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STRESS INDUCED PHASE TRANSFORMATION IN NITI SHAPE MEMORY ALLOYS

By

Gie Hong Kang

A DISSERTATION

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

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ABSTRACT

STRESS INDUCED PHASE TRANSFORMATION IN NITI SHAPE MEMORY ALLOYS

By

Gie Hong Kang

Stress induced martensitic transformation modes in near-equiatomic NiTi alloys have been investigated by using in-situ X-ray diffraction of samples mounted on a tensile stage. Tensile deformation studies have also been conducted to determine the stress-strain-temperature relationship in these alloys. Through differential scanning calorimetry studies, it is shown that both the martensitic start temperature, M, and the premartensitic transformation temperature, T, are strong functions of the thermomechanical history of the sample. Samples given a fixed amount of plastic deformation (30% reduction in thickness by rolling) before annealing, show a monotonic decrease in T with increasing annealing temperature up to about 600°C. In a purer NiTi alloy, the M temperature increases monotonically with increasing annealing temperature when the samples are given the same amount of deformation (30%) before annealing. It is observed that even a small amount of impurities,

influence the M_s temperature as well as the deformation mode. It is suggested that a strong interaction between impurities and dislocations, in these alloys, can influence the nucleation mechanism for the martensitic and the premartensitic phases. In the less purer alloy, the impuritydislocation interaction is strong enough to produce highly localized bursts of transformations, during tensile deformation, giving rise to Lüders band type of surface marking along with discontinuities in the stress-strain curve.

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1 INTRODUCTION

A diffusionless martensitic phase transformation, in a certain class of alloys, can be induced by cooling the alloy below its martensitic start temperature, M. More martensite forms as the temperature is lowered below M and ultimately, at a martensite finish temperature, M, the alloy is 100% martensitic. Upon reheating, the martensite starts to retransform back to the high-temperature parent phase (commonly designated as the austenite phase) at the austenite start temperature, A_{g} , and this phase reversal is completed at the austenite finish temperature, A,. In general, the alloys which undergo such a phase transformation can be grouped together in two distinct classes. In one class of alloys (such as Fe-C, Fe-Ni etc.), the thermal hysteresis associated with the forward and reverse transformation is relatively large, i.e., $A_s >> M_s$. In the second class of such alloys (such as Au-Cd, Cu-Zn-Al, Ti-Ni etc.) the transformation hysteresis is relatively small, i.e., $A_{e} \approx M_{e}$. The later group also manifests an interesting set of properties such as shape memory effect, pseudo-elasticity, pseudo-plasticity etc.

It is now well documented that the martensitic phase transformation is a shear dominent, displaceive phase change involving atomic movements less than interatomic distances (1). Thus, the transformation does not require long-range

atomic diffusion and thermodynamically, this is a "firstorder" phase change. Because of the shearing nature of this transformation, the martensitic phase change can also be induced by deformation at or near the M_s temperature. In general, a critical upper limit of temperature exists, above which stress induced martensite transformation can not occur. This temperature is called deformation-induced martensite start temperature, M_d , and $M_a > M_s$.

In thermo-elastic group of martensitic alloys, a thermo-elastic equilibrium, between the amount of martensite, stress and temperature, exists at a temperature $T \leq M_d$. Such a stress-induced martensitic transformation, in these alloys, is fully reversible.

Although the martensitic transformation is generally believed to be first-order type, i.e., at a discrete temperature (M_g) parent-phase \rightarrow product-phase upon extraction of heat energy, there are numerous experimental evidence which indicate that there are gradual (second-order type) dynamical changes of the parent-phase lattice as a sample is cooled toward the M_g temperature (2~4). These premartensitic or pre-cursor changes are especially pronounced in the thermo-elastic group of martensitic alloys (2~12).

Examples of such a precursor phenomenon, upon cooling, are found in the form of a gradual broadening and progressive splitting of specific parent-phase diffraction peaks (3, 4), anomalous magnetoresistance (2), softening of

elastic constants (5), appearance of extra reflections in selected area electron diffraction pattern (6) and so on. Although an ample evidence of the pre cursor phenomena associated with the thermally induced martensitic transformation is found in the literature, a corresponding study related to stress-induced transformation is currently lacking.

The purpose of the present study, therefor, is to investigate the parent phase instability of a thermoelastic martensitic alloy with respect to an applied stress. The alloy chosen for this study is TiNi (~50 at. % Ni), since the precusor phenomena associated with thermally induced phase change in this alloy system has been well documented. Further, noting the fact that thermo-mechanical history (including thermal cycling, annealing temperature and testing temperature) of this alloy influences the martensitic transformation parameters (Mg, M, Ag, A) during cooling and heating transformations, attention is also paid in characterizing the effects of thermomechanical history in stress-induced martensitic transformation in a NiTi alloy. Stress-strain response of a thermoelastic martensitic alloy is influenced by both the martensitic and pre-martensitic transformations (13, 14), if the deformation is given at a temperature T, such that $M_{s} \le T \le M_{s}$. Stress-induced transformation produces a plastic-yielding type of response when the applied stress, at a given temperature, reaches a

critical value to produce stress-induced martensitic transformation. The associated strain, during this "yielding" is due to the transformation strain rather than due to dislocation motion as is the case in ordinary yielding. This transformation yielding is also influenced by the premartensitic transformation (13, 14) and secondary discontinuitics are observed in the stress-strain curves. Thus, the deformation mode in this alloy has also been studied as a function of thermomechanical history of the alloy.

2 BACKGROUND

2-1 Summary of Techniques Used for Phase Transformation Studies in NiTi.

Many different methods can be used to study martensitic phase transformation in NiTi alloys. A few of the more common ones are briefly discussed below.

2-1-1 Transmission Electron Microscopy (TEM).

The most important advantage of transmission electron microscopy is that it can provide an almost complete characterization of the microstructure (as indicated by the scheme shown in figure 1). Today electron microscope is very popular in phase transformation studies since it is possible to resolve substructural details down to a few Angstroms and atomic plane spacing as low as 1 Å can be resolved (15).

2-1-2 Optical Microscopy.

Metallographic technique is a very common method, but the lack of detailed optical metallographic information in case of NiTi alloy is the significant factor contributing to the uncertainty about the physical metallurgy of the shape memory effect of this alloy.



Figure 1. Scheme illustrating the main features of electron microscopy.

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Dunne, et al (16) introduced three techniques for metallographic examination of NiTi alloys.

- Mounted specimens were mechanically prepared and then etched. The most effective of the etching reagents was an aqueous solution containing 10% HNO and 5% HF.
- 2) Mounted and mechanically polished specimens were electropolished in an attempt to remove the surface layer. Of the electrolytes used, the best one was a solution containing 8% perchloric acid in methanol.
- 3) Small unmounted specimens, polished to a 0.25 μ m diamond finish, were electropolished in a Struers Tenupol twin-jet polisher, to prepare polished disks about 3 mm in diameter. The most satisfactory electrolyte was a solution of 5% perchloric acid and 25% glycerol in ethanol.

