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## PHASE TRANSFORMATIONS IN TERNARY TINIX ALLOYS

Ву

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## A THESIS

Submitted to Michigan State University in partial fulfillment of the requirements for the degree of

MASTER OF SCIENCE

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#### ABSTRACT

## PHASE TRANSFORMATIONS IN TERNARY TINIX ALLOYS

By

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The charge density wave (CDW) and thermoelastic martensitic transformations, in ternary TiNiX alloys, were studied using electrical resistance as a function of temperature measurements. Electron microscopy and electron diffraction studies were performed at ambient temperatures. The TiNiX shape memory alloys studied, consist of component X being Al, Fe and Cu. Thermal cycling and aging effects were investigated. The martensitic phase is effected by complete thermal cycling, evident by the depression of the  $M_s$  temperature. It also exhibited a slower austenite recovery  $(A_S \text{ to } A_f)$  curve. Thus, multiple thermal cycles produces lattice defects and some degree of plastic deformation (dislocations) in the parent lattice. Aging effects were more prevalent in the premartensitic transition (CDW) but also effected the martensite phase of these alloys. These effects were attributed to precipitation and subsequent changes in the matrix composition in their vicinity. The longer aging times gave greater changes in the martensitic transformation.

#### I. INTRODUCTION

The unusual behavior and properties of the intermetallic compound TiNi, a well-known shape memory alloy, has been the subject of numerous investigations since the discovery of its shape memory properties by a group at the U.S. Naval Ordance Laboratory. Of the dozen or so known alloys that exhibit the shape memory effect TiNi possesses the best combination of physical and mechanical properties. The shape memory effect (SME) is defined as, when a material is deformed beyond an apparent yield point, yet recovers all or nearly all strain upon stress release and, on heating.

The binary TiNi alloy displays several solid state phase transformations, undergoing thermoelastic martensitic transformation slightly above room temperature. Immediately above the martensitic start ( $M_s$ ) temperature the TiNi exhibits a premartensitic instability, believed to be charged density wave (CDW) phenomena and associated phase transitions (1-10).

In this study minor additions of the transition elements Fe, Al, and Cu, to the binary TiNi alloy, produces a large temperature separation between the premartensitic transitions and the martensitic transformation. This occurs since the contribution of these minor additions is as

impurity atoms. These impurity atoms trap vacancies, decreasing the density of free vacancies thus lowering the martensite start temperature (11). The density of vacancies is greater at higher temperatures. Thus, quenching from high temperatures gives a high density of vacancies; with the vacancy density of the parent phase influencing the martensitic transformation.

The charge density wave and thermoelastic martensitic transformation, in ternary TiNiX alloys, were studied using electrical resistance as a function of temperature measurements. Electron microscopy and electron diffraction studies were performed at ambient temperatures. Thermal cycling and aging effects were investigated for five alloys.

Each alloy studied contained the CsCl(B2) ordered crystal structure for the high-temperature parent phase (1-10,12,13). Then, on cooling, the alloys Ti<sub>50</sub>Ni<sub>45</sub>Fe<sub>5</sub>, Ti<sub>50</sub>Ni<sub>47</sub>Fe<sub>3</sub> and Ti<sub>59.4</sub>Ni<sub>38.7</sub>Al<sub>1.9</sub> forms the "premartensitic" phase, where diffraction studies produce satellite spots at 1/3 positions of the basic B2 reciprocal lattice structure. Finally, when the strains presumably reaches a critical level (M<sub>S</sub> temperature) the continuous reversible premartensitic behavior gives way to a discontinuous change in crystal structure and martensite plates begin to form.

For the  $Ti_{40}Ni_{45}Cu_5$  alloy the parent phase transforms to a martensitic phase with similar morphology and lattice

parameters to those of the binary TiNi alloy (14). The predominant structure that is formed is a slight monoclinic distortion of the orthorombic B19 structure noted for many years in Au-rich AuCd (15). The distortion often comes from the oblique shear along the main shear plane. For the TiNi-3.8% Cu alloy it is not known, definitely, if the parent phase proceeds to the premartensitic or martensitic transformation. TEM studies were done at room temperature, the parent phase for this alloy, thus they were inconclusive.

