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ABSTRACT

Martensitic transformations generally result in a lattice invariant shear such as twinning. TiNi shape memory alloys typically exhibit submicron twinning upon transforming from high temperature cubic austenite to low temperature monoclinic martensite. Previous studies have discussed the presence of $(11\bar{1})$, (011) and (010) twinning in the martensite of the binary alloy. The substitution of between 15% and 30% Cu for Ni results in a ternary alloy having the same B2 austenite structure but an orthorhombic martensite structure. Although many orthorhombic grains exhibit (011) twinning, some grains exhibit no twinning. The crystallographic nature of this twinless martensite based on transmission electron microscopy (TEM) observations and x-ray diffraction (XRD) will be discussed. *In situ* TEM heating and cooling experiments are conducted in an attempt to establish the orientation relationships between the austenite and martensite phases. A simple mathematical transformation may explain how the twinless orthorhombic structure is derived from the parent cubic phase. In addition, the shape memory aspects of these ternary alloy are discussed.

1. INTRODUCTION

Binary TiNi has been extensively studied, both with regards to its shape memory properties and the crystallography of its martensitic transformation [1-4]. Upon cooling, the cubic, B2 austenitic structure transforms to monoclinic, B19' martensite [4,5]. The martensite typically exhibits fine submicron twinning, with the monoclinic $(11\bar{1})$, (011) and (010) twin planes being observed [6,7,8]. Knowles and Smith [8] have applied the martensitic transformation theories of Wechsler, Lieberman and Read [9, 10] to the binary TiNi system. Although the addition of third elements often strongly alter the martensitic transformation temperature M_S, the addition of Cu has been shown to have little effect on M_S [11]. Generally only small ternary additions may be made without changing the crystallographic structures and diminishing or cancelling the shape memory effect. However, up to 30% Cu may be substituted for Ni and still retain the shape memory properties. Whereas the austenite structure remains B2 as Cu is added [12], the martensitic structure changes for higher Cu

(>10%) ternary alloys. Both monoclinic [13] and orthorhombic [14] martensites have been observed for ternary alloys containing 15—25% Cu. Although the equilibrium martensite structure of the higher Cu alloys is determined to be orthorhombic, the structure also appears to depend on processing [15]. Ternary alloys containing ~10% Cu undergo two martensitic transformations upon cooling, with an orthorhombic martensite present over a 10 °— 20 °C range prior to transforming to monoclinic martensite [15, 16, 17]. The present analysis considers the various twinning systems observed in the Cu containing alloys and applies the mathematical transformation theories to the TiNiCu system.

2. EXPERIMENTAL PROCEDURE

Different ternary alloys of TiNiCu were prepared from high purity (99.99%) metals by vacuum plasma-melted and casting into one kilogram ingots. Due to the large discrepancy between the individual melting temperatures of the elements, care was taken to make sure that the ingots were of the proper weight after casting. Different composition alloys of $Ti_{50}Ni_{(50-x)}Cu_x$, for x= 5,10,15,20, and 25, were cast. As has been discussed in reference [15], the as-cast material is not guaranteed to be of an equilibrium structure, thus solution anneals were obtained at greater than $0.85T_m$. Due to the easy oxidation of each of these elements (and alloys consisting of these elements), all annealing was performed in high vacuum annealing furnaces. Since the annealing temperature was above the melting temperature of pure Cu, some Cu may have been lost from the surfaces of the annealed material. Thus material that was observed microscopically, was also analyzed to determine that the compositions were as desired. Although the Cu concentration may vary, the Ti to Ni+Cu ratio must be 1 to 1, in order to prevent the formation of a second phase [12].

