SHAPE MEMORY ALLOYS

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I. INTRODUCTION

In some alloys, a given plastic strain recovers completely when the concerned alloy is heated above a certain temperature. This phenomenon, shape memory effect (SME), was observed in Au-Cd (1) and In-Tl (2) alloys in the first half of 1950s. However, SME was not a focus of research until it was found in a Ti-Ni alloy (3) in 1963, when the phenomenon was first termed the shape memory effect. A similar phenomenon was found in a Cu-Al-Ni alloy as well (3a). At that time, however, SME was considered to be a peculiar phenomenon limited to the specific Ti-Ni alloy.

In 1970, Otsuka & Shimizu (4, 4a) unambiguously demonstrated a one-to-one correspondence between SME and the thermoelastic martensitic transformation in a Cu-Al-Ni alloy. Thus, they concluded that SME is characteristic of alloys exhibiting thermoelastic martensitic transformations. They ascribed the origin to the crystallographic reversibility of the thermoelastic transformation and the presence of a recoverable deformation mode, i.e. twinning, in thermoelastic alloys. Since then, there

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have been a great number of investigations (5, 5a) of SME and various phenomena related to thermoelastic transformations (see Section III). As a result, SME is currently understood in the following way (6): An apparent plastic strain introduced into a material by twinning deformation in martensite and/or by the stress-induced martensitic (SIM) transformation in the parent phase at a temperature below A_s[1] vanishes completely with the reverse transformation upon heating to a temperature above A_f.[1] Typical alloys exhibiting SME, i.e. shape memory alloys (SMAs), widely known at present are listed in Table 1. All the SMAs exhibit a thermoelastic transformation, and most of them are ordered.

Complete shape recovery by SME depends on the following two conditions: (a) the transformation is crystallographically reversible,[2] and (b) slip is excluded in the whole deformation process. The first condition is in general characteristic of thermoelastic transformations or the martensitic transformations in ordered alloys (4, 7), and thus the complete SME is realized primarily in the alloys exhibiting a thermoelastic transformation.[3] The relation between atomic order and crystallographic reversibility are discussed in Section III. The second condition is obvious: If stress or strain is too high, and all the deformation modes, i.e. SIM transformation in the parent phase and twinning in martensite, are consumed, slip may be introduced, which results in plastic strain and incomplete shape recovery.

In brief, SME is a phenomenon essentially associated with a martensitic transformation. In Section II the crystallographic aspects of SMAs, i.e. crystal structures of parent and martensite phases and the transformation between them, are described. Section III is devoted to the description of various unique mechanical properties of SMAs, i.e. SME and other effects related to thermoelastic transformations and the martensites themselves. In Section IV, thermal and mechanical stability of SME characteristics are discussed; in Section V, applications of SMAs are reviewed briefly.

For information on overall features of martensitic transformations, including the thermoelastic and nonthermoelastic types, readers can refer to excellent textbooks (9–11) in the bibliography of this article; some

[1] The characteristic temperatures of martensitic transformations, M_s, M_f, A_s, and A_f stand for martensite-start, martensite-finish, reverse transformation-start and reverse transformation-finish temperatures, respectively.

[2] This means that not only the crystal structure but also the orientation of the parent phase is restored after the reverse transformation.

[3] Although Fe-Mn-Si alloys undergo nonthermoelastic transformations, the alloys exhibit SME under some limited conditions (8) (see Section III).

references (6, 7, 12–22) may also be useful for a deeper comprehension of
the whole nature of SMAs.

II. CRYSTALLOGRAPHIC ASPECTS

Crystal Structures of Parent and Martensite Phases and the Intermediate "Premartensitic" State

PARENT PHASE   Crystal structures of parent phases of the SMAs are
fundamentally either of body-centered cubic (bcc) or face-centered cubic
(fcc) lattice, as seen in Table 1. Before martensitic transformations, the
parent phases, except In-Tl, Mn-Cu, and Fe-Pd alloys, are usually ordered
into a $B2$, DO_3, $L2_1$ or $L1_2$ type superlattice structure. Cu-Zn-Al SMAs
possess both $B2$ and DO_3 ordered structures in the parent phase, according
to composition or heat treatment for a given composition (23).

When parent phases with various types of order are examined at ambient
temperature by transmission electron microscopy (TEM), characteristic
fine structures termed "mottled" or "tweed" (24) are observed. Cor-
responding electron diffraction reveals the presence of plate- and/or rod-
like diffuse scattering and moreover some "extra spots," which are not
expected to appear in these types of order (24). These fine structures clearly
indicate that the parent phases do not have simple ordered structures;
their appearance prior to martensitic transformations is often a termed
"premartensitic" phenomenon (see below).

The SMAs from Ag-Cd to Ni-Al in Table 1 are the so-called β phase
alloys, and the parent phases with DO_3, $B2$, and $L2_1$ order are usually
denoted by β_1, β_2, and β_3, respectively, regardless of alloy systems (10).