2-1-3 X-ray Technique.

X-ray data are most important in this work because knowledge of the crystal structure is a necessary prerequisite to any understanding of phase transformations. For continuous observation of stress induced martensitic transformation, X-ray measurements can be carried out using a diffractometer with a cooling/heating and strain device. The order of the transformation can be determined by closely

examining the change in the line profiles during the transformation (17). If the transformation is of the first order type, then the lattice change is discontinuous. Thus, the matrix reflections do not shift, and martensite reflections appear discontinuously during the transformation. On the other hand, if the transformation is of the second or higher order type, then the lattice change is continuous. Thus, the matrix reflections must change continuously i.e., shifting, broadening and splitting of the parent phase reflections during the progress of martensitic transformation.

2-1-4 Differential Scanning Calorimetry.

Differential Scanning Calorimetry (DSC) is the most widely used of all thermal analysis techniques. DSC is used routinely to measure fundamental thermal properties, such as transition temperatures and heats of transitions. The DSC characteristics of a sample of NiTi alloy shows two major transitions: One is for premartensitic change and the other for the martensitic transformation. These transition temperatures provide a qualitative information of phase transformations in the NiTi alloy, while the peak integration quantitatively measures the heat of phase transformation during cooling and heating (18).

2-1-5 Stress-Strain Curves.

In NiTi alloys, two-stage yielding points were observed by Suzuki and coworkers (19). They reported that there were two plateaus in the stress-strain curves in the low temperature range. The critical stress for the second plateau corresponds to the stress necessary for martensitic transformation σ_m , but that for the first plateau was suggested to be due to the stress required for rearrangement of the rhombohedral phase variants, which appear prior to the onset of the martensitic transformation, during cooling in the absence of stress. Since then a two stage yielding behavior associated with R-phase transition has been confirmed (13, 14).

2-2 Crystal Structures of the Martensitic Phase in NiTi Alloys.

Equilibrium phase diagram of the NiTi system is shown in figure 2. For the near-equiatomic composition, the high temperature phase (γ in the phase diagram) has an ordered CsCl type (B2) structure. For the martensitic phase, varios crystal structures such as hexagonal, triclinic, etc. have been proposed in the past (7, 20~22). However, the generally accepted crystal structure of the martensitic phase, in this alloy, is a distorted B19 structure (23).



Ni-Ti Nickel-Titanium

Figure 2. Binary equilibrium phase diagram for the NiTi system.

Dautovich and Purdy (7) studied 50 and 51 a/o NiTi alloys by using resistivity technique, powder X-ray diffraction, and transmission electron microscopy. They concluded that the ordered "bcc" alloy can undergo a continuous (second-order) transition prior to the formation of a triclinic martensitic phase (a = 4.60 Å, b = 2.86 Å, c = 4.11 Å, $\alpha = 90.1^{\circ}$, $\beta = 90.9^{\circ}$, $\gamma = 96.7^{\circ}$,).

Nagasawa, et al (21) showed the presence of 12R, 4H and cubic phase with a 9Å cell in NiTi alloys.

Mukherjee, et al (22) showed that stacking modulations with increasing Ni content are 2H-4H-3R and 9R.

Otsuka, et al (23) studied the crystal structure of martensite which was identified to be nearly of the B19 type, more like a distorted B19 structure shown in figure 3. The unit cell is monoclinic with the c axis slightly inclined (=96.8°). The atomic arrangement in the unit cell, however, might not be exactly as assumed by Otsuka, et al, since the (001) line was observed in the X-ray diffraction patterns.

Three slightly different uniy cell dimensions of the distorted B19 structure of the martensite have been proposed. Hehemann and Sandrock (24), Michal and Sinclair (25) and Otsuka, Sawamura and Shimizu (23). These are as follows:

	Ref.(24)	Ref.(25)	Ref.(23)
a	2.883	2.885	2.889
b	4.623	4.622	4.120



Unit cell of TiNi martensite. $a = 2.889 \text{ A}, b = 4.120 \text{ A}, c = 4.622 \text{ A}, \beta = 96.8$.

Figure 3. Unit cell of NiTi martensite, according to Otsuka, et al (23).

с	4.117	4.120	4.622
ß			96.8°
γ	96.8°	96.8°	

Thus, within the experimental errors, this is a good agreement for the martensitic unit cell.

2-2-1 Premartensitic Phase.

Dautovich and Purdy (7) suggested that the martensitic transformation is preceded by a second-order, diffusionless transformation which produces a rhombohedral phase with a = 6.02 Å and $\gamma = 90.7^{\circ}$.

Chandra and Purdy (20) showed the existence of <210> and <321> streaks in electron diffraction, which they interpreted in terms of a large-amplitude, short-wavelength atomic displacement wave, reflecting an incipient mechanical instability of the B2 lattice. They re-indexed the powder patterns obtained by Dautovich et al in terms of a rhombohedral cell with a = 9.03 Å and $\gamma_{\rm min}$ = 89.3°.

2-2-2 Crystallographic Steps for the B2 to Martensite Transformation.

Saburi, et al (26) proposed crystallographic steps for the B2 to martensite transformation. Figure 4 shows the





(c)

Figure 4. Change in interatomic relations on transformation. (a) B2 (b) martensite, homogeneous distortion and shear XA ' (c) martensite, homogeneous distortion and shear $XA_2^{1'}$.

change in interatomic relations on transformation, involving i) a homogeneous distortion (expansion along $[011]_{B2}$, contraction along $[100]_{B2}$ and expansion along $[0\bar{1}1]_{B2}$) and ii) a combination of elementary shears in opposite directions, [011] and $[0\bar{1}\bar{1}]$, between two adjacent closepacked planes.

Hehemann and Sandrock (24) proposed crystallographic steps for the conversion from B2 to martensite as shown in figure 5. In addition to the Bain strains shown in figure 5 (c) and (d), $(001)_{H}[010]_{H}$ planar shuffles are required within the unit cell, as shown in figure 5 (e). The magnitude of this shuffle is approximately $1/8[010]_{H}$.

Michal, et al (27) proposed that the atomic movements which occur for the B2 structure can be described in three stages. The three steps are: a homogeneous shear, a homogeneous shuffle and a slight atomic readjustments. The lattice correspondence between the B2 and martensite phase is shown in figure 6. The first crystallographic step is a homogeneous shear on the (112) plane in the [111] direction. The second crystallographic step is a homogeneous shuffle of alternate (011) planes in \pm [110] direction in figure 7 (a), the effect of which is shown in figure 7 (b). The third step is shown in figure 8, which is a projection on the (011) plane (the basal (001)_H plane). The direction of atomic motion is indicated by small arrows in the upper drawing. This also induces a shuffle of alternate (010)_H plane in the [100]_H direction.



(a) B2 cells with fct cell delineated



Figure 5. Crystallographic steps for the B2 to martensite transformation.