The premartensitic phenomena is associated with charge density wave transitions. "A charge density wave is a static modulation of the conduction electrons, which is a Fermi-surface-driven phenomenon usually accompanied by a periodic lattice distortion" (4). Formation of a CDW requires a favorable Fermi surface geometry where the Fermi surface shape is connected by the same wave vector. CDW phemonena has been reported in one and two dimensional materials but is rare in three-dimensional materials because of the unlikeliness of favorable Fermi surface nesting. Although, it is possible for Fermi surface nesting to occur in the transition metals. This is attributed to the complicated geometry of the Fermi surface of the transition metals which is due to complex overlapping of d and f bands. Any change in the concentration of the valance electron due to the addition of another alloying element will result in

significant changes in Fermi energy. If an element is alloyed with another element having a higher valency, then the Fermi energy will increase. This is the case in adding the transition elements Fe and Al to the TiNi binary alloy. Thus, it would seem this contributes to the CDW transitions. However, if an element with a higher valency is alloyed with an element with a lower valency, then the Fermi energy will decrease. In the Ti<sub>50</sub>Ni<sub>45</sub>Cu<sub>5</sub> alloy, and most Cu additions, the premartensitic phase is inhibited, probably due to an unfavorable Fermi surface. The change in Fermi energy will distort the Brillouin Zone structure because of the change in the filled state in the Brillouin Zone of the binary alloy. Strong electron-phonon coupling is required to form a CDW, permitting ionic displacements to reduce the prohibitive CDW Coulomb energy. "Precursor phenomena such as a soft phonon mode (Chan and Heine 1973) might occur above the transition temperature to assist the CDW instability. These soft phonon modes are seen in the phonon dispersion spectrum as a 'giant' Kohn anomaly (Woll and Kohn 1962) near  $Q=2K_{f}$  (4).

A CDW can be studied by electron diffraction, where satelite reflection's appear near the Bragg reflections of the parent lattice as a result of a new superlattice formation. Two distinct phase transitions are associated with CDW formation. The first "premartensitic" transition is a second order "normal-to-incommensurate" transition. A

second "premartensitic" transition, occurring at a lower temperature than the first transition, is a first order "incommensurate-to-commensurate" transition (1-10). Thus, the sequence of transformations, upon cooling, for the alloys containing the "premartensitic" phase is as follows: "parent phase (B2) + incommensurate phase (distorted cubic) + commensurate phase (rhombohedral) + martensitic phase (monoclinic)" (2).

The thermoelastic transformation is defined as one in which a given plate or domain of martensite grows or shrinks as the temperature is lowered or raised, and the growth rate appears to be governed only by the rate of change in temperature. When the temperature of the specimen is lowered, plates of martensite form. As the temperature is decreased further the martensite plates continue to grow, until the structure is completely martensitic at the martensite finish temperature. The behavior for the reverse transformation shows that the martensite plates contract continuously with increasing temperature, until the structure is completely austenitic at the austenite finish temperature (16-21). It has been found that the martensite plate produced last on the initial transformation, is the first to undergo the reverse transformation (16). The growth and shrinkage of the martensite plates occur under a balance between thermal and elastic effects, making the transformation reversible. Other possibilities for their

occurrence are, small lattice deformation for the deformation, martensites containing internal twins that can be easily detwinned and martensites having an ordered structure that can't be destroyed by slip (11). An important thermoelastic characteristic is a small volume change upon transformation. The volume change for TiNi is 0.16 pct, according to the lattice paramters. This is compared to steel which has a volume change of 3 to 4 pct, which exhibits a large hysteresis (16). This, apparently is another important characteristic of thermoelastic martensite, a small temperature hysteresis ( $\Delta t = A_s - M_s$ ). In contrast, ordinary martensitic transformations in ferrous alloys accompanies usually a plastic deformation as well as an elastic strain, giving a large temperature hysteresis. For example  $\Delta t$  is about 400°C in Fe<sub>70</sub>Ni<sub>30</sub> alloy (19) compared to 4°C to 28°C for the alloys in this study.

Thermal cycling effects on TiNi alloys have been investigated by Sandrock et al (20), studying incomplete thermal cycling and by Wayman and Cornelis (21), studying complete thermal cycling. Incomplete cycling consists of cooling below  $M_s$ , but not as far as  $M_f$ , followed by heating to reverse some, but not all of the martensite. This acts as a form of "cold working" by producing dislocations. Complete cycling consists of cooling to form essentially all martensite followed by a complete reversion to the high temperature parent phase. This produces dislocations,

although, the effect is not as great as in incomplete thermal cycling. Thus, multiple thermal cycles produces lattice defects and some degree of plastic deformation (dislocation) in the parent phase. The presence of dislocations presumably acts as an impediment to further martensite formation and the result is a stabilization effect i.e. lowering of the M<sub>g</sub> temperature.