The alloys were analyzed using X-Ray Diffraction, X-Ray Fluorescence, and Energy Dispersive X-Ray Spectroscopy. In addition, the microstructures of the different alloys were observed using optical microscopy to establish that primarily only one phase was present, and transmission electron microscopy (with Philips EM400 and EM430 microscopes) to determine the structure of the phases present. TEM samples were prepared by electropolishing foils in an electrolyte of 75 vol.% methanol—25 vol.% nitric acid at -15 °C and 12 volts [18].
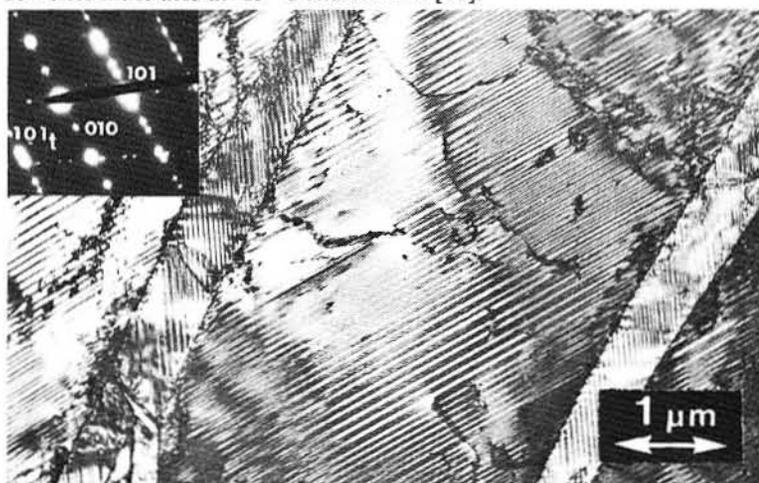

Figure 1. (010) twinning in $Ti_{50}Ni_{40}Cu_{10}$ monoclinic martensite.

3. EXPERIMENTAL RESULTS

The $Ti_{50}Ni_{(50-x)}Cu_x$ alloys with less than 10% Cu exhibit a monoclinic martensite with approximately the same B19' structure as the binary TiNi alloy. All grains of martensite exhibit fine twinning with the predominant twin plane being $(11\bar{1})$. However, (010) twinning is more prominent in the 10% Cu alloy (figure 1) than has been observed in binary TiNi. After annealing two hours at 1050 °C, the 20% Cu alloy exhibits an orthorhombic martensite with lattice parameters of a=0.2889 nm, b=0.4514 nm, and c=0.4265 nm, as determined by x-ray diffraction. The x-ray diffraction spectrum (figure 2) also displays peaks that are attributed to the added presence of monoclinic martensite. (The monoclinic martensite is believed caused by the presence of the top free surface, as will be discussed in more detail in the discussion of *in situ* TEM experiments.) The predominant twinning plane in the orthorhombic martensite of the high Cu-containing alloys is the (011) plane; and the twins (figure 3) are not as finely spaced as in monoclinic martensite. Additionally, some grains of orthorhombic martensite exhibit no twinning (figure 4).
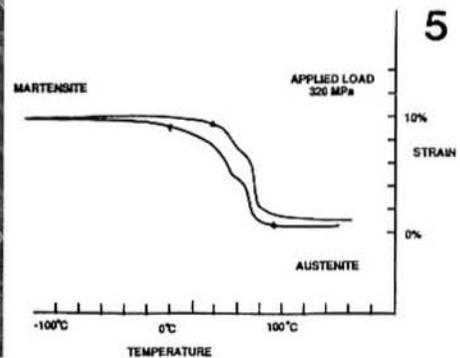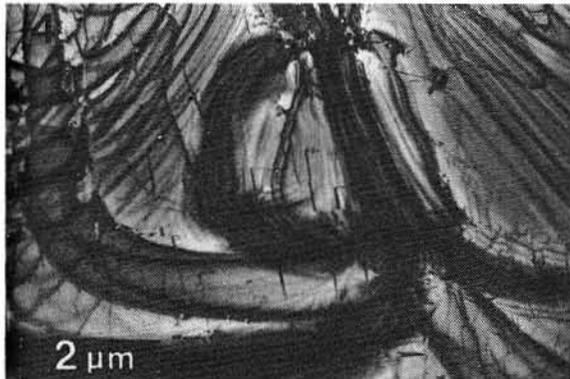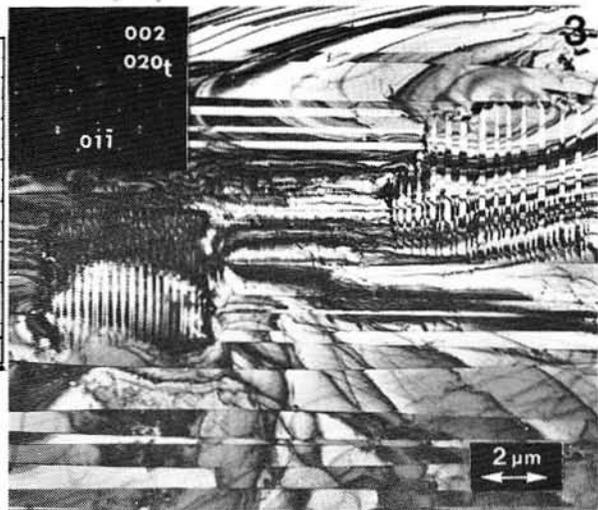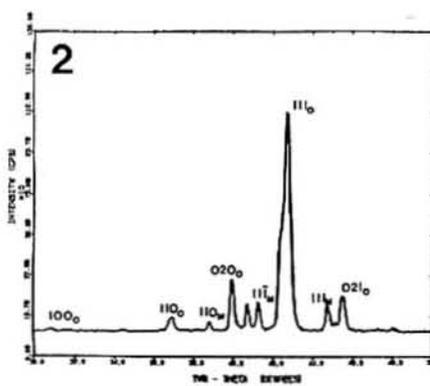