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Figure 6. A schematic drawing of the B2 lattice, showing the lattice correspondence between the B2 (β) and martensite (M) phase and ($\overline{112}$)[$1\overline{11}$] shear mode. A tetragonal cell (heavy line) within four B2 unit cell is a useful reference.



Figure 7. A schematic drawing showing the effects of a (110)[110] shuffle (equivalent to (001) [010] in martensite indices). Nearest neighbor distances have been assumed to remain unchanged.

HALF SHADED CIRCLES ± 1/2 [001]



Figure 8. A projection of the atoms on the (001) plane. The atomic movements in the final resettling step are indicated, such that the lower picture now represents the martensite crystal structure. Figure 9 shows the pure lattice distortion (Bain Strain) which carries a tetragonal cell (delineated in the parent B2 structure) into the monoclinic cell of the product as proposed by Knowles and Smith (28). The correspondence is identical with that used for gold-cadmium. In an orthonormal basis parallel to the cube directions [110], [110] and [011], the deformation is represented by the matrix

$$T_{1}' = 1/a_{o} \qquad \begin{vmatrix} b/\sqrt{2} & 0 & 0 \\ 0 & c \sin\beta/\sqrt{2} & 0 \\ 0 & c \cos\beta/\sqrt{2} & a \end{vmatrix}$$

where a_{0} is the lattice parameter of the parent and a, b, c, and β are those of the monoclinic product. In an orthonormal system parallel to the cube axes, the deformation is represented by the matrix

$$\mathbf{T}_{1} = \begin{pmatrix} \alpha_{1} & \beta_{1} & 0 \\ \beta_{1} & \alpha_{1} & 0 \\ \delta_{1} & \delta_{1} & \gamma_{1} \end{pmatrix}$$

where

$$\alpha_{1} = \frac{\sqrt{2}}{4a_{o}} (b + c \sin\beta)$$

$$\beta_{1} = \frac{\sqrt{2}}{4a_{o}} (-b + c \sin\beta)$$

$$\gamma_{1} = \frac{a}{a_{o}}$$

$$\delta_{1} = c \cos\beta/2a_{o}$$



o Ni atoms



Figure 9. (a) The untransformed B2 phase in which a tetragonal cell is delineated. The orthonormal vectors (i.j.k) are along the cube axes. The orthonormal vectors (i'.j'.k') are along the cube directions [110]. [110] and [001]. (b) The martensite cell into which the tetragonal cell is transformed. The vectors (a.b.c) define the monoclinic lattice. The orthonormal vectors (i'.j'.k') and (i.j.k) are also shown. Using an analysis based on the Wechsler-Lieberman-Read (WLR) theory of martensitic crystallography (28), the twin fraction of the martensitic product phase is found to be (twinned on $(111)_{\mu}$, derived from $(011)_{c}$, 0.32.

2-3 Some Premartensitic Phenomenon Associated with the Transition.

The martensitic transformation exhibits a premartensitic phenomenon just above the martensitic start temperature (M_g) . The R-phase transition is known to contribute to deformation due to the rhombohedral distortion of the unit cell (4, 8-10, 28). There are at least three factors which contribute to the R-phase transition in NiTi alloys. These are:

- 1) increasing Ni content (8)
- 2) annealing at a low temperature immediately after cold work (19)
- 3) thermal cycling (29~31)

There are several phenomena associated with this transition.

- Extra diffraction spots at 1/3 positions of the B2 reciprocal lattice (6)
- 2) An increase in electrical resistance prior to the martensitic transformation (4, 7, 8~11)
- 3) A splitting in the (011) and (211) B2 reflections (7, 12)
- 4) A two stage yielding observed at certain temperatures (13)

In addition, anomalies in physical or mechanical properties are reported, such as decrease in the velocity of sound (29, 32), elastic modulus (5), internal friction (5, 33), specific heat (34, 35), and so on.

2-4 Shape Memory Effect (SME).

Consider a specimen in the low temperature martensitic condition, subject to a certain amount of deformation. If the specimen is now heated, a total relaxation of stress occurs and the specimen regains its original undistorted shape. The shape recovery occurs during the reverse transformation of martensite to its high-temperature parent phase. This is called the shape memory effect (SME). A number of interrelated mechanisms which contribute to this basic phenomenon are discussed next.

2-4-1 One-Way SME.

Figure 10 shows a schematic diagram of the one-way shape memory effect (36). Two initial states and mechanisms can be



Figure 10. A schematic description of the shape memory effect: (a) a straight parent phase wire: (b) cooled through the athermal transformation range M to M, producinga straight martensite wire: (c) a deformed martensite wire: (d) the deformed wire straightens out when heated through the reverse transformation range from P to P, reproducing the straight parent phase wire. It should be noted that there is typically a slight hysteresis between the forward and reverse transformation ranges, so that the transformation P → M on cooling occurs over a slightly lower range (M to M) than that (P to P) for the transformation M → P on heating. M is the temperature below which martensite can be stress induced from the parent phase. differentiated.

- The specimen initially consists of the parent phase; the deformation causes stress-induced martensite to form which is retransformed by heating.
- 2) The specimen initially consists of the martensitic phase formed by cooling; the deformation causes stress-induced displacements in the martensitic structure which, on heating, first revert into the original microstructural configuration and are then immediately followed by retransformation of the martensitic phase to the parent phase.

2-4-2 Pseudoelasticity.

A NiTi specimen can be deformed by an applied stress to strains up to ~16% (i.e., much higher than elastic limit for ordinary metals) and when the applied stress is released, the strain is completely reverted "pseudoelastically" such that the original shape is restored isothermally. By complete analogy to the basic SME, two initial states and mechanism can be differentiated.

- 1) The initial structure consists of parent phase; the deformation (at $T \ge A_f < M_d$) induces martensite which reverts to the parent phase on the release of the applied stress.
- 2) The initial state is martensitic; the deformation

(at T < M_f) induces displacements of reversibly
movable plates and twin interfaces; these
displacements revert to original microstructural
state of the martensitic phase on the release of the
applied stress.

2-4-3 Two-Way SME.

A specimen is thermally cycled through the martensitic transformation range M_r thru A_r and an applied external stress is superimposed during the cycling. Figure 11 shows the two-way shape memory effect (37). This effect is due to a non-random distribution of orientation variants of the martensite plates which are formed during cooling under an applied stress and revert to the matrix phase by shrinkage during heating. The shape changes of the individual plates collectively produce a shape change in the specimen. The preferred orientation of the growing plates is caused by the existence of persistent nuclei with preferred orientation, which can be induced by plastic deformation of the matrix and/or of the martensite, or by inducing the first transformation under an applied stress (38).

2-5 The Primary Mechanism of the Shape Memory Effect.

The primary mechanism of the shape memory effect is



Figure 11. Examples of the two-way shape memory.

generally considered to be the interaction of stress with the martensitic transformation (10, 39~42). Depending on the deformation temperature with respect to M_g , one or more of the following three mechanisms may be operative in NiTi alloys (43).