Aging effects on the binary TiNi alloys have been found to decompose eutectoidally, from the high temperature B2 structure, into fcc Ti<sub>2</sub>Ni and hexagonal TiNi<sub>3</sub> (23-28). This decomposition is preceded by the formation of an intermediate precipitate as in the investigation by Koskimaki et al (23). At the beginning of precipitation, there is a stage at which the atomic arrangement of fine precipitates is coherent with the matrix. This obstructs the shape change for the martensite transformation thus, initiation of transformation is more difficult and the  $M_s$ temperature decreases. M<sub>S</sub> has been reported to be very strongly dependent on the alloy composition; decreasing the Ti content leads to a rapid lowering of  $M_s$  (14). The titanium composition of the matrix is reduced with precipitation of the fcc Ti<sub>2</sub>Ni phase. This usually occurs in Ti-rich alloys, such as the ones in this study. A certain amount of different phases have been found in previous studies. This is generally assumed to be  $Ti_2Ni_1$ , TiNi3 or a complex oxide or nitride (20). The use of dark

field illumination is often valuable when carrying out observations on foils containing more than one phase. For example, if there are two different kinds of precipitates in a foil, and each gives rise to diffraction spots other than those from the matrix, then by using one of the precipitate diffraction spots to form the dark field image it is possible to show up the location of many of the corresponding precipitates in a given area (29). Unfortunately this technique was unavailable for this investigation.

Thermal cycling apparently effects the martensitic transformation, depressing the  $M_S$  temperature with an increasing number of cycles and suppressing the martensitic hysteresis loop. While aging apparently effects CDW transitions, giving a more enhanced premartensitic hysteresis; it can also, suppress the martensitic transformation.

#### **II. EXPERIMENTAL PROCEDURE**

Five alloys Ti59 4Ni38 7All 9, Ti50Ni47Fe3, Ti<sub>50</sub>Ni<sub>45</sub>Fe<sub>5</sub>, Ti<sub>50</sub>Ni<sub>45</sub>Cu<sub>5</sub> and TiNi-3.8%Cu were used in this study. They were sectioned into disc specimens, 3mm in diameter, for use in TEM studies. Electrical resistance samples were sectioned to be approximately 5cm in length and 1 mm in diameter. The samples were annealed at 900°C for 10 minutes in evacuated quartz tubes and then quenched into ice brine. The aged samples were annealed and quenched as above, heat treated at temperatures and 400°C and 600°C for times of 1 hr. and 4 hrs. in evacuated quartz tubes, then quenched in ice brine. Thin foils for TEM observations were made by jet polishing at room temperature using an electrolyte consisting of perchloric (8%) and glacial acetic acids (92%). Electron diffraction and transmission electron microscopy were performed on the Phillips 300 and Hitachi HU-11A. A continuous measurement of electrical resistance as a

function of temperature is achieved by using an omnigraphic 200 x-y recorder with a fast response time (22). The cooling medium is liquid nitrogen vapor in a deep, wide mouth Dewar vessel. The cooling, or heating, rate is easily adjusted by varying the rate of sample immersion or

withdrawal into or out of the liquid nitrogen vapor. This was done using a Hurst stepping motor, model LAS, with a linear travel of 0.0013 inches per step, and stepping motor controller. A variable resistor controls the stepping rate helping to obtain an optimum cooling rate. An Omega signal amplifier with common mode noise rejection is used to optimize the resistivity curve from the x-y recorder. Four copper leads were spot welded to the ends of the sample. The outer two leads connect to the d.c. power supply and the inner two, for potential measurements, connect to the x-y recorder. A copper-constantan thermocouple (.005 in. wire) was spot welded to the center of the sample. The wire leads were connected to a terminal strip; mounted perpendicular to an aluminum holding rod 3 feet long. This is connected to a 3 foot lead screw which moves through the stepping motor. The sample could be lowered into the cooling bath by engaging the motor, and raised by activation of microswitches which automatically cycle the sample.

A regulated d.c. power supply served as a current source. 140v were applied across the sample, with a 1000 ohm resistor, giving a current of 140 ma. This high resistance, which is high relative to that of a typical specimen, means the power supply can be considered to be producing a constant current.

## III. RESULTS AND DISCUSSION

The electrical resistance versus temperature for a full thermal cycle between room temperature and liquid nitrogen temperature for a Ti<sub>59.4</sub>Ni<sub>38.7</sub>Fe<sub>1.9</sub> alloy is given in Fig. The bright field image of the parent phase, with no 1. microstructure other than extinction contours, is shown in Fig. 2(a), its corresponding diffraction patterns in Figs. 2(b) and 2(c), identified as [111] B2 and [120] B2 zones, respectively. On cooling the B2 parent phase transforms to the first "premartensitic" phase at Tp, evident by the increase in electrical resistance. The second "premartensitic" transition begins at T<sub>d</sub> where the curve seems to show an inflection point (1,2). The martensitic transformation starts at  $M_s$ , with an abrupt decrease in resistance, until the martensite finish temperature  $M_f$  is reached. On heating, the martensitic transformation exhibits a large hysteresis with the reverse transformations of the martensite phase beginning at the austenite start temperature  $A_s$ , with completion at the austenite finish temperature  $A_f$ . A small hysteresis occurs around  $T_d$ , the second premartensitic transition, while no hysteresis occurs at  ${\tt T}_{p}{\tt .}$  The transformation temperatures and thermal cycling effects of TiNiAl, TiNiFe and TiNiCu alloys are given in









Fig 2. Transmission electron micrograph and corresponding diffraction patterns of the parent phase for a Ti59.4Ni38.7Al1.9 alloy. (a) Electron micrograph mag. 40,000x; (b) [111] B2 Zone diffraction pattern.