MARTENSITE PHASE   Most of the martensites in the β phase SMAs possess
a long period stacking order (LPSO) structure, such as $2H$, $9R$ ($18R_1$),
and $18R_2$ in the Ramsdell notation.[4] Basal planes of the LPSO structures
are derived from $\{220\}_{\beta_1,\beta_3}$ or $\{110\}_{\beta_2}$ planes of parent phases. Hence, for
example, $9R$ and $18R_1$ structures are fundamentally the same if atomic
order is disregarded. The martensites with $6R$, $18R_1$, $18R_2$, and $2H$ struc-
tures produced from β_1 parent phase are usually denoted by α'_1, β'_1, β''_1,
and γ'_1, respectively, and similarly those with $3R$, $9R$, $18R_2$, and $2H$
structures produced from β_2 parent phase by α'_2, β'_2, β''_2, and γ'_2, respectively.
Among these martensites, the $18R_2$ structure is rather less common; it has
been observed only in Cu-Al-Ni (25, 26), Au-Cd (27), and Cu-Zn-Al (28)

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[4] The two kinds of $18R$-type LPSO structures are explicitly distinguished by the Zhdanov
notation as follows: $(2\bar{1})_6$ for $18R_1$ and $(1\bar{1}3\bar{1})_3$ for $18R_2$.

Table 1 Alloys exhibiting perfect shape memory effect and pseudoelasticity

Alloy	Composition (at.%)	Structure change	Hysteresis (K)	Ordering
Ag-Cd	44-49 Cd	$B2 \to 2H$	~15	Ordered
Au-Cd	46.5-50 Cd	$B2 \to 2H$	~15	Ordered
Cu-Zn	38.5-41.5 Zn	$B2 \to M9R$	~10	Ordered
Cu-Zn-X (X = Si, Sn, Al, Ga)	A few at.%	$B2(DO_3) \to 9R$, $M9R$ ($18R$, $M18R$)	~10	Ordered
Cu-Al-Ni	28-29Al	$DO_3 \to 2H$	~35	Ordered
	3-4.5 Ni			
Cu-Sn	~15 Sn	$DO_3 \to 2H$, $18R$	—	Ordered
Cu-Au-Zn	23-28 Au	$L2_1 \to M18R$	~6	Ordered
	45-47 Zn			
Ni-Al	36-38 Al	$B2 \to 3R$	~10	Ordered
Ti-Ni	49-51 Ni	$B2 \to$ monoclinic	~30	Ordered
		$B2 \to$ rhombohedral $\to$ monoclinic		
Fe-Pt	~25 Pt	$L1_2 \to$ ordered bct	~4	Ordered
In-Tl	18-23 Tl	fcc $\to$ fct	~4	Disordered
In-Cd	4-5 Cd	fcc $\to$ fct	~3	Disordered
Mn-Cu	5-35 Cu	fcc $\to$ fct	—	Disordered
Fe-Pd	~30 Pd	fcc $\to$ fct	—	Disordered

SMAs so far and can be produced by stress only from a $2H$-type structure (29).

The crystal structure of the martensite in a Au-~ 50 at.%Cd alloy is distinctly different from the LPSO structures (30) and thus denoted by ζ'_2. The ζ'_2 martensite possesses a rhombohedral lattice with space group $P\bar{3}1m$, similar to the so-called R phase in Ti-Ni(-Fe) SMAs (see below).

The crystal structure of the martensite in near equiatomic Ti-Ni alloys was debated for a long time. Recently, however, Kudoh et al (31) explored the crystal structure of the Ti-Ni alloy martensite by a single-crystal x-ray diffraction method and proposed a definite structure model. The unit cell dimension of the monoclinic lattice and the atomic parameters have been refined until the R-factor of the analysis was reduced to 4.5%. Formerly, the crystal structure of the Ti-Ni alloy martensite was regarded as one of the LPSO structures, i.e. $2H$. But the new structural model does not possess such a close-packed plane of atoms as basal planes in the LPSO structures; it is a three-dimensionally close-packed one. In this respect the martensite structure is distinguished from those of the β phase SMAs.

Thermoelastic Fe-Pt martensite possesses a base-centered tetragonal superlattice structure, and the axial ratio with respect to the fundamental body-centered tetragonal (bct) lattice, c/a, is as large as 1.11 (32). The high tetragonality is ascribed to the $L1_2$ order of the austenite prior to the martensitic transformation. On the other hand, the thermoelastic martensite recently found in an ausaged Fe-Ni-Ti-Co alloy is also bct with an axial ratio much larger than that of the Fe-Pt martensite, i.e. 1.14 (33). The higher tetragonality is due to the existence of coherent γ' Ni$_3$Ti ordered precipitates evenly dispersed in the disordered austenite matrix.

Although the bct martensite in disordered Fe-Pd alloys is non-thermoelastic and does not display SME, the face-centered tetragonal (fct) martensite in the same alloy is thermoelastic (34), as well as for the Fe-Pt alloys (35).

"PREMARTENSITIC" STATE   It is widely known that parent phases prior to martensitic transformations exhibit various anomalies termed "premartensitic" phenomena; so far they have been observed in elastic constants (15), electrical resistivity (36), magnetoresistance (37), electron diffraction (24), x-ray diffraction (38), neutron diffraction (39), TEM image (24), acoustic emission (40), and extended x-ray absorption fine structure (41). However, it is to be noted that the term "premartensitic" is often used loosely and thus all the anomalies are not truly precursory phenomena of the subsequent martensitic transformations (42).