- 1) Stress induced martensite formation from the β phase.
- 2) Reorientation of thermally induced martensite variants through the twin interface motion.
- 3) Variation in twin thickness within individual variant plates.

2-6 Shape Memory Properties.

2-6-1 Chemical Composition.

A wide disagreement exists between the reported M_g temperatures for NiTi alloys as shown in figure 12. It is obvious, from such observations, that factors other than composition must also be significant in affecting the transformation behavior, and presumably also the related properties of the compound (44).

Nickel-rich compositions show a major variation

 in transformation behavior with the prior heat treatment. This is ascribed to the incomplete precipitation
 of nickel, and the consequent supersaturation of the
 β structure.



Figure 12. Previously reported data on the effect of composition on the recovery temperature of NiTi alloys.

2) Titanium-rich compositions show relatively minor variations in transformation behavior, consistent with the very limited tolerance of the NiTi structure for excess titanium.

Eckelmeyer (45) reported that the recovery temperature can be seen to increase substantially with small departures from stoichiometry in the titanium rich end. After this initial increase, further additions of titanium have no effect on the recovery temperature. He also reported that increase in the recovery temperature is obtained by substituting zirconium for titanium or gold for nickel. Substitutions of aluminum and manganese for titanium decrease the recovery temperature. It is also known that substitutions of cobalts or iron for nickel decrease the recovery temperature.

Mercier and Melton (46) observed that displacing the $M_{_{5}}$ temperature by compositional adjustments changed the details of the transformation.

2-6-2 Shape Recovery Temperature.

According to Kaplow, et al (47), in the near-equiatomic NiTi alloy, certain processing factors significantly affect the shape recovery temperature T_{f} , and the extent of shape recovery, while others do not. The lowest recovery temperature and the best shape recovery were obtained by annealing between 450° C and 500° C. Varying the annealing temperature resulted in the largest change in these two parameters, causing an increase of 20° C in T_r and a decrease of 13% in the shape recovery if the annealing temperature was increased much above 500° C. Increasing the strain leads to an increase of 10° C in T_r at 500° C. Larger increases are observed at other annealing temperatures, without any effect on the extent of shape recovery. Altering the annealing time had a relatively small effect.

2-6-3 Orientation Dependence.

According to Saburi, et al (48), the orientation dependence in the shape memory strain is significant in NiTi alloy samples. This knowledge ought to be quite important in improving the shape memory capacity in polycrystalline NiTi alloys. After developing a texture in a material, the memory capacity in a certain direction can be improved.

2-6-4 Grain Size Effect.

Saburi and coworkers (48) reported that single crystal specimens of the 50.5 a/o NiTi alloy do not behave pseudoelastically at any temperature. Polycrystal specimens of the same alloy, on the other hand, show complete pseudoelasticity above A. The pseudoelasticity becomes

pronounced as the grain size decreases. The reduction in grain size is very effective in improving the pseudoelasticity and thus the role of the grain boundaries is important in the pseudoelasticity of NiTi alloys.

2-6-5 Effect of Sample Geometry on Shape Memory Response.

Cross, et al (49) performed a study on the shape memory response of NiTi rods, wires of varying diameters and foils of varying thicknesses. They selected a final annealing temperature of about 500°C, as the optimum for shape memory, and studied the effect of material form and amount of strain, on shape memory. They reported that, irrespective of the form, 100 percent recovery could be obtained if the strain did not exceed 6 to 8 percent.

2-7 Metallurgical Variables in Shape Memory Phenomenon.

Metallurgical variables, which can be manipulated for the shape memory phenomenon, can be divided into two groups as follows (47.);

Group I: Extrinsic parameters

- i) final annealing temperature.
- ii) annealing time.
- iii) amount of strain.
 - iv) number of thermal cycles.

Group II: Intrinsic parameters

i) internal structures with precipitates.

ii) internal structures with dislocations.

iii) internal structures with precipitates and dislocations.

iv) grain size.

2-8 Factors Causing a Decrease in the M_g Temperature.

The R-phase transition usually appears prior to the martensitic transformation when the M_s point is lowered. There are many factors which cause the M_s point to decrease. They are as follows:

- 1) increasing Ni content (45, 50)
- 2) aging after solution treatment (32, 51, 52)
- 3) annealing at temperatures below the recrystallization temperature (9, 51)
- 4) thermal cycling (29~31)
- 5) substitution of a third element such as Fe (51, 53)

The first factor lowers the M_g temperature in a solidsolution state.

The second and third factors produce precipitations and/or dislocations which suppress the matensitic transformation by forming back stress around themselves which interacts unfavorably with the transformation strain.

The fourth factor can also be associated with

dislocations which are introduced upon repeated reverse transformation.

The last factor is also effective in making the R-phase appear over a wide temperature range. However, the cause for depressing the M_s temperature, in this case, is not the back stress field. In this case the strain field (as evidenced by the surface relief) of the R-phase, most likely interact with the martensitic missfit strain and thus a further supercooling is needed for the martensite nucleation.

2-9 Applications of Shape Memory Behavior.

Applications have taken clever advantage of two main characteristics of the transformation.

- 1) the shape change on heating through a certain temperature range.
- 2) the stored potential energy (back-stress) if this reverse transformation is opposed.

These two parameters, the reverse strain and reverse stress respectively, have already been combined to invent a wide variety of heat-activated fasterners, switches, couplings, controls, deployment devices, and even heat engines. There have been some interesting medical and dental applications, including teeth braces, orthopeadic bone straightening and fracture aligning devices, blood clot filters, intracranial aneurism clips, prosthetic muscles for an artifical heart etc. Also under development are applications such as thermostatic radiator valves and cooling fan clutches for automobiles, automatic window openers for greenhouses and many other ingenious inventions based on the unique behavior (36).

2-10 Prospects and Limits of SME Application.

1) The useful stress range

The inherent elastic softness of SME alloys limits their usefulness at higher stress levels where the SME is degraded by plastic deformation.

2) The useful strain range

The recoverable shape strain is determined by:

- i) the magnitude of the macroscopic shear of the transformation.
- ii) the structural properties of the martensitic phase permitting structurally reversible shears to occur.
- iii) the possible occurence of a second martensitic variant extending the range of transformation strain to that of two consecutive transformations.
- 3) The usable number of SME cycles.

For both the use of the SME as such, and for utilizing the high fatigue life and internal friction of SME alloys, the stresses applied and the recovery properties of each alloy play a decisive role. 4) The usable temperature range.

Martensitic transformation temperatures, and thus the range of usable SME properties can be adjusted in wide range by composition variation.

5) The usable efficiency for energy conversion machines.