Fig 2. (Continued). (c) [120] B2 Zone diffraction pattern.

Table 1. In Fig. 3, a plot of electrical resistance versus temperature for the 50th full thermal cycle for Ti<sub>59.4</sub>Ni<sub>38.7</sub>Al<sub>1.9</sub> alloy is given. The effects of thermal cycling are more significant on the martensitic transformation. The hysteresis is depressed with  $M_S$ decreasing 17°C, also a slower austenite recovery from  $A_S$  to A<sub>f</sub> occurred, as compared to the uncycled sample. An example for Ti<sub>59.4</sub>Ni<sub>38.7</sub>Al<sub>1.9</sub> alloy cycled 50 times through the transformation range is shown in Fig. 4. No significant numbers of dislocations were evident in the uncycled state. The cycled sample, however, exhibited a relatively high density of dislocations.

Electrical resistance versus temperature curves for TiNiFe alloys are given in Fig. 5 and Fig. 6 for  $Ti_{50}Ni_{47}Fe_3$ and  $Ti_{50}Ni_{45}Fe_5$  respectively. In Fig. 5 the plot contains both the premartensitic transition and the martensitic transformation, similar to Fig. 1. In Fig. 6 while the premartensitic transition is evident the martensitic transformation is believed to occur below liquid nitrogen temperature. Thermal cycling of the  $Ti_{50}Ni_{45}Fe_5$  alloy doesn't effect the premartensitic transition. Fig. 7 shows the electrical resistance versus temperature curve for the 50th full thermal cycle for a  $Ti_{50}Ni_{47}Fe_3$  alloy. The hysteresis loop for the martensitic transition is suppressed without changing the martensite or austenite transformation temperatures, see Table 1.

Alloys	Ms	Mf	As	Α <sub>f</sub>	Тp	Tđ
<u>Tinial</u>						
59.4-38.7-1.9 lst cycle 50th cycle	-68 -85	-160 -170	-40 -42	-11 -18	26 25	18 18
TiNiFe						
50-47-3 lst cycle 50th cycle	-96 -97	-196 -196	-90 -90	-60 -61	-2 -2	-13 -13
50-45-5 lst cycle 50th cycle	<-196 <-196	<-196 <-196	<-196 <-196	<-196 <-196	-52 -52	-70 -70
TiNiCu						
50-45-5 lst cycle 200th cycle	61 45	48 30	65 50	79 61	- -	- -
50-46.2-3.8 lst cycle 200th cycle	5 5	-21 -21	3 5	13 14	-	-

TABLE I. Thermally Cycled: Compositional (at.%) Dependence of Transformation Temperatures (°C) in TiNicu, TiNiFe and TiNiAl Alloys



Fig. 3. Electrical resistance vs. temperature for a full thermal cycle between room temperature and liquid nitrogen temperature, 50th full thermal cycle,  $TI_{59.4}NI_{38.7}AI_{1.9}$  alloy.



Fig. 4. Transmission electron micrograph of a Ti59.4Ni38.7Al1.9 alloy thermally cycled, 50 times, through the transformation range; mag. 80,000x.



Electrical Resistance (Arbitrary Units)

Fig. 5 Electrical Resistance vs. temperature for full thermal cycle between room temperature and liquid nitrogen temperature,  $Ti_{50}$  Ni<sub>47</sub> Fe<sub>3</sub> alloy.



## Electrical Resistance (Arbitrary Units)





The electrical resistance versus temperature curve for Ti<sub>50</sub>Ni<sub>50</sub>Cu<sub>5</sub> is given in Fig. 8. On cooling, the B2 parent phase transforms to the martensitic phase (12-14,30). The electrical resistance increased abruptly at the M<sub>S</sub> temperature on cooling and it decreased at the As temperature on heating. These results were reversed as compared to other ternary TiNiX alloys. In Fig. 9 the bright field image for the Ti50Ni45Cu5 alloy is shown exhibiting the martensitic structure. Fig. 10 shows the electrical resistance versus temperature curve for the 200th complete thermal cycle for the Ti50Ni45Cu5 alloy. The Ms temperature decreased 16°C. Comparing this alloy to the Ti<sub>59.4</sub>Ni<sub>38.7</sub>Al<sub>1.9</sub> alloy, 200 complete thermal cycles instead of only 50 complete thermal cycles, a four-fold difference, were needed to obtain a similar shift in M<sub>S</sub>.