Recently, notable progress has been made in understanding the nature of the premartensitic state in Ti-Ni(-Fe) SMAs. Matsumoto & Honma (43)

demonstrated that when a part of Ni in the equiatomic Ti-Ni alloy is substituted by Fe up to a composition of $Ti_{50}Ni_{47}Fe_3$, the premartensitic, and the subsequent martensitic transformations, which overlap in the binary alloys, take place with a large temperature interval (about 100 K). This situation has made it possible for the premartensitic state to be explored without the interference of martensitic transformation. In fact, the premartensitic state in the ternary alloy has been investigated extensively by means of x-ray, electron, and neutron diffractions, and TEM (44). As a result, it has been revealed that the following two kinds of phase transitions are involved prior to the martensitic transformation: a second-order phase transition from the $B2$ parent phase to an incommensurate (IC) phase and a first-order transition from the IC phase to a commensurate (C) phase occurring about 12 K below the onset of the $B2 \rightarrow$ IC transition. The structure of the IC phase remains cubic; meanwhile the structure of the C phase is rhombohedrally distorted along a $\langle 111 \rangle$ direction of the cubic matrix, and thus termed simply the R phase. Salamon et al (39, 45) interpreted these two successive phase transitions in terms of charge density waves (CDWs). However, the origin of these premartensitic transitions is controversial. Yamada et al (46) pointed out recently that the incommensurability depends on the Brillouin zone, thus contradicting a simple charge density and/or lattice wave description of the IC phase; they proposed another model termed "modulated lattice relaxation" (MLR). Thus, much more work is required to clarify the nature of the incommensurability.

Crystallography of Martensitic Transformations

PHENOMENOLOGICAL THEORY OF MARTENSITIC TRANSFORMATIONS   Crystallographic characteristics of martensitic transformations are well understood by the phenomenological crystallographic theory (9–11). The theory enables one to predict shape strain, habit plane, and orientation relationship between parent and martensite phases, etc. Thus, it is useful for analyzing the self-accommodating formation of thermally induced martensite variants (6), the SIM transformations, and transformation pseudoelasticity (17) (see below).

The phenomenological theory assumes that the martensitic transformation is described by an invariant plane strain (IPS), $\mathbb{P}_1$, which is described by the product of the following three operators: (a) the lattice deformation, $\mathbb{B}$, which creates a martensite lattice from a parent lattice, (b) a lattice invariant shear (LIS), $\mathbb{P}_2$, as slip, faulting, or twinning in martensite, and (c) a lattice rotation, $\mathbb{R}$. The magnitude of LIS as a macroscopic quantity can be determined so that the product, $\mathbb{P}_2\mathbb{B}$, has an undistorted plane. A lattice rotation $\mathbb{R}$ is then obtained so that the

undistorted plane is not further rotated. Consequently, for a set of input data (i.e. a specific lattice correspondence between parent and martensite phases, lattice parameters of both the phases, and a suitable system of LIS), four general sets of solutions of IPS are obtained.

The LIS, $\mathbb{P}_2$, in the phenomenological theory is important, because it is introduced so that an invariant plane, i.e. a habit plane, is present for the transformation. However, the LIS is not necessarily required, depending on the lattice deformation. In fact, a few SMAs are known (30) in which no traces of LIS are present in martensite.

RECENT IMPROVEMENT OF CONSISTENCY BETWEEN THEORY AND EXPERIMENT   The phenomenological theory has been applied to various martensitic transformations in many alloy systems so far. But overall agreement between theory and experiment was not very good, except in a few cases (9, 11). For example, in a Cu-Al-Ni alloy (47), where the $\beta_1 \rightarrow \gamma'_1$ martensitic transformation is thermally or stress-induced, a rather significant discrepancy was noted between locations of the experimental $\{121\}_{\gamma'_1}$ Type I twinning plane and the theoretical one. Recently, however, Okamoto et al (48) has solved the inconsistency by adopting the $\langle 111 \rangle_{\gamma'_1}$ Type II twinning as LIS, which was in fact experimentally found in deformed γ'_1 martensite single crystals.

Type II twinning as LIS has also been observed in the monoclinic Ti-Ni martensite recently. Matsumoto et al (49), using single crystals of the Ti-Ni alloy, for the first time, simultaneously measured most of the crystallographic parameters and compared them with the theoretical predictions obtained by adopting the two twinning modes as LIS, as suggested by Knowles & Smith (50), $(11\bar{1})$ Type I and $[011]$ Type II twinning. As a result, overall consistency between theory and experiment was found for the $\langle 011 \rangle$ Type II twinning. Step structures in an atomic scale, which are consistent with the Type II twinning, have recently been observed along twin boundaries in the Ti-Ni monoclinic martensite (51) by lattice-imaging technique of TEM.

CRYSTALLOGRAPHY OF SELF-ACCOMMODATION OF MARTENSITE FORMATION   In general, in a single crystal of the parent phase, 24 martensite variants with different but crystallographically equivalent habit planes can be formed at temperatures below M_f. These martensite variants are termed "habit plane variants" (6). Although the formation of each martensite variant is accompanied by a definite shape strain, the macroscopic shape of the material does not change as a whole before or after the transformation. This is due to the so-called self-accommodation of martensite formation, which can be understood from phenomenological consider-

ations, as demonstrated by Saburi & Nenno (6) for the β phase SMAs. According to their analysis, the 24 possible habit plane variants consist of six groups, and four habit plane normals in each group are symmetrically clustered around one of the six {110} poles of parent phase. The four habit plane variants are actually formed side by side in a characteristic diamond-shaped morphology upon cooling. Such grouping is a result of self-accommodation because the average shape strain in each group is essentially zero.