These machines utilize the temperature difference between two reservoirs to generate mechanical work by a device based on the "one-way" or the "two way" shape memory effect. It has been shown that the calculated efficency of such an engine is small (54). But since such an engine can operate by extracting heat energy from a high-temperature reservoir at a temperature as low as ~50°C, efficency is not an important factor. Such a heat source, for example, could be inexpensive solar heating etc.

3 PREVIOUS WORK

3-1 Differential Scanning Calorimetry.

Mukherjee, et al (18) reported that a distinct twostage heat evolution is observed in near-equiatomic NiTi alloys on cooling, whereas a single calorimetric peak is observed on reheating. These two cooling peaks are well separated in temperature. The first peak is asymmetric and it has a broad shoulder, but the second peak is more symmetric. What is most noteworthy is the fact that the combined area of the two cooling peaks is exactly equal to the area of the single heating peak. Such a correspondence implies that the first event on cooling brings the parent phase energetically closer to the final martensitic product phase.

Dautovitch, et al (55) were able to detect a small calorimetric peak (82 cal/g mole) in 51 a/o NiTi alloys due to a premartensitic transition.

Wasilewski and coworkers (56) noted a small exothermic peak during cooling at about 10° C above the transformation temperature in an alloy of Ni 48 a/o Ti 52 a/o.

Johnson, et al (57) observed premartensitic peak in a NiTi alloy. They noted that in the martensitic reaction a second peak appeared at a higher temperature than the M_g and it was believed to be the premartensitic reaction.

Dautovich and coworkers (55) reported the heat of transformation to be 370 \pm 20 cal/g mol in 51 a/o NiTi alloy.

Goldstein, et al (58) also reported two separate peaks representing the formation of R structure and its subsequent conversion into martensite, during continued cooling. The subsequent merge of the two peaks into a single peak with thermal cycling demonstrated that the R structure is metastable. Specimens that are in equilibrium have only a single major peak during the heating or the cooling transformation.

3-2 X-ray Diffraction Effects Associated with Thermally Induced Phase Transformation.

Mukherjee and coworkers (3) showed that the $(110)_{\beta}$ peak in a NiTi alloy (polycrystalline 51.3 a/o NiTi alloy) undergoes a systematic change during cooling. The $(110)_{\beta}$ peak broadening and splitting were observed by using a specially designed cooling stage such that the sample could be cooled or heated at temperature intervals of 0.5°C with \pm 0.01°C error. They observed that in the transition temperature range, the $(110)_{\beta}$ peak first broadened and then split. Also a symmetric shift and separation of the split peaks become more pronounced at temperatures approching the M₂ temperature.

Another observation was reported by R. Kaplow et al (4) in a 49.96 a/o NiTi alloy. While the integrated intensity

remains constant, there is a decrease in peak height and an increase in FWHM below T_R , reaching a resolvable splitting of the peak. Apparently, there is a compositional dependence of the (011) integrated intensity below T_R , as a small increase (~5%) was observed in Ni₅₁Ti₄₉ and a much larger change (~40%) in TiNi_{45.3}Fe_{4.7}. The two subpeak intensities then remain approximately constant as the 20 separation between them increases with lowering temperature.

Otsuka et al (17) studied phase transformation in a 49.75 a/o NiTi alloy. The result shows that the $\{110\}_{B2}$ line becomes weak with decreasing temperature, without losing its sharpness and without a line shift: no splitting of the line is observed although the reflection plane is a mirror plane in the matrix. It is also observed that the reflections from the martensite phase are independent of the Bragg angles during the cooling process. It is noted that none of the reflections shift during the transformation process. This is of course within the range of experimental errors.

3-3 X-ray Diffraction Effects Associated with Stress Induced Phase Transformation.

Kaplow, et al (59) observed that during strain, virtually all of the β phase in a nearly equiatomic NiTi alloy was converted to martensite at about 6% strain. The transformation was exothermic, which accounted for the

observed temperature increase during this step.

Washburn, et al (43) reported that some growth of the already existing martensite occurs at the expense of the retained high temperature phase. According to their report, the stress induced transformation of the most favourably oriented martensite would be expected to occur at the expense of unfavourably oriented martensite phase and/or retained high temperature phase. Based on their result, it can be seen that after giving 3% total elongation, at room temperature the integrated intensities of (020), (111) and (002) martensite diffraction lines increased at the expense of the (110), integrated intensity.

According to Kaplow (4), there is a shift in X-ray intensity from $\{hkl\}_{R}$ to $\{\bar{h}kl\}_{R}$, on tensile-stressing the specimen below T_{R} . This is consistent with stress-induced domain reorientation, resulting in a preferred arrangement of domains in the R-phase. The geometry of the situation is explained schematically in figure 13. A rhombohedral distortion of the cubic unit cell can be regarded as an elongation along a <111> $_{B2}$ direction. Below T_{R} , <111> $_{B2}$ directions are converted to <111> $_{R}$ or < $\bar{l}11>_{R}$ while (011) $_{B2}$ planes become either (011) $_{R}$ or (011) $_{R}$. Thus in a given crystal grain, domains may form with either <111> $_{R}$ or < $\bar{l}11>_{R}$ along the <111> $_{B2}$ axis, the probability being 1/4 for <111> $_{R}$ and 3/4 < $\bar{l}11>_{R}$. The multiplicity factor for (011) $_{R}$ and (011) $_{R}$



Figure 13. Schematic of R-phase strain accommodation during tensile straining.

approximately equal number of $(011)_R$ and $(0\bar{1}1)_R$ planes parallel to the diffracting surface, resulting in similar Xray intensities for the two diffraction peaks initially. The $(hkl)_R$ have larger interplanar spacing than $(\bar{h}kl)_R$ planes, and hence when aligned, are more accommodating with respect to the external tensile stress. The above changes are reflected in the increase of the $(0\bar{1}1)$ X-ray intensity and the corresponding decrease of the (011). They also observed that the martensite intensities vary linearly with strain, i.e., the amount of martensite formed is proportional to the induced strain.

2

3-4 Two-Stage Yielding in Stress-Strain Curves.

Otsuka, et al (14) reported that there are two stages in the stress-strain curve for the $Ti_{50}Ni_{47}Fe_3$ alloy. In the first stage, a small strain appears at a low stress. In the second stage there is a large strain at higher stresses. According to them, the first stage was interpreted as corresponding to the rearrangement of R-phase variants into a variant more favourable under the applied stress, and the second one due to stress-induced martensitic transformation. This interpretation is supported by the fact that test temperature lies between M_s and T_R , the first stage being associated with a small strain and second, with a large strain, and the critical stress for the second stage having a positive

temperature dependence.

Otsuka, et al (13) also reported that there are two stages in the stress-strain curve for a binary NiTi alloy. A clear two-stage yielding was observed, reproducibly, at a temperature below the T_R point. The pseudoelasticity associated with the martensitic transformation appears at temperatures above A_r but the pseudoelasticity associated with the R-phase transition is not clearly observed even above T_R . The lack of clear evidence for the pseudoelastic behavior for the first stage may be due to the following two reasons:

1) the transformation strain associated with the stressinduced R-phase is so small that it is hard to detect the pseudoelastic strain in the first stage.