In Fig. 11 the electrical resistance versus temperature curve for a TiNi-3.8%Cu alloy is given. On cooling from the B2 parent phase the electrical resistance increased abruptly similarly to the Ti<sub>50</sub>Ni<sub>45</sub>Cu<sub>5</sub> alloy, and also, exhibited a decrease in resistance on heating. Thus, we might conclude that the transformation is similar to that of the Ti<sub>50</sub>Ni<sub>45</sub>Cu<sub>5</sub> alloy.

The possibility of, one-third reflections or premartensitic instability reported by T. Tadaki and C. M. Wayman (12), and this study being conducted at room temperature prevents a conclusive answer. Thermal cycling of the





Fig. 9. Transmission electron micrograph for a Ti<sub>50</sub>Ni<sub>45</sub>Cu<sub>5</sub> alloy taken at room temperature; mag. 60,000x.



Electrical Resistance (Arbitrary Units)



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TiNi-3.8%Cu alloy didn't appear to effect the transformation temperatures. This prompted questions since, thermal cycling usually effects the martensitic transformation, but not the "premartensitic" transition.

The aging effects on TiNiAl, TiNiFe and TiNiCu alloys are given in Table 2. The aging effects of electrical resistance versus temperature for a full thermal cycle between room temperature and liquid nitrogen temperature for a Ti<sub>59.4</sub>Ni<sub>38.7</sub>Al<sub>1.9</sub> alloy are given in Fig. 12, Fig. 13 and Fig. 14 for aging @ 400°C for 1 hour, @ 400°C for 4 hours and @ 600°C for 1 hour respectively. These curves compared to Fig. 1, the unaged specimen, reveal an enhanced hysteresis loop around  $T_d$  in the premartensitic transition. Also from these curves and data given in Table 2 it is apparent that M<sub>S</sub> is slightly depressed by aging @ 400°C for 1 hour, with a significant change when aged @ 400°C for 4 hours. It appears that the other transformation temper tures M<sub>f</sub>, A<sub>s</sub> and A<sub>f</sub> were not as greatly effected; neither was the martensitic transformation for aging @ 600°C for 1 hour.

Fig. 15(a), the transmission electron micrograph of Ti59.4Ni38.7Al1.9 alloy aged at 400°C for 1 hour, exhibits an intermediate precipitate phase (23) and its corresponding diffraction pattern, Fig. 15(b). This exhibits the [110] B2 zone axis, with a [110] fcc zone superimposed pattern

Alloys	Ms	Mf	As	Af	Τp	т <sub>d</sub>
TINIAL					<u></u>	
59.4-38.7-1.9 400°C (1 hr.) 600°C (1 hr.) 400°C (4 hrs.)	-68 -70 -68 -83	-160 -160 -160 -160	-40 -41 -40 -40	-11 -10 -12 -12	25 25 25 25	18 18 18 18
<u>TiNiFe</u>						
50-45-5 400°C (1 hr.) 600°C (1 hr.) 400°C (4 hrs.)	<-196 <-196 <-196 <-196	<-196 <-196 <-196 <-196	<-196 <-196 <-196 <-196	<-196 <-196 <-196 <-196	-52 -52 -52 -52	-70 -70 -70 -70
50-47-3 400°C (1 hr.) 600°C (1 hr.)	-96 -97 -97	-196 -196 -196	-90 -90 -90	-60 -63 -63	-2 -3 -6	-13 -14 -17
TiNiCu						
50-45-5 400°C (1 hr.) 600°C (1 hr.) 400°C (4 hrs.)	61 61 60 65	48 48 49 46	65 65 65 65	79 78 79 85	- - -	- - -
50-46.2-3.8 400°C (1 hr.) 600°C (1 hr.) 400°C (4 hrs.)	5 5 6 4	-21 -21 -21 -26	-3 -4 -12	13 13 14 18	- - -	- - -

TABLE II. Aging Effects: Compositional (at.%) Dependence of Transformation Temperatures (°C) in TiNiAl, TiNiFe and TiNiAl Alloys.













attributed to the  $Ti_2Ni$  precipitate phase, also, containing the hexagonal  $TiNi_3$  structure.

Fig. 16(a), the transmission micrograph of Ti59.4Ni38.7Al1.9 alloy aged at 400°C for 4 hours, exhibits a finer precipitate plate than previous shown in Fig. 15(a). This is probably the Ti<sub>2</sub>Ni precipitate that results from the decomposition of the intermediate phase (23). Fig. 16(b) shows the diffraction pattern [332] B2 zone diffraction pattern with [116] fcc superimposed pattern.