Figure 2. XRD scan of orthorhombic $Ti_{50}Ni_{30}Cu_{20}$.   Figure 3. (011) twinning in $Ti_{50}Ni_{30}Cu_{20}$ orthorhombic martensite.   Figure 4. Twinless orthorhombic martensite in $Ti_{50}Ni_{30}Cu_{20}$. Figure 5. Transformation hysteresis for strain vs. temperature in $Ti_{50}Ni_{40}Cu_{10}$.

The 10% Cu alloy exhibits a 2-step transformation during strain (elongation) vs. temperature or resistivity vs. temperature tests. Figure 5 displays a plot of elongation due to an applied stress of 320 MPa as a 0.45 mm diameter wire is cooled and heated through the transformation temperature. This 2-step transformation is still evident after subsequent thermal cycling. The intermediate step is indicative of the presence of an intermediate martensite phase having an orthorhombic structure. *In situ* TEM heating and cooling experiments were unable to observe the intermediate orthorhombic phase, as the B2 cubic austenite transformed directly to monoclinic martensite upon cooling.

Additional *in situ* TEM experiments were conducted to determine if the orthorhombic martensite of the high (>15%) Cu alloys would transform to a monoclinic martensite at low temperatures. The orthorhombic martensite remained stable upon cooling to liquid nitrogen (-186 °C) temperature. After heating *in situ* to cause transformation to cubic austenite, however, the TEM thin foils would transform to monoclinic martensite with subsequent cooling. The lack of orthorhombic martensite after thermal cycling indicates the monoclinic structure to be preferred in a thin foil. This dependence of structure on macroscopic sample geometry and processing history indicates how both monoclinic and orthorhombic structures could have been observed by previous authors [13, 14], and precludes using TEM alone to investigate the crystallographic orientation relationships between austenite and orthorhombic martensite.

