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A. W. Westerberg and G. Stephanopoulos, "Studies in Process Synthesis—I," *Chem. Eng. Sci.* 30, 963 (1975).

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SHALE OIL. See Oil shale.

SHAPE-MEMORY ALLOYS

The shape-memory effect is based on the continuous appearance and disappearance of martensite with falling and rising temperatures. This thermoelastic behavior is the result of transformation from a phase stable at elevated temperature to the martensite phase. A specimen in the martensite condition may be deformed in what appears to be a plastic manner but is actually deforming as a result of the growth and shrinkage of self-accommodating martensite plates. When the specimen is heated to the temperature of the parent phase, a complete recovery of the deformation takes place. Complete recovery in this process is limited by the fact that strain must not exceed a critical value which ranges from 3–4% for copper memory-effect alloys to 6–8% for the Ni–Ti system. A number of other characteristics associated with shape memory are referred to as pseudoelasticity or superelasticity, two-way shape-memory effect, martensite-to-martensite transformations, and rubberlike behavior.

Martensite is a metastable phase that forms when a phase stable at elevated temperature, such as austenite in steel, is cooled at a certain rate, thereby suppressing the formation of phases that are diffusion-controlled (see Steel). A characteristic of martensite is the relationship between the parent-phase crystal and the martensite. For steel, the austenitic phase is fcc. When it transforms to martensite, the orderly shift to a bct (body-centered tetragonal) structure takes place (see Fig. 1). The structure stable at elevated temperature varies with the alloy system, and the martensite varies from a simple bcc to a more complex structure which may have as many as 18 atom layers to define the unit cell.

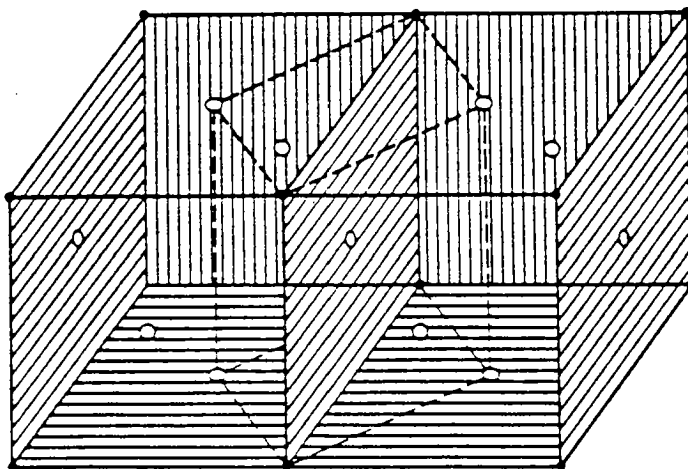


Figure 1. The original fcc structure (γ) changes to the bct with $(111)\gamma \parallel (110)\alpha$ and the $[110]\gamma \parallel [111]\alpha$.

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The temperature at which martensite starts to form on cooling is referred to as the M_s , and the temperature at which the elevated temperature phase has been completely transformed is the M_f . On heating a martensitic specimen, the temperature at which the reaction reverses to the elevated temperature phase is designated A_s ; the reaction is completed at a higher temperature designated A_f (see Fig. 2).

Thermoelastic behavior was first discussed in 1938 in a study of a Cu-Zn alloy which showed that martensite could be made to appear and disappear with a change in temperature (1). In a later study in the USSR, the phase relationships in brass between the high temperature β phase and martensite were examined (2). The length changes that occur on martensite transformations under load in the Fe-Ni system were determined (3). A later investigation of the shape-memory effect in Au-Cd alloys demonstrated that useful force could be generated in this type of transformation. These findings led to research on the practical applications for the shape-memory effect, and investigation of the martensite transformation kinetics in the Ni-Ti system (4). This system is commonly referred to as Nitinol (Nickel-Titanium Naval Ordnance Laboratory). The essential features of the martensite transformation are common to all alloy systems exhibiting the memory effect, whether they be 2H, 3R, 9R, or 18R structures (5-6). In some alloy systems, the various martensites are both internally faulted or internally twinned and may possess different crystal structures. However, in all cases studied to date, an initial parent phase transforms to self-accommodating martensite plates that are characterized by six plate groups, each consisting of four variants. Because of the self-accommodating character of the transformation, the average shape deformation in a particular plate group is effectively zero.

Table 1 lists the martensite alloy systems that have been investigated with respect to thermoelasticity, pseudoelasticity, shape-memory effect, and two-way shape-memory effect. The bcc (β) phase is the dominant parent because of the comparatively large thermodynamic difference between the martensite transformation from a bcc parent to 3R, 2H, 18R, or 9R, and from an fcc parent to bcc or bct. The former is typical for nonferrous alloys, whereas the latter accounts for the hardening of steel.

For an excellent general review of martensite kinetics, microstructure, and thermodynamics as they relate to shape memory, see ref. 7 and the First International Conference on Shape Memory (8).