For a given transformation, several different but crystallographically equivalent lattice correspondences are present between the parent and martensite lattices. A martensite with a specific lattice correspondence is termed a "correspondence variant" (6). A habit plane variant thus consists of one correspondence variant when internally faulted and two when internally twinned.

The morphology of self-accommodating martensite groups differs according to the type of martensitic transformations. In fact, a square-shaped morphology was recently observed for the R phase transformation in a Ti-Ni SMA single crystal (52). On the other hand, a triangle-shaped morphology was recently observed in Ti-Ni(-Cu) alloys (53, 54) upon martensitic transformations.

III. MECHANICAL PROPERTIES

Shape Memory Effect

Suppose that a single-crystal material that exhibits a thermoelastic martensitic transformation is cooled to a temperature below its M_f. In the material, 24 habit plane variants are formed, consisting of six self-accommodating plate groups (see above). When such a material is stressed by external force, the conversions between the correspondence variants take place, first within each martensite plate (if the martensite is internally twinned), next within each plate group, and finally between plate groups. It was clearly demonstrated by Saburi & Nenno (6) that the intervariant conversions are nothing but twinning by many twinning systems in martensite. The material can thus be deformed until a single correspondence variant, i.e. a single crystal of martensite, is attained, which gives rise to the maximum elongation or compression strain in the material. The strain remains upon unloading because the martensite is stable below M_f. Upon heating to a temperature above A_f, however, the surviving variant transforms to the parent phase with the original orientation, following the unique lattice correspondence between them and resulting in recovery of shape. This is SME. It is thus seen that the maximum recoverable strain by SME is determined by the Bain strain for the surviving correspondence

variant (6), and that the driving force for shape recovery is the difference in chemical free energy between parent and martensite phases. Only the parent phase with the original orientation nucleates upon the reverse transformation because the transformation is crystallographically reversible, and because of this, the SME is complete.

The crystallographic reversibility is assured if an alloy is ordered (55). Unless the reverse transformation occurs in such a way that the original orientation of parent phase is restored, it inevitably leads to the destruction of the original atomic order in the parent phase and results in a structure with higher energy. Because of this, thermoelastic reversible martensitic transformations occur mostly in ordered alloys. In fact, such a strong correlation between the occurrence of thermoelastic transformation and atomic order is experimentally demonstrated in Fe-Pt SMAs (56). However, the disordered In-Tl, Mn-Cu, and Fe-Pd alloys exhibit thermoelastic transformations also. It is thus obvious that atomic order is not a necessary but a sufficient condition for the occurrence of thermoelastic transformations. The crystallographic reversibility in disordered alloys is explained by the simple lattice correspondence and the extremely small Bain strains (55).

In Fe-Ni-Co-Ti SMAs recently developed (33), the austenite is disordered. But, by ausaging, coherent and fine γ' precipitates with $L1_2$ order are evenly dispersed in the austenite matrix and undergo the martensitic transformation and its reversion with the austenite matrix. Hence, the presence of such ordered precipitates is responsible for the crystallographic reversibility.

The SME associated with the $B2 \rightleftarrows R$ transformations in Ti-Ni SMAs. has been shown to be unique (52) among other SMAs: Deformation in the Ti-Ni alloys proceeds with intervariant conversions of the R phase under stress, as in other SMAs, but shape recovery upon heating, after a single crystal of the R phase is achieved, proceeds with no parent/martensite interface movement. Shape recovery gradually takes place with increasing temperature until the reverse transformation temperature is reached. Such a shape change is due to the temperature-dependent rhombohedral distortion of the R phase (45).

The SME recently found in Fe-Mn-Si alloys is also unique in the following points (8): The alloys are disordered, and the associated fcc $\rightleftarrows$ hexagonal close-packed (hcp) transformations are not thermoelastic. Complete shape recovery occurs upon heating only when deformation is achieved by the stress-induced fcc $\rightarrow$ hcp transformation. Thus, the origin of SME in the alloys is explained by the preferential multiplication of a single type of Shockley partial dislocation occurring during the fcc $\rightarrow$ hcp transformation.

Transformation Pseudoelasticity

Martensitic transformations can be induced by stress even above M_s (7). In a material exhibiting a thermoelastic martensitic transformation, the SIM becomes unstable at temperatures above A_f under no stress and upon unloading immediately reverts to parent phase. Accompanying the SIM transformation and its reversion, the material exhibits a nonlinear elasticity that is characterized by closed stress-strain (S-S) curves. The nonlinear elasticity is termed Transformation Pseudoelasticity[5] (Transformation PE) because it is evidently associated with the transformations (19). The driving force of strain recovery is the difference in chemical free energy between parent and martensite phases as a function of stress; complete shape recovery is again due to the crystallographic reversibility of the transformation, as in SME. Transformation PE is, therefore, essentially the same as SME, except that the reverse transformation is caused by heating material to a temperature above A_f. In fact, almost all the alloys undergoing thermoelastic martensitic transformations exhibit Transformation PE as well as SME (19).