2) micro-plastic deformation induced during the preceding tensile test may affect the following deformation in the first stage.

3-5 Thermal Cycling

Wayman, et al (10) reported that additional thermal cycling further depressed the M_s temperature and increased the resistivity peak height. The most obvious feature of the thermal cycling was that the resistivity peak was enhanced, and in no case did the peak appear upon heating.

Sandrock, et al (30) have attributed this peak to a

softening of vibrational modes, and have suggested that the peak behavior is intrinsic, but masked by the onset of the martensitic transformation. The peak becomes more evident upon subsequent cycles, simply because the M is lowered.

Buehler and Wang (61) noted that thermal cycling within the transition range increased the area under the cooling leg of the electrical resistance curve and lowered the temperature value of its peak. Perkins (62) subsequently showed that such thermal cycling produced dislocations.

Mukherjee, et al (63) showed that with increasing cycles the hardness level of the parent phase of the alloy increased and they concluded that interfacial dislocations are left behind during successive reversals.

Goldstein and coworkers (58) reported that internal stresses can be generated in nickel-rich, supersaturated, near-equiatomic TiNi alloys by the early stages of precipitation of TiNi₃ during annealing. Thus a specimen studied at room temperature, for the shape memory effect, may have residual stresses which could have originated from one of the following sources:

1) incomplete annealing.

2) precipitation hardening.

3) cold work after annealing treatment.

They also noted that matrix composition and stresses present following annealing are interacting parameters which influence the transformation structures formed and the

temperatures at which they form.

3-6 Trasmission Electron Microscopy Analysis.

Wayman and coworkers (64) reported that the sequence of transformation events (upon cooling) in the $Ti_{50}Ni_{47}Fe_3$ alloy were thus described as follows: Parent phase (CsCl type) \rightarrow incommensurate phase (distorted cubic) \rightarrow commensurate phase (rhombohedral) \rightarrow martensitic phase (monoclinic, B19'). They also reported that three kinds of internal defects appeared in the $Ti_{50}Ni_{47}Fe_3$ martensite: (111) transformation twins, stacking faults on the (001) basal planes, and APB's. They proposed that three-dimensional charge density wave phenomenon and associated phase transitions were involved in the premartensitic behavior of the NiTi alloys. The first of two premartensitic transition was suggested to be a second order "normal-to incommensurate" transition. A second premartensitic transitions was thought to be a first order "incommensurate-to-commensurate" transition.

Sinclair, et al (65) proposed that the extra reflections observed in electron diffracion patterns of NiTi above M_s were interpreted in terms of lattice displacement waves (LDW) confined to discrete regions of 100-500 Å in diameter. LDW's of the type 1/2<110><110>, 1/2<110><001>, 1/2<111><111> and 1/3<112><111> were associated with atomic motions of the subsequent martensitic reaction.

4 EXPERIMENTAL PROCEDURES

Two NiTi alloys of slightly different compositions were used in this research.

The chemical compositions of these two alloys are shown in Table I.

Alloy Composition	A w/o	B w/o
Nİ	53.70	54.00
Ti	45.70	45.60
Fe	.20	.10
Al	0	.10
Si	. 30 ·	.10
С	.02	.09
S	.007	.008

Table I. Alloy composition.

The specimens were hot rolled. Finally the specimens were reduced to the final thickness (1mm) by cold working (30% reduction) and cut by a shear machine to get the required dimension of 1mm x 10mm x 60mm. The specimens were mechanically polished to remove the oxidized layer and encapsulated in a quartz tube under vacuum to avoid oxidation. Then the samples were annealed for 1 hour at

oxidation. Then the samples were annealed for 1 hour at 450°C, 500°C, 550°C, and 600°C respectively followed by quenching in water at room temperature.

Prior to the X-ray diffraction study, the samples were mechanically polished and etched. X-ray diffraction measurements were made by mounting the samples on a heating stage with a strain device on a G.E. diffractometer as depicted in figure 14. Two different testing temperatures were chosen: 24°C and 32°C. The sample temperature was controlled by using a sensitive temperature controller attached to a hot air blower. A thermocouple was attached to the back surface of the sample. This sensing thermocouple controlled the on off switch of the blower via the temperature controller.

For Differential Scanning Calorimetry (DSC), the specimens were cold worked and were cut by a shear machine to prepare small pieces weighing approximately 8 to 12 mg and then annealed at four different temperatures. This size could fit into the pan of the Differential Thermal Analyzer.

The equipment used was a Dupont 990 Differential Thermal Analyzer. The heating and cooling rates were 10° C per minute. For specimens having a rather low M_s temperature, a cold cell filled with either liquid N₂ or dry ice and alcohol was used to provide adequate cooling.

For the tensile test, the specimens were cold worked and were cut by a shear machine to produce a size of $1 \times 3 \times 50$ mm



Figure 14. Strain device on a G. E. diffractometer.

and then annealed at four different temperatures. Specimens were deformed by tensile elongation in an Instron Tensile Testing Machine using a friction grip. The strain rate was maintained at 8.33 x 10^{-3} sec⁻¹. The extent of deformation ranged up to about 10% elongation.

Thin foils for TEM study were obtained from these specimens by the following procedure. The samples were first mechanically polished on a series of 120, 240, 400, and 600 grit SiC papers to reduce the thickness to ~ 0.15mm. Discs of 3mm diameter were punched out. After a vacuum annealing, the discs were thinned in a solution containing 7% perchloric acid in acetic acid with 40V applied voltage at room temperature using a Tenupol 2 electropolisher. The foils were then examined in a Hitachi H-800 electron microscope operated at 200 KV. 5 RESULTS

5-1 Differential Scanning Calorimetry

Differential scanning calorimetry results show two exothermic peaks during cooling in specimens annealed at 450° C, 500° C, and 550° C, and one exothermic peak during cooling in the specimens annealed at 600° C, in both alloys A and B (see Table II and III). Examples of these calorimetric peaks for alloys A and B, annealed at 450° C, 500° C, 550° C and 600° C are shown in figures 15 and 16.

With the help of calorimetric studies, the heat effects associated with the formation of an intermediate R-phase can be isolated from that of the martensitic transformation, in the transformation sequence of the parent to the martensite phase transition.

It can be seen that the two cooling peaks are well separated on the temperature axis. The separation interval between the first and second peak becomes smaller with increasing annealing temperature as shown in figures 17 and 18. The annealing temperature is effective in making the Rphase appear over a wide temperature range. It is observed that the M_s temperature increases monotonically with increasing annealing temperature in alloy A but in alloy B this relationship is more complex. The temperature range over which the R-phase is stable gets wider with decreasing

transformation	annealing temperature (^O C)			
temperature	450	500	550	600
TT1 (T _R)	45	38	35	34
TT2 (M _S)	0	4	16	-

Table II. Calorimetric data for alloy A showing effect of annealing temperature.