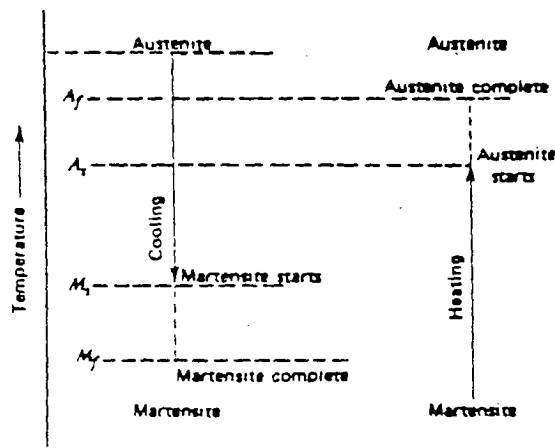


Table 1. Alloys Exhibiting Martensitic Effects

Thermoelastic	Pseudoelastic	Shape memory	Two-way shape memory
Ag-Cd	Ag-Cd	Ag-Cd	Cu-Al
Au-Cu-Zn	Au-Cd	Au-Cd	Cu-Zn-Al
Cu-Al-Ni	Au-Cu-Zn	Au-Cu-Zn	In-Tl
Cu-Zn	Cu-Al-Mn	Cu-Al	Ti-Ni
Cu-Zn*	Cu-Al-Ni	Cu-Al-Ni	
Fe-Pt	Cu-Au-Zn	Cu-Zn	
Ti-Ni	Cu-Zn	Cu-Zn-Al	
	Cu-Zn-Al	Cu-Zn-Ga	
	Cu-Zn-Sn	Cu-Zn-Si	
	Cu-Zn-X	Cu-Zn-Sn	
	Fe ₃ Be	Fe-Pt	
	Fe ₃ Pt	Fe-Ni	
	In-Tl	In-Cd	
	Ni-Ti	In-Tl	
	Ti-Ni	Ni-Al	
		Ni-Ti	
		304 stainless steel	
		Ti-Nb	
		Ti-Ni	

* With ternary additions of Ni, Ag, Au, Cd, In, Ga, Si, Ge, Sn, and Sb.

The behavior of shape-memory-effect (SME) alloys is exactly opposite to that of normal metals in the following essential feature: as the temperature rises above A_s and martensite is increasingly converted to the β phase, the modulus of elasticity increases. This change is spectacular for Cu-Al-Zn SME alloys where the Young's modulus changes by a factor of 50 from 0.4 GPa (58,000 psi) at the A_s to 20.7 GPa (3×10^6 psi) near the A_f . Obviously, a spring tension or torsion device develops a greater force with increasing temperature and this force can be either static or it can be used to produce a controlled motion. The force that can be developed by an SME device is as much as 200 times the force that could be developed by a bimetallic element of the same size or volume.

The Crystallographic Nature of Shape Memory

The martensitic memory or marmem effect occurs in alloys where both the parent and the martensite are ordered and exhibit crystallographically reversible, thermoelastic martensite transformations (7,9-10).

It has been demonstrated in one of the simplest systems, Cu-Zn, that a single orientation of the bcc β phase transforms on cooling below the M_f to self-accommodating variants of martensite. The habit planes for the transformation are symmetrically disposed around the (110) family of planes, of which there are six in the cubic system. Habit planes are the planes in the parent phase from which transformation takes place. Thus, for the plane (011) the four variants are (2 11 12), (2 12 11), ($\bar{2}$ 12 11), and ($\bar{2}$ 11 12); this set is termed a plate group. The six (110) planes offer a total of 24 martensite variants. When the martensite group is deformed, deformation proceeds by a gradual conversion of four variants to a single martensite plate rather than by grain-boundary sliding or slip. The surviving orientation depends on whether the strain

is tensile or compressive and whether the growth or shrinkage is such as to minimize strain-energy accumulation. Upon heating, the reverse transformation from martensite to the β phase occurs between A_1 and A_2 and the single crystal (plate) of martensite transforms to a single β crystal with the original orientation of the parent phase. In the case of Cu-Zn and other systems with relatively complex ordered martensite structures (9R or 18R), the reverse transformation is crystallographically restricted. Thus, although there are many variants that can develop on transformation from parent to martensite, only a single-parent orientation is possible in the reverse, or shape-recovery, transformation.

When a martensite group is deformed to coalesce into a single orientation, the dominant mechanism is twinning. Each twin is actually an alternative variant of the martensite crystal. Thus, for the four variants that cluster about the (110) habit, each orientation is a twin of another, and by this degenerate variant-twin relationship, a group of martensite plates formed from a single parent crystal can, on deformation, coalesce to a single crystal (single variant) of martensite.

The parent phase is usually ordered B_2 or DO_3 symmetry, although initially a transformation can take place from disordered to an ordered or superlattice structure. This ordered structure transforms to one of the four martensite crystal forms 2H, 3R, 9R, or 18R that exhibit shape memory. These designations refer to the sequence of stacking of planes to form the ordered structure. A sequence could be *abab*, *abcabc* or *abcbcacab* or similar variations. The repetition of these planes to define a unit cell is then 2, 3, and 9, respectively.

Typical alloys that transform to these various martensites are

2H, Cu-Al-Ni and Ag-Cd
3R, Ni-Al
9R, Cu-Zn
18R, Cu-Zn-Al.

A distinction exists in the habit and deformation characteristics of the 2H and 3R types and the 9R and 18R martensites. The former are internally twinned and deformation occurs by a detwinning of a variant plate. The latter are internally faulted and deformation proceeds by variant-to-variant coalescence followed by group-to-group coalescence. Although these structural differences exist, the self-accommodating habit-plane grouping with respect to an (011) plane is common to all systems exhibiting the marmem effect. The 9R martensite is derived from a B_2 parent, whereas the 18R transforms from a DO_3 superlattice. The difference in the stacking of (110) planes is because of the requirement for an invariant plane strain that involves a restricted stacking of close-packed planes. In order to obtain the required invariant plane-strain condition, both the 9R and 18R martensite contain stacking faults to provide the necessary accommodation. The sequence of β to β_2 to orthorhombic 9R for a Cu-Zn alloy is shown in Figure 1.

As noted previously, the atoms in each plane are displaced relative to those above and below and from a repetitive sequence of a nine-plane group. These complex atomic displacements take place by a combined process of shuffling and shear to arrive at the 9R structure. The 3R martensite twin plane is identical to the 9R and 18R fault plane. In the case of 2H martensites, no such twin-fault correspondence exists, and the twin is derived from a different parent (110) plane.

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