However, for the occurrence of Transformation PE, the critical stress for slip must be higher than for SIM transformations. For example, near equiatomic Ti-Ni alloys are easily subjected to slip when they are as-solution-treated and do not exhibit Transformation PE, irrespective of Ni content. However, it has been clearly demonstrated that annealing after cold-working, aging for Ni-rich Ti-Ni alloys, and refining of grain size cause prominent increases in critical stress for slip, resulting in Transformation PE (57–59). The occurrence of Transformation PE is also affected by crystal orientation, alloy composition, and sense of applied stress [see Otsuka & Shimizu (7) for more detail].

In a SIM transformation, a particular habit plane variant with the largest Schmid factor for the shear component of shape strain is first induced among the possible habit plane variants (7). By increasing applied stress, monocrystallization in martensite is eventually accomplished through intervariant conversions. Further stress induces another transformation from the existing martensite to another, as typically demonstrated in Cu-Al-Ni SMAs by Otsuka et al (29). The first transformation from parent to martensite and the subsequent one from the martensite to another martensite constitute two-stage Transformation PE. The martensite-to-martensite Transformation PE can also occur upon a SIM transformation from a thermally induced martensite to another and its reversion. Transformation PE associated with a martensite-to-martensite

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[5] The term "superelasticity" is used in some references (19).

transformation has been found in many SMAs (7) such as Cu-Al-Ni, Cu-Zn, Cu-Zn-Al, Au-Cd, Au-Ag-Cd, and Ti-Ni SMAs. In the Ti-Ni alloys, not only the martensitic transformation but also the R phase transformation is stress-induced, and evidence for the two-stage Transformation PE associated with the two kinds of transformations is provided by Miyazaki & Otsuka (60) in the thermomechanically treated alloys.

Two-Way Shape Memory Effect

As seen in the foregoing discussion, the shape remembered by SME is that of the parent phase, and in this sense the SME is often called one-way SME. Meanwhile, when a material in the fully martensitic state is deformed beyond a recoverable strain by SME, some permanent strain remains even after heating to a temperature above A_f. However, upon subsequent cooling, the shape in the martensitic state is only partially regained. This spontaneous shape change disappears upon heating. Afterward, the material takes the shapes of both the phases upon repeated cooling and heating. Thus, such a SME is called two-way SME (TWSME) or reversible SME (13, 61). The origin of TWSME is considered as follows: Excessive deformation in the martensitic state introduces dislocations that stabilize martensite plate configurations. Upon heating, the martensites disappear, but the dislocations remain. Upon subsequent cooling, the same configurations of martensite plates are formed so that the stress fields formed by the dislocations are accommodated. The preferential formation of specific martensite variants brings about a macroscopic shape change of the material, and thus TWSME appears repeatedly as long as the dislocation configurations persist.

Various methods causing TWSME, other than the one described above, have been proposed: excess deformation in the SIM transformation mode at temperatures above M_s (13), SME training (62), SIM training (62), combined training of SME and SIM (63), constraining in the martensitic state followed by heating to a temperature above A_f in the constrained condition (64), and use of some precipitates (65).

All Round Shape Memory Effect

Nishida & Honma (66) found that a Ni-rich Ti-Ni alloy exhibits a peculiar phenomenon termed "all round shape memory effect" (ARSME) when appropriately aged under constraint. When a curved strip of the alloy is cooled after heat treatment, it straightens spontaneously; with further cooling it curves to the opposite side, but the original curved shape is recovered by subsequent heating. It is suggested (66) that ARSME is caused by interactions between internal stress fields built up by the formation of some precipitates during aging and the two successive trans-

formations, i.e. the R phase and the martensitic. In this sense, ARSME is essentially the same as ordinary SME.

The precipitates concerned have recently been explored by TEM, electron diffraction, and energy dispersive x-ray microanalysis (67–69). As a result, the precipitates with a lenticular morphology have been shown to possess a rhombohedral structure with a composition of Ti_3Ni_4 and that the formation builds up tensile stress fields along $\langle 111 \rangle$ directions of the parent phase. It is supposed (68, 70) that the tensile stress fields around the precipitates induce the preferential formation of particular variants of the R phase and the martensite, which results in a macroscopic shape change.

Reverse Shape Memory Effect

When a SMA is deformed somewhat heavily at a temperature below or slightly above M_s and then heated to a temperature above A_f, the shape recovery due to SME is incomplete. But, with further heating, the shape moves toward the direction of applied stress. This kind of shape change is time dependent, while that due to SME occurs instantly. Such a phenomenon was first found by Pops (71) in a Cu-Zn-Si SMA and termed "reverse shape memory effect" (RSME). It was demonstrated that the reverse shape change is associated with the bainitic transformation occurring in the alloy.

Twinning Pseudoelasticity

It is widely known that in some SMAs strain recovery takes place upon unloading immediately after deformation in the martensitic state. It is to be noted that no martensitic transformations are associated with the attained strains (14, 19). This phenomenon has been observed so far not only in Au-Cd, In-Tl, and Cu-Al-Ni martensitic alloys but also in Au-Cu-Zn, Cu-Zn-Al, and Cu-Zn ones. In the former alloys, the martensites are known to be internally twinned, while in the latter they are to be internally faulted. The strain recovery is attributed to reversible movement of twin boundaries in the former alloys and of intervariant interfaces in the latter ones. However, the intervariant conversions are equivalent to twinning in martensites (16) (see above). A suitable terminology, "Twinning Pseudoelasticity" (Twinning PE) (19), which was formerly termed "rubber-like behavior" or "ferroelasticity" (19), is given to this phenomenon. Aging is essential for such a phenomenon to occur in some of the alloys; in others it is not needed at all, depending on temperature and crystal orientation [see Otsuka & Shimizu (19) for more detail].