Table III. Calorimetric data for alloy B showing effect of annealing temperature.

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transformation	annealing temperature (^O C)			
temperature	450	500	550	600
TT1 (T _R)	37	21	-2	10
TT2 (M _S)	-26	-34	-47	-3



Figure 15-1. Results of differential scanning calorimetry of alloy A, annealed at 450°C and 550°C.



Figure 15-2. Results of differential scanning calorimetry of alloy A, annealed at 500°C and 600°C.

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Figure 16-1. Results of differential scanning calorimetry of alloy B, annealed at 450°C and 550°C.

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Figure 16-2. Results of differential scanning calorimetry of alloy B, annealed at 500°C and 600°C.



Figure 17. Change in T and M temperature with increasing annealing temperature in alloy A.



Figure 18. Change in T and M temperature with increasing annealing temperature in alloy B.

annealing temperature (see figures 15 and 16). This phenomenon is analogous to the effect observed when a third element is added to the alloy system (13).

These results also indicate that with decreasing annealing temperature the difference in the the T_R and M_S temperatures increases. This is also achievable in NiTi alloys by addition of a third element, which causes the difference in the T_R and M_S temperatures to increase (13).

In alloy A, the T_R temperature decreases with increasing annealing temperature, but the M_s temperature increases. Loci of these two temperatures intersect at one particular temperature. Thus, annealing at or above 600°C produces a β phase which can directly transform to martensite without the intervention of the R-phase

In alloy B, initially both M_s and T_R decrease with increasing annealing temperature. But at temperatures above 550° C, the M_s and T_R temperature starts to increase with increasing annealing temperature. The exact cause for this inflexion point is not known. However, precipitation of the NiTi₂ phase within the alloy matrix might be the cause since reflexions from NiTi₂ phase is clearly seen in the X-ray diffraction pattern of the sample annealed at 550° C to 600° C.

The other important observation regarding these peaks is that the combined enthalpy change during cooling is exactly equal to that during heating.

The calorimetric results for A and B alloys are
summarized in tables IV and V. The measured enthalpy changes are designated as ΔH_1 and ΔH_2 on cooling and ΔH_2 on heating.

The total enthalpy change increases with increasing annealing temperature. It is also observed that the enthalpy change in the formation of R-phase is much smaller than that due to martensite transformation.

5-2 The Change of X-ray Diffraction Pattern with Increasing Strain.

Three types of transformations, due to introduction of stress, have been observed. These are:

- 1) parent phase to martensite.
- 2) parent phase to R-phase to martensite.
- 3) R-phase to martensite.

Figures 19 and 20 respectively show the change in X-ray diffraction peaks, with increasing strain, for specimens annealed at 450° C, 500° C, 550° C and 600° C for 1 hour (for both alloys). It is observed that the intensities of the side peak of (011)_{B2}, resulting from R-phase transition, and the peaks from martensite phase, shift while the intensities of the peaks from the parent phase decrease with increse in strain. All X-ray diffraction peaks corresponding to the B2 phase are accountable. All 20 values observed, correspond to those calculated in terms of the d-spacing of the B2 phase and the calculated intensities (as shown in table VI) compare well

Table IV. The calorimetric results for alloy A (53.70% Ni,45.70% Ti); various enthalpy changes.

Annealing Temp.	Enthal C AH.	Lpy Change al/g	A 11
C	1	1 ''2 ·	Δ'nr
450 ⁰ C	1.64	5.08	6.72
500 ^o c	2.03	5.23	7.26
550 ^o c	1.70	5.82	7.52
600 ^o c		9.15	9.15

Table V. The calorimetric results for alloy B (54.00% Ni, 45.60% Ti); various enthalpy changes.

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Annealing Temp.	Enthal C	.py Change :al/g	
°c	AH ₁	ΔH ₂	∆ ^H r
450 ⁰ C	2.37	3.80	6.17
500 °c	2.53	4.20	6.73
550 °c	2.10	5.35	7.45
600 ^o c		8.66	8.66



Figure 19-1. X-ray diffraction VS strain. Sample annealed at 450°C and tested at 24°C. Alloy A.



Figure 19-2. X-ray diffraction VS strain. Sample annealed at 500°C and tested at 24°C. Alloy A.



Figure 19-3. X-ray diffraction VS strain. Sample annealed at 550°C and tested at 24°C. Alloy A.



Figure 19-4. X-ray diffraction VS strain. Sample annealed at 600°C and tested at 24°C. Alloy A.



Figure 19-5. X-ray diffraction VS strain. Sample annealed at 450°C and tested at 32°C. Alloy A.



Figure 19-6. X-ray diffraction VS strain. Sample annealed at 500°C and tested at 32°C. Alloy A.



Figure 19-7. X-ray diffraction VS strain. Sample annealed at 550°C and tested at 32°C. Alloy A.



Figure 19-8. X-ray diffraction VS strain. Sample annealed at 600°C and tested at 32°C. Alloy A



Figure 20-1. X-ray diffraction VS strain. Sample annealed at 450°C and tested at 24°C. Alloy B.



Figure 20-2. X-ray diffraction VS strain. Sample annealed at 500°C and tested at 24°C. Alloy B.



Figure 20-3. X-ray diffraction VS strain. Sample annealed at 550°C and tested at 24°C. Alloy B.



Figure 20-4. X-ray diffraction VS strain. Sample annealed at 600°C and tested at 24°C. Alloy B.



Figure 20-5. X-ray diffraction VS strain. Sample annealed at 600°C and tested at 32°C. Alloy B.

h k l	d _{cal}	^d obs	Relative intensity %
1 1 0	2.13	2.10	100
200	1.51	1.50	4
2 1 1	1.23	1.22	20
220	1.07	1.06	7
3 1 0	0.95	0.95	3
222	0.87	0.87	10

Table VI. Comparison of observed d-spacings with calculated ones (B2).

CsC1 (B2) a_o = 3.015

with the observed intensities.

The peaks from the X-ray diffraction pattern of the martensitic phase can be indexed as shown in table VII.

As the peaks from the R-phase are very weak, they are very difficult to index. Therefore, in this case the $(011)_{B2}$ peak splitting in the X-ray diffraction pattern and electron diffraction pattern are used to identify the existence of the R-phase. This is because the $(011)_{B2}$ peak splitting has been associated with a further phase transformation, i.e., from the B2 to a rhombohedrally distorted phase (4).

Fortunately, at larger strains (say ~9%), the peaks from martensite phase are intense enough to be indexed and thus the location of these martensite peaks could be interpolated at smaller strains. Thus, knowing the martensitic and β -phase peak positions, the very weak R-phase peaks could be tentatively identified. Finally, the results of this work has been compared with the results for thermally induced transformation obtained by Otsuka et al (23). Both results show good agreement with each other in d-spacing. However, relative intensities of the martensitic peaks obtained by strain are different from those for thermally induced transformation. For example, $(020)_{\mu}$ peak is the highest intensity peak in the present work but (111), is the highest one in Otsuka's work. This is believed to be due to the formation of preferred variants (resulting in a strong texture) in the stress induced transformation.