4. DISCUSSIONS

A 2-dimensional projection can depict how the (001) orientations of both the orthorhombic and the monoclinic unit cell are derived from a (110) orientation of the cubic unit cell (figure 6). In the case of the monoclinic structure, a (010) twin plane may prevent large atom displacements during the transformation. Using the analysis of Knowles and Smith [8] for the monoclinic structure, the distortion matrices for the two twins are written with respect to cube directions $[1\bar{1}0]$, $[110]$ and $[001]$

$$T_{1'} = \begin{bmatrix} c/\sqrt{2}a_o & 0 & 0 \\ 0 & b(\sin\gamma)/\sqrt{2}a_o & 0 \\ 0 & b(\cos\gamma)/\sqrt{2}a_o & a/a_o \end{bmatrix}$$

$$T_{2'} = \begin{bmatrix} c/\sqrt{2}a_o & 0 & 0 \\ 0 & a/a_o & b(\cos\gamma)/\sqrt{2}a_o \\ 0 & 0 & b(\sin\gamma)/\sqrt{2}a_o \end{bmatrix}$$

where, using the first monoclinic setting of Michal [5], the lattice parameters are a=0.2889 nm, b=0.4622 nm, c=0.412 nm, the angle between a and b axes: γ=96.8°, and a_0=0.3016 nm for the B2 cubic unit cell. From equation (8) of Wechsler [9], the rotation matrix relating the two twins is

$$\Phi = \begin{bmatrix} 1 & 0 & 0 \\ 0 & \cos\phi & -\sin\phi \\ 0 & \sin\phi & \cos\phi \end{bmatrix}$$
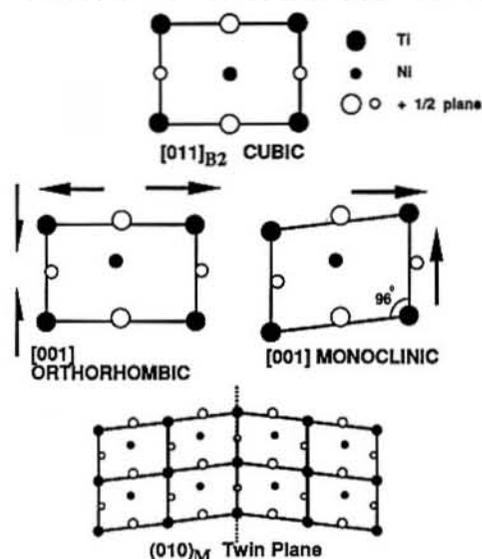
where ϕ=76.4°.

Figure 6. Two-dimensional projection of orthorhombic and monoclinic (001)orientations derived from cubic (110), with (010) twinning.
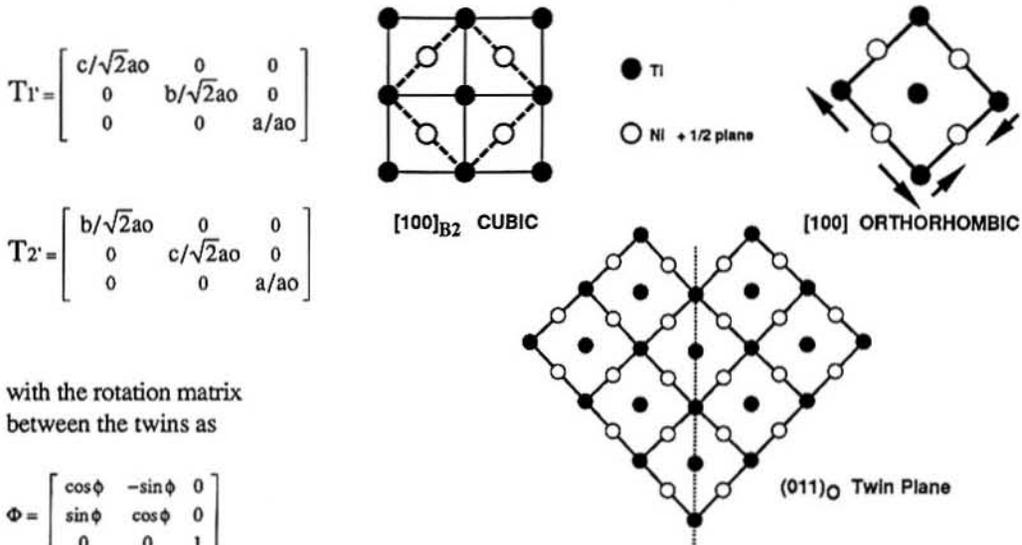
Following the mathematical description of Lieberman's analysis [10] from equation (13) through equation (41), the mathematical solutions for the twin fractions are 0.41 and 0.59, which agree with the relative twin fractions observed in figure 1.