The mechanism of Twinning PE is not clear yet; those formerly proposed have been critically reviewed (14). However, it is interesting to note that, as clearly demonstrated in a Cu-Al-Ni alloy (72), the twin boundaries

displaced under stress do not return exactly to the stabilized positions after aging. Thus the relaxation process during aging does not occur at the boundaries, but through the entire volume of material. In this sense, the pseudotwinning mechanism proposed by Zangwill & Bruinsma (73) is not likely either. A mechanism termed "lattice relaxation" more recently proposed by Sakamoto & Shimizu (74) is compatible with the volume relaxation, but clearly definite experimental evidence is needed.

Pseudoelasticity appearing only upon bending, which is observed in a Cu-Al-Ni alloy single crystal consisting of single variant of γ' twinned martensite, is due to elastic interaction of twinning dislocations (19). The pseudoelastic behavior found in the same alloy after cyclic deformation and in a heavily cold-worked Ti-Ni alloy that shows an unusual elastic strain (up to 4.2%) is considered to be due to the same mechanism as above (19).

IV. THERMAL AND MECHANICAL STABILITY OF SME CHARACTERISTICS

Aging

In some SMAs, SME characteristics deteriorate with time even at ambient temperature. Such pronounced aging phenomena occur in Cu-based SMAs in particular and in both parent and martensite phases of them, depending on alloy composition and temperature (22).

The ordering reactions in Cu-based SMAs occur upon quenching, but may not always be completed. In addition, excess quenched-in vacancies are introduced in parent and/or martensite phases. Upon aging at temperatures below roughly 473 K, the ordering reactions proceed further, assisted by quenched-in vacancy migration, and result in some changes of transformation temperatures. In fact, the increase of $B2$ order in Cu-Zn alloys causes a decrease of M_s (75), while the increase of DO_3 order in Cu-Zn-Al (75) and Cu-Al-Ni (76) alloys causes increases of M_s. Meanwhile, it is reported (77) that DO_3 order depresses M_s in Cu-Sn alloys.

Aging at higher temperatures eventually causes the precipitation of γ phase in many Cu-based SMAs (76, 78). The existence of fine precipitates depresses the martensitic transformation initially, but the depletion of solute atoms accompanying the growth of the precipitates brings about an increase of M_s, and concurrently the shape recovery ability decreases (76, 78).

Aging effects occurring in a martensite are termed "stabilization of martensite" because the reverse transformations are inhibited or prohibited by the aging. Primarily two mechanisms have been proposed for

the stabilization of martensite:[6] (a) pinning of parent/martensite and martensite/martensite interfaces by quenched-in vacancies (80, 81) and (b) reordering in martensite (80, 82), where atomic rearrangement in martensite results in some change of relative stability between parent and martensite. The former mechanism seems to be inconsistent with the fact that stabilization occurs even in a single crystal of martensite (83). Recently, however, it has been observed by TEM (84) that preferential nucleation of γ phase precipitates occurs at intervariant interfaces in a Cu-Zn-Al alloy. On the other hand, an x-ray diffraction study (85) has proved that some atomic rearrangement occurs in martensite during stabilization so that the monoclinic angle (β) of the β'_2 or β'_1 martensite (86, 87) approaches 90°. Thus, both mechanisms are likely to occur.

As mentioned in Section III, Twinning PE is brought about by martensite aging in some SMAs. Meanwhile, strain-aging in the martensitic state causes the change from Twinning PE to SME (14), i.e. restabilization. Effects of stabilization disappear after the martensite transforms back to its parent phase (88), and aging effects in parent and martensite phases can be diminished by air-cooling, step-quenching, or preaging (77). This occurs because the diffusion coefficient in a bcc parent phase is larger than in a martensite phase by the order of 10^4.

Thermal Cycling

Thermoelastic martensitic transformations were once considered to be ideally reversible. But it is now widely known that thermal cycling, by which the forward and reverse transformations are repeated, eventually causes the accumulation of many dislocations in the parent phase. Accompanying such a change in substructure of parent phase, shifts of transformation temperatures have been observed in many SMAs (see below).

A recent study (89) on a Cu-Al-Ni SMA single crystal showed that the M_s temperature is considerably depressed by thermal cycling when the number of cycles is increased up to 10^4 times, and that the depression is closely related to the next nearest neighbor disordering in a parent phase with DO_3 order. In Cu-Zn-Al SMAs, on the other hand, it is clearly demonstrated (90) that thermal cycling effects differ according to whether the parent phase is of $B2$ order or DO_3 order, i.e. M_s of the alloys with $B2$ order is increased by a great number of thermal cycles, while M_s of the alloys with DO_3 order is decreased. These changes in M_s can be explained in terms of disordering in the parent phase.