Fig. 17 the transmission electron micrograph of a Ti<sub>59.4</sub>Ni<sub>38.7</sub>Al<sub>1.9</sub> alloy exhibits a coarse precipitate believed to be the intermediate precipitate. Ti<sub>2</sub>Ni and TiNi<sub>3</sub> are the expected products from the decomposition of the intermediate precipitate. The finer precipitates shown in Fig. 17(a), are apparently these precipitates. Fig. 17(b), gives the [110] B2 zone diffraction pattern with hexagonal (TiNi<sub>3</sub>) superimposed pattern.

Fig. 18 and Fig. 19 shown the effects of aging on the electrical resistance versus temperature measurements for a  $Ti_{50}Ni_{45}Fe_5$  alloy @ 400°C for 1 hour and @ 600°C for 1 hour respectively. Compared to Fig. 6, the unaged specimen, a more enhanced hysteresis loop for the premartensitic transition around  $T_d$  is evident. The sample aged @ 400°C for 1 hour, was effected greater than the sample aged @ 600°C for 1 hour and @ 400°C for 4 hours, not shown.







Fig. 15. Transmission electron micrograph and diffraction pattern for a Ti59.4Ni38.7Al1.9 alloy, aged at 400°C for 1 hr. (a) Electron micrograph, mag. 54,000x; (b) [110] B2 zone diffraction pattern, [110] fcc and hexagonal superimposed patterns.



Fig. 16. Transmission electron micrograph and diffraction pattern for a Ti59.4Ni38.7Al1.9 alloy, aged at 400°C for 4 hrs. (a) Electron micrograph, mag. 54,000x; (b) [332] B2 zone diffraction pattern with [116] fcc superimposed pattern.



Fig. 17. Transmission electron micrograph and diffraction pattern of a Ti<sub>59.4</sub>Ni<sub>38.7</sub>Al<sub>1.9</sub> alloy aged at 600°C for 1 hr. (a) Electron micrograph, mag. 54,000x; (b) [110] B2 zone diffraction pattern with hexagonal superimposed pattern.









Electrical Resistance (Arbitrary Units)

In Fig. 20, is the transmission electron micrograph of Ti<sub>50</sub>Ni<sub>45</sub>Fe<sub>5</sub> aged at 400°C for 1 hour and its corresponding diffraction patterns. In Fig. 20(b) [152] fcc diffraction pattern is shown. This pattern is similar to the intermediate phase diffraction pattern described by Koskimaki et al (23). The omega phase precipitate (31) shown in Fig. 20(c) is not commonly found in the TiNi alloys and could be the result of heat treatment, or in manufacturing the alloy.

In Fig. 21, the transmission electron micrograph of  $Ti_{50}Ni_{45}Fe_5$  aged at 600°C for 1 hour and its corresponding diffraction patterns are given. Fig. 21 (a) exhibits precipitate plates similar to the intermediate phase. The very fine plates could be the fcc  $Ti_2Ni$  phase. Fig. 21(b) gives the [110] bcc zone diffraction pattern with [114] fcc and hexagonal ( $TiNi_3$ ) superimposed patterns. In Fig. 21(c) the [111] B2 zone diffraction pattern with [115] fcc superimposed pattern is shown. These fcc precipitate phases are believed to be  $Ti_2Ni$ .

The aging effects for a full thermal cycle between room temperature and liquid nitrogen temperature for a  $Ti_{50}Ni_{47}Fe_3$  alloy is given in Fig. 22 for aging @ 600°C for 1 hour. For the  $Ti_{50}Ni_{47}Fe_3$  alloy, the martensite and austenite transformation temperatures are relatively constant, see Table 2. The premartensitic transition is effected as in the other alloys, giving a more enhanced hysteresis. The TiNiFe alloys appear to be the least



Fig. 20. Transmission electron micrograph of a Ti<sub>50</sub>Ni<sub>45</sub>Fe<sub>5</sub> and its corresponding diffraction patterns, aged at 400°C for 1 hr. (a) Electron micrograph, mag. 54,000x; (b) [152] fcc diffraction pattern.



Fig. 20. (Continued). (c) Hexagonal, omega phase observed.



Fig. 21. Transmission electron micrograph and its corresponding diffraction patterns, for a TisONi45Fes alloy aged at 600°C for 1 hr. (a) Electron micrograph, mag. 54,000x; (b) [110]B2 zone diffraction pattern with [114] foc and hexagonal superimposed patterns.



Fig. 21 (Continued). (c) [111] B2 zone diffraction pattern with [115] fcc superimposed pattern.





effected samples studied, possibly due to the Fe impurity affect on the vacancy density of the parent phase (11).

