> and a transverse field of 254.65 kA/m caused the sample to deform under load, doing work that increased up to 1.3 J/kg with increasing volume fraction of stress-induced martensite<sup>[61]</sup>. James and Wuttig reported a free strain of 0.5% in single crystals of FePd at -17 °C<sup>[62]</sup> and a field induced, free strain of 1.3% below 0 °C in stress-cooled, non-stoichiometry, single crystal of  $\text{Ni}_2\text{MnGa}$ <sup>[61]</sup>.

The present author's research group is now just studying the mechanism of the magnetically controlled SME and the relationship among the  $M_s$  temperature, field-induced strain, force, alloy composition and processing in  $\text{Ni}_2\text{MnGa}$ . Polycrystalline  $\text{Ni}_2\text{MnGa}$  alloy with non-stoichiometry possessing better formability and SME is expected to be developed for practical applications.

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