The Burgers vector of dislocations accumulating in the parent phase

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[6] The influence of other factors is discussed in detail in (79).

after thermal cycling was examined by the image matching technique in TEM (91, 92) for Cu-Zn and Cu-Zn-Al alloys and was determined to be $\langle 100 \rangle$ in the $B2$ lattice (equivalently $\frac{1}{2}\langle 100 \rangle$ in DO_3 lattice). On the other hand, the feature of disordering revealed by x-ray diffraction suggested that the Burgers vectors are $\frac{1}{2}\langle 100 \rangle$ and/ or $\frac{1}{2}\langle 111 \rangle$ in a Cu-Al-Ni alloy (89), and $\frac{1}{2}\langle 111 \rangle$ and $\frac{1}{4}\langle 111 \rangle$ in the Cu-Zn-Al alloys with $B2$ order and DO_3 order, respectively (90). The formation of the $\langle 100 \rangle$ type dislocations in Cu-Zn alloys is explained by stress relaxation associated with the volume change upon the transformation (92). Meanwhile, in the Cu-Zn-Al alloys, the $\frac{1}{2}\langle 100 \rangle$ or $\langle 100 \rangle$ type dislocations were considered to be produced by the reaction between the partial dislocations corresponding to stacking faults in martensite (93).

Thermal cycling effects in Ti-Ni SMAs depend on the thermomechanical treatment (94). That is, the aged alloys and the alloys annealed after cold-working are much less affected by thermal cycling than those that have been solution-treated. But, extended thermal cycling (up to 10^4 cycles) brings about significant shifts not only in M_s but also in the R phase transformation temperature (T_R), even in an aged Ni-rich Ti-Ni alloy; It is interesting to note that M_s decreased, while T_R increased (95). This change in transformation temperatures may be accounted for by the relaxation of the tensile stress fields built up around the Ti_3Ni_4 precipitates by thermal cycling. Thermal cycling causing only the $B2 \rightleftarrows R$ transformations results in almost no change in the transformation temperatures and shape recovery force (96).

Cyclic Deformation and Fatigue

Sakamoto et al (97) demonstrated that when a Cu-Al-Ni SMA single crystal is cyclically deformed in the SIM transformation mode above A_f, the shape of the PE loop in an S-S curve is stable and almost unchanged up to about 10^3 cycles. This is because the alloy with DO_3 order in the parent phase has a high critical stress for slip, σ_c, and thus dislocations are difficult to introduce during the deformation cycling.

In general, however, the shape of S-S curves changes with deformation cycles because of the introduction of slip (98). In polycrystals, in particular, slip relaxes some stress concentration at grain boundaries because of elastic or plastic strain compatibility among neighboring grains. Even at temperatures above A_f, SIMs are stabilized by the stress field of the dislocations, which results in residual strains upon unloading. On subsequent loading, the SIM formation may be assisted by the stress field, and thus the critical stress for SIM formation decreases.

As mentioned in Section III, Ti-Ni SMAs that have been solution-treated are subject to slip, but the σ_c can be raised considerably by ther-

momechanical treatments so that the alloys exhibit stable Transformation PE for deformation cycling more than 10^2 cycles (99).

Fatigue life of Cu-based SMAs strongly depends on the deformation mode (100): It is long in the order of elastic deformation, reorientation of martensite variants, and SIM transformation, i.e. the deformation mode involving the movement of parent/martensite interfaces has the worst effect on the fatigue life. This is verified in both single- and polycrystalline states. It thus seems that the movement of the parent/martensite interface itself is accompanied by some irreversible processes, such as the production of dislocations.

In alloys with high σ_c, such as Cu-Al-Ni SMAs, fatigue life in the polycrystalline state is shorter than in the single-crystalline state, irrespective of the deformation mode. In particular, the fatigue life of a Cu-Al-Ni alloy polycrystal is about two to four orders shorter than that of the single crystal in elastic deformation and SIM transformation modes, respectively. This is because slip rarely occurs in the alloy, and thus intergranular cracking (IGC) easily takes place in the polycrystalline state. Two causes for stress concentration leading to IGC have been proposed: high elastic anisotropy in parent phase (101) and large transformation strain accompanied by SIM formation (100).[7] Meanwhile, the difference between single- and polycrystalline states is little for the martensite reorientation mode (100) because many twinning systems are operable in the martensitic state, and the strain incompatibilities among neighboring grains can be accommodated by them.

In a Cu-Zn-Sn SMA, however, it is observed (98) that the fatigue life in the polycrystalline state is significantly longer than that in the single-crystalline state, even for the SIM transformation mode. This is because of the ease of slip in the alloy.

In general, however, fatigue properties in the SIM transformation mode of Cu-based SMAs are poor even in the single-crystalline state since the fatigue life is the order of 10^3 cycles at most (100, 103). According to Sade et al (104), in a Cu-Zn-Al alloy single crystal subjected to cyclic deformation in the SIM transformation mode, some arrays of dislocation tangles are observed along the intersection between the basal plane and habit plane of β'_1 martensite, which leads to nucleation of a crack.

Ti-Ni SMAs exhibit superior fatigue properties in such a way that the 10^7 cycle fatigue limit exists in the polycrystalline state even for the SIM transformation mode (105). It is also to be noted that in the Ti-Ni SMAs fatigue limit is higher for the SIM transformation mode than for the

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[7] Recently, segregation of oxygen atoms at grain boundaries has been suggested as the origin of IGC in the Cu-Al-Ni SMA (102) (see below).

martensite reorientation mode, according to Melton & Mercier (105). However, Miyazaki et al (106) showed that the fatigue life of a Ti-Ni alloy is only as long as 3×10^3 cycles for the SIM transformation mode, although they also showed that it can be extended one order by thermomechanical treatments. Thus, much more work is needed to clarify this point.