Fig. 23 gives the transmissions electron micrograph of  $Ti_{50}Ni_{47}Fe_3$  alloy aged at 400°C for 1 hour and its corresponding diffraction pattern. Fig. 23(a) exhibits a fine precipitate believed to be  $Ti_2Ni$  from the diffraction pattern, Fig. 23(b). The [100] B2 zone diffraction pattern with [114] fcc superimposed pattern is shown.

Fig. 24 gives the transmission electron micrograph of Ti<sub>50</sub>Ni<sub>47</sub>Fe<sub>3</sub> alloy aged at 600°C for 1 hour and its corresponding diffraction patterns. Fig. 24(a) exhibits fine precipitates formed at the extinction contour believed to be Ti<sub>2</sub>Ni from the diffraction pattern, Fig. 24(b). The [120] B2 zone diffraction pattern with [113] fcc superimposed pattern is shown. Fig. 25 shows the effects of aging on a TiNi-3.8%Cu alloy @ 400°C for 4 hours, on the electrical resistance versus temperature measurement. On cooling, the electrical resistance increases much slower than in the unaged specimen. On heating, slower recovery is evident, similar to aging effects on the martensitic transformation. On cooling, the initial point, where the electrical resistance increases, is 5°C lower than the corresponding point in the unaged specimen, Fig. 11. Again this is similar to aging effects on the martensitic transformation.

Fig. 26 and Fig. 27 shows the aging effects on Ti<sub>50</sub>Ni<sub>45</sub>Cu<sub>5</sub> alloy aged @ 400°C for 1 hour and @ 400°C for 4





Fig. 23. Transmission electron micrograph and diffraction pattern for a Ti<sub>50</sub>Ni<sub>47</sub>Fe<sub>3</sub> alloy, aged at 400°C for 1 hr. (a) Electron micrograph, mag. 62,000x; (b) [100] B2 zone diffraction pattern with [114] fcc superimposed pattern.





Fig. 24. Transmission electron micrograph and diffraction pattern for a Ti<sub>50</sub>Ni<sub>47</sub>Fe<sub>3</sub> alloy aged at 600°C for l hr. (a) Electron micrograph, mag. 54,000%; (b) [120] B2 zone diffraction pattern with [113] fcc superimposed pattern.



Electrical Resistance (Arbitrary Units)





hours. The curve for the sample aged  $(400^{\circ}C)$  for 1 hour is nearly identical to the unaged specimen, Fig. 8. There apparently is no effect on the TiNiCu alloy when aged for short periods of time (lhr.), see Table 2. The curve for the sample aged  $(400^{\circ}C)$  for 4 hours, also, shows a slower austenite A<sub>S</sub> to A<sub>f</sub> recovery, but M<sub>S</sub> is increased by 4°C rather than decreasing as in the other alloys.

The aging effects on these alloys is due to precipitation, suppressing the martensitic transformation and slowing the recovery of the premartensitic transition to the parent phase.

#### IV. SUMMARY

The effects of thermal cycling on the martensitic transformation consists of depression of the  $M_S$  temperature and a slower austenite recovery in the Ti<sub>59.4</sub>Ni<sub>38.7</sub>Al<sub>1.9</sub> and Ti<sub>50</sub>Ni<sub>45</sub>Cu<sub>5</sub> alloys, suppression of the hysteresis loop in the Ti<sub>50</sub>Ni<sub>47</sub>Fe<sub>3</sub> alloy, but, no apparent effect on the TiNi-3.8%Cu alloy. These effects are attributed to dislocations that apparently act as a barrier to the formation of martensite plates, and are responsible for the stabilization of a high temperature phase.

The aging effects are due to precipitation of an intermediate phase which decomposes to fcc (Ti<sub>2</sub>Ni) and hexagonal (TiNi<sub>3</sub>) phases. The fcc Ti<sub>2</sub>Ni precipitate appears in most cases, presumably because they are Ti-rich. The hexagonal TiNi<sub>3</sub> appears in the Ti<sub>59.4</sub>Ni<sub>38.7</sub>Al<sub>1.9</sub> alloy aged at 400°C and 600°C for 1 hour and also for the Ti<sub>50</sub>Ni<sub>45</sub>Fe<sub>5</sub> alloy aged at 600°C for 1 hour. Another hexagonal phase, an omega precipitate, appears for the Ti<sub>50</sub>Ni<sub>45</sub>Fe<sub>5</sub> alloy aged at 400°C for 1 hour. For a longer aging time, the intermediate precipitate apparently decomposes to a finer precipitate, as in the Ti<sub>59.4</sub>Ni<sub>38.7</sub>Al<sub>1.9</sub> alloy aged at 400°C for 4 hours.