In the orthorhombic structure, however, the (010) plane is a plane of symmetry and is not a twin plane. The transformation of the cubic structure to the orthorhombic structure can follow directly the theory applied by Lieberman for AuCd [10]. Using the lattice parameters listed above for the orthorhombic unit cell, the distortion matrix is written with respect to the orthorhombic axes as

$$T_{1'} = \begin{bmatrix} b/\sqrt{2}a_o & 0 & 0 \\ 0 & c/\sqrt{2}a_o & 0 \\ 0 & 0 & a/a_o \end{bmatrix}$$

The principal distortion $c/\sqrt{2}a_o = 0.99993$, is almost unity, and allows for a homogeneous distortion. This implies the distortion of the martensitic transformation may be accounted for without twinning [10], which is the case observed in figure 4. (The slight discrepancy between the distortion and unity may be accounted for by dislocation slip during transformation and/or occasional twinning that was not observed by electron microscopy.)

Using the same lattice parameters for the orthorhombic structure, it is possible to consider twinning on the (011) plane, which is not a plane of symmetry. Figure 7 is a 2-dimensional projection of the (100) orientation of the orthorhombic unit cell as derived from a (100) orientation of the cubic unit cell. It is quite readily discernible that little distortion is required, as compared to the monoclinic twinning. The distortion matrices for the two twins are written with respect to the orthorhombic axes

$$T_{1'} = \begin{bmatrix} c/\sqrt{2}a_o & 0 & 0 \\ 0 & b/\sqrt{2}a_o & 0 \\ 0 & 0 & a/a_o \end{bmatrix}$$

$$T_{2'} = \begin{bmatrix} b/\sqrt{2}a_o & 0 & 0 \\ 0 & c/\sqrt{2}a_o & 0 \\ 0 & 0 & a/a_o \end{bmatrix}$$

with the rotation matrix between the twins as

$$\Phi = \begin{bmatrix} \cos\phi & -\sin\phi & 0 \\ \sin\phi & \cos\phi & 0 \\ 0 & 0 & 1 \end{bmatrix}$$

where $\phi = 3.25°$.

Figure 7. Two-dimensional projection of (100) orthorhombic orientation, with (011) twinning.

Again following the mathematical description of Lieberman's analysis from eqn. (13) through eqn. (41) [10], and accounting for the (011) twin plane, the mathematical solutions for the volume

fraction of the twins are 0.999 and 0.001. These values are approximately unity and zero, seeming to imply that a twinless transformation should occur. However, such mathematical solutions also imply that it does not matter which twin forms or which distortion occurs. This solution could account for random twinning, as is actually observed in figure 3. Since the distortions are minimal, the twins do not need to be fine. The twinned structure observed in figure 3 is more a result of nucleation variations rather than as a necessity to satisfy twin volume fractions of the transformation theory. Twins, once nucleated, tend to traverse the entire grain. As would be expected for random twinning, the overall volume fraction of each twin in an individual grain is ~ 0.5.

4. CONCLUSIONS

1) When large concentrations of Cu (up to 30%) are substituted for Ni in TiNi alloys, the shape memory properties are modified, most importantly by the narrowing of the temperature range of the transformation hysteresis.

2) Ternary TiNiCu alloys with greater than 10% Cu exhibit an orthorhombic martensite. Although many orthorhombic grains exhibit (011) twinning, some grains exhibit a twinless martensite.

3) The twinned (and twinless) orthorhombic martensite, as well as the twinned monoclinic martensite in the 10% Cu alloy, correspond with the mathematical solutions based on transformation theories of Lieberman, Wechsler, and Read [10].

4) The 10% Cu ternary alloy exhibits a two-step transformation upon cooling from B2 austenite to orthorhombic martensite to monoclinic martensite, which in turn provides this alloy with a two-step reversible shape change.

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