Improvement of SMAs

Various attempts have been made to improve thermal and mechanical stability of the SME characteristics of SMAs, especially for the most promising ones, such as Ti-Ni, Cu-Zn-Al, and Cu-Al-Ni alloys. The thermomechanical treatments adopted for near equiatomic Ti-Ni alloys are one of the typical examples (see above). Meanwhile, preaging or step-quenching is effective for retardation of aging effects in Cu-based SMAs. However, one of the most noteworthy improvements to be made for Cu-based SMAs may be in their fatigue and fracture characteristics because they are fatal defects of the alloys. As mentioned above, the ease of fracture and fatigue is due to the difficulty of relaxation of stress concentrations at grain boundaries. Hence, the main point of improvement is to refine the grain size of those alloys.

Grain refining by small additions of alloying elements is being attempted most extensively. Effects of various elements such as Ti, Zr, V, Pb, B, and so on have been examined in Cu-Al-Ni and Cu-Zn-Al SMAs (22). Among them, the influence of Ti addition to Cu-Al-Ni SMAs is to be noted in particular, since the grain size is reduced to 15 μm, while the usual size is roughly 1 mm (107). According to Sugimoto et al (108), the mechanism of grain refinement can be accounted for by the presence of finely dispersed Ti-rich "X-phase" particles that may act as obstacles to grain boundary migration. On the other hand, Sure & Brown (109) and Lee & Wayman (102) suggest that although Ti atoms are concentrated primarily in the X-phase, the grain growth retardation appears to be due to the small concentrations of Ti atoms in the solid solution. The mechanism is thus not clearly understood yet. According to Adachi et al (110), two kinds of precipitates are present in the Ti-added alloy, termed X_L and X_S phases. The X_L and X_S precipitates, typically several μm and several 10 nm in size, respectively, are both identified to possess $L2_1$ order, but with different proportions of the constituent atoms. By such a grain refining, the fracture strength, the strain to fracture, and the fatigue life are all improved to a great extent (107).

An Auger electron analysis by Lee & Wayman (102) indicated that oxygen atoms are present at grain boundaries in a Cu-Al-Ni ternary alloy, while they are not in the Ti-added alloy. It was then suggested that oxygen segregation at grain boundaries in the ternary alloy may be the major

cause of intergranular fracture, and that oxygen trapping of Ti atoms changes the fracture mode from intergranular to transgranular.

In addition to the above alloying element addition method, powder metallurgy (111), rapid solidification (112), and more recently sputtering (113) methods have been used for grain refinement.

V. APPLICATIONS

Because of SME itself and other unique mechanical properties, as mentioned above, SMAs are now being used or have the potential to be used for various purposes. The uses of SMAs in practice may be divided into two categories: irreversible and reversible uses. Irreversible use includes use of only shape recovery and use of shape recovery and the reverse transformation stress. The use of SMAs as a thermal actuator and for energy conversion from thermal energy to mechanical energy are examples of the reversible use. Typical examples of ways to use SMAs are described here only briefly. For more details of the applications, several excellent references (7, 16, 22) are available.

Use of only shape recovery is simple but quite useful in inaccessible places such as interiors of nuclear reactors and vacuum apparatus, deep sea, and space. A self-erectable antenna developed by NASA is one of the most interesting examples.

Pipe coupling is a typical use of shape recovering and the reverse transformation stress. Recently, a notable improvement has been achieved in Ti-Ni pipe couplings (114). The improved Ti-Ni alloy has a much wider temperature hysteresis (~ 150 K) than any previously reported (30–50 K) and the hysteresis loop is wide enough to position ambient temperature within it. Hence, the couplings can be shipped and stored at ambient temperature in the martensitic condition, i.e. in the deformed state, then installed by using any appropriate heating technique.

One example of reversible use of SMAs is actuators. In order to utilize SME repeatedly, an appropriate bias spring, by which the SMA can be deformed below M_s, is necessary. For use of SMAs as thermal actuators, the thermal hystereses are desired to be as small as possible; this can be realized by adjusting the strength of the bias springs or by utilizing a martensitic transformation with small hysteresis (1.5 K), such as the R phase transformation in Ti-Ni alloys. Actuators driven by electric current for robots and artificial hearts and kidneys represent other applications.

The principle for conversion of thermal energy to mechanical energy is as follows: Work that is necessary to deform a martensitic SMA is in general much smaller than that generated when the deformed martensitic SMA reverts to its original undeformed state by heating above A_f. Heat

engines with various mechanisms have been proposed. A turbine engine made by Tanaka et al (115) generates the largest electric power at present (665 W).

Transformation PE is also worth using because of its unique characteristics, such as the large amount of recoverable strain, constancy of stress during transformation, and large elastic strain. In fact, it is utilized in dental arch wires and frames for plastic eye glasses. Sugimoto & Otsuka (116) suggested using Transformation PE for energy storage.

VI. SUMMARY

The understanding of the crystallography of the martensitic transformations, including the premartensitic transitions, in SMAs has been greatly advanced by recent studies, in particular by those utilizing single crystals of SMAs. The mechanism of SME and other unique mechanical characteristics in SMAs have been clarified to a great extent from the crystallographic point of view. However, several fundamental and practical problems remain to be solved, including the origin of the premartensitic transitions and twinning PE, and drastic improvement of thermal and mechanical stability.

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