Precipitation changes matrix composition, effecting both the premartensitic and martensitic transitions. Precipitates could change the Fermi energy, distorting the

Brillouin Zone thus, effecting the premartensitic transition. For the martensitic transformation, precipitation of fcc Ti<sub>2</sub>Ni phase reduces the Ti content, depressing the M<sub>S</sub> temperature. Precipitates can obstruct the shape change for the martensitic transformation thus, initiation of transformation is more difficult and the M<sub>S</sub> temperature decreases. The contribution of either of these is not fully understood. This study conducted at room temperature presents some problems, such as, inconclusive results for the TiNi-3.8%Cu alloy. Also, the lack of the dark field illumination technique prevented positive identification of the precipitation phases.

The  $M_S$  temperature is a function of impurity content, prior thermal history and composition. The sensitivity of TiNi to many variables makes it unreliable to generalize these results beyond the range of alloys and heat treatments in this investigation.

#### LIST OF REFERENCES

- C. M. Hwang and C. M. Wayman, Scripta Met., <u>1</u>, 381 (1983).
- C. M. Hwang and C. M. Wayman, Scripta Met., <u>17</u>, 2345 (1983).
- C. M. Hwang and C. M. Wayman, Scripta Met., <u>17</u>, 1449 (1983).
- C. M. Hwang, M. Meichle, M. B. Salamon and C. M. Wayman, Phil Mag. A, <u>47</u>, No. 1, 9 (1983).
- 5. C. M. Hwang, M. Meichle, M. B. Salamon and C. M. Wayman, Phil Mag. A, <u>47</u>, No. 1, 31 (1983).
- C. M. Hwang, M. B. Salamon and C. M. Wayman, Phil. Mag. A, <u>47</u>, No. 2, 188 (1983).
- 7. C. M. Hwang and C. M. Wayman, Met. Trans., <u>15A</u>, 1155 (1984).
- C. M. Hwang, M. Meichle, M. B. Salamon and C. M. Wayman, Res Mechania, <u>10</u>, 1 (1984).
- 9. C. M. Hwang and C. M. Wayman, Acta. Met., <u>32</u>, No. 1, 183 (1984).
- 10. C. M. Hwang and C. M. Wayman, Scripta Met., <u>17</u>, 385 (1983).
- 11. Z. Nishiyama, Martensitic Transformations, C. M. Wayman ed., Academic Press, New York, 276 (1978).
- 12. T. Tadaki and C. M. Wayman, Metallography, <u>15</u>, 233 (1982).
- 13. T. Tadaki and C. M. Wayman, Metallography, <u>15</u>, 247 (1982).
- 14. K. N. Melton and R. H. Bricknell, ICOMAT 1979 p. 171.
- 15. R. F. Hehemann and G. D. Sandrock, Scripta Met., <u>5</u>, 801 (1971).

- 16. K. Otsuka, T. Sawamura and C. M. Wayman, Met. Trans., 2, 2583 (1971).
- 17. R. J. Wasilewski, Scripta. Met., 5, 127 (1971).
- 18. J. Perkins, Met Trans., 4, 2709 (1973).
- 19. N. Nakaniski, Y. Murakami and S. Kacki, Scripta Met., <u>5</u>, 433 (1971).
- 20. A. D. Sandrock, A. J. Perkins and R. F. Hehemann, Met. Trans. 2, 2769 (1971).
- 21. C. M. Wayman and I. Cornelis, Scripta Met., <u>6</u>, 115 (1972).
- 22. K. A. Thornburg, D. P. Dunne and C. M. Wayman, Met. trans. 2, 2302 (1971).
- 23. D. Koshimaki, M. J. Marchinkowski and A. S. Sastri, Trans. TMS-AIME, 245, 1883 (1969).
- 24. P. Duwez and J. L. Taylor, AIME Trans., <u>188</u>, 1173 (1950).
- 25. G. R. Purdy and J. Gordon Parr, TMS-AIME Trans., <u>221</u>, 636 (1965).
- 26. H. Margolin, E. Ence and J. P. Nielsen, AIME Trans., 197, 243 (1953).
- 27. W. J. Buehler and R. C. Wiley, ASM Trans., <u>55</u>, 269 (1962).
- 28. R. J. Wasilewski, S. R. Butler and J. E. Hanlon, J. Metal Science, <u>1</u>, 104 (1967).
- 29. G. Thomas, Transmission Electron Microscopy of Metals, p. 253, John Wiley and Sons, Inc., New York, 1962.
- 30. Toshio Honma, Minoru Matsumoto, Yoshiro Shugo, Minoru Nishida and Isao Yamazaki, Titanium Science and Technology, R. Jaffe ed., 3, 1433 (1980).
- 31. T. N. Duerig, G. T. Terlinde and J. C. Williams, Met. Trans. A, 11A, 1987 (1980).

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