	Present Study		Otsuka	, et al (23)
h k l	d _{obs}	Relative intensity % (observed)	d _{obs}	Relative intensity % (observed)
1 1 0	2.32	5	2.34	18 .
002	2.28	7	2.30	64
1 1 Ī	2.16	8	2.18	81
020	2.05	100	2.06	55
1 1 1	2.01	45	2.01	100
1 1 2	1.66	2	1.73	12
022	1.53	5	1.53	24
200	1.43	3	_	-

Table VII. Comparison of observed d-spacings for stress-induced martensite with those for thermally induced martensite (reported by Otsuka, et al(23)).

monoclinic

a	=	2.889
b	=	4.120
С	=	4.622
β	=	96.8 ⁰

An inhomogenious transformation, in the form of banded surface markings is observed during stress induced transformation as shown in figure 21. A larger volume percent of martensite is formed inside the band. This is demonstrated by X-ray diffraction pattern taken from the banded region (see figure 22).

5-3 Observation of Internal Structures by Transmission Electron Microscopy

Two slightly different samples were annealed at four different temperatures, and the internal structure showed a single phase of the B2 type, with precipitates and dislocations. This type of structure was also reported by Otsuka, et al (23). This is clearly shown in figure 23 for alloy A which has a transformed needle like R-phase, since room temperature is located between T_{R} and M_{S} points. The results for alloy B were the same except for the absence of a transformed phase, because the M temperature is much lower than the room temperature. While alloy A exhibited a fine and scattered distribution of precipitates and the presence of transformed needle like R-phase, alloy B showed a dense distribution of the same, along with a large number of dislocations as shown in figure 24. Figure 25 shows a single phase of the B2. 1/2(111) superlattice reflections were revealed after 10 thermal cyclings, in alloy B as shown in



Figure 21. Banded surface marking (similar to Lüder band) observed in alloy B. Magnification x250.



Figure 22-1. X-ray diffraction pattern from an area within the band. Sample annealed at $600^\circ C$ and strained and tested at $24^\circ C$. Alloy B.



Figure 22-2. X-ray diffraction pattern from the unbanded area. Sample annealed at 600°C and strained and tested at 24°C. Alloy B.







a)



ь)

Figure 24. a) Transmission electron microscoph of alloy B annealed at 500°C showing a high dislocation density.
 b) Transmission electron microscoph of alloy B annealed at 600°C showing both dislocations and

precipitates.



a)



b)

Figure 25. a) bright field image of alloy B annealed at 550°C. b) diffraction pattern of the same area showing the B2 reflection in the [111]_{B2} zone. figure 26. This reflection became stronger on thermal cycling, corresponding to a marked increase in the magnitude of the premartensitic electrical resistivity peak (37). Sharp diffraction spots indicate a rearrangement of dislocation which minimizes the stress field present around them after annealing treatment. Distorted parent phase diffraction spots, after thermal cycling, indicate that eigen-strain (stress-free strain) is introduced after thermal cycling. These diffraction spots, however, are sharper in annealed samples when the repeated transformation induced dislocations are absent.

5-4 Stress-Strain Behavior Associated with Stress Induced Phase Transformation

Two similar alloys used in this investigation show different deformation behavior, which is shown in figures 27, 28, 29, and 30, as a function of annealing temperature and thermal cycling. It is observed that there is no two stage yielding in the annealed samples in alloy A, but there is a two stage yielding after thermal cycling. On the other hand, there is a two stage yielding in both annealed and thermally cycled samples in alloy B.

The variation in the stress-strain curve due to thermal cycling is similar for alloys A and B:

In the initial stages, for very low strains, the stress



a)



ь)

Figure 26. a) bright field image of alloy B annealed at 500°C.
b) diffraction pattern of the same area showing the 1/2 B2 extra reflections in the [111]_{B2} zone axis after 10 thermal cyclings.



Figure 27-1. Stress-strain curves in alloy A, annealed at 450°C, and 500°C.

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Figure 27-2. Stress-strain curves in alloy A, annealed at 550° C, and 600° C.



Figure 28. Stress-strain curves after 10, 30 and 50 thermal cycles in alloy A, annealed at 500°C.



Figure 29. Stress-strain curves in alloy B, annealed at 450°C, 500°C, 550°C and 600°C.



% STRAIN

Figure 30. Stress-strain curve after 10, 30 and 50 thermal cycles in alloy B, annealed at 500°C.

level for a given amount of strain is very similar, for samples cycled 10, 30, and 50 times. Both alloys exhibit the same behavior. However, at higher strains the difference in the stress, for a given strain is large. This is because of the phenomenon of work hardening.

In alloy A, two stage yielding is pronounced after thermal cycling, but the shape of the stress-strain curves is similar, irrespective of the number of thermal cycles. In alloy B, two stage yielding still exist after thermal cycling, but the stress-strain curve after 50 thermal cycles does not show two stage yielding.

It is quite clear from figures 29 and 30 that the greater the number of thermal cycles, higher is the stress for the same amount of strain, at higher strain values. The phenomenon is analogous to work hardening, in which the parent matrix is "transformation hardened" through repeated transformation. This hardening could be conceived of in term of structural defects such as interfacial dislocations, which accumulate during repeated transformations. So the dislocation entanglements increase the critical stress and therefore the strength. This behavior is identical to that exhibited by the hardness values as a function of thermal cycling as reported by Mukherjee, et al (49). They observed that the hardness progressively increased with increased number of transformation cycles. The rate of increase in hardness, however, is rapid during the initial few cycles and

it slows down as the number of transformation cycles increases.

5-5 Formation of Banded Surface Marking.

As has been mentioned before, unique bands are formed during elongation as shown in figure 31. These bands are quite similar to Lüder's band, except that within these bands, phase transformation occurs.

It is observed that there are some specific characteristics of these bands:

- 1) The bands make 45° angles with the stress axis.
- 2) No new bands are developed with increasing strain.
- 3) The bands appear with ~2% strain and disappear with ~5% strain.
- 4) The bands become deeper and broader simultaneously and then shallower and finally disappear with increasing strain.
- 5) The bands disappear with the release of strain, in samples annealed at temperatures below 600°C. The bands do not disappear completely with the release of strain, in samples annealed at temperatures ≥ 600°C.



6 DISCUSSION

It has been suggested in the past that premartensitic transformation, in NiTi alloys, is observed only when the martensitic start temperature is suppressed either by alloy additions (such as Fe) or by thermal cycling between ${\bf A}_{_{\rm S}}$ and A, (13). However, we have clearly demonstrated, from our calorimetric results, that for a given alloy composition, the premartensitic transformation temperature (T_c) is a strong function of annealing temperature (see figures 15-1, 15-2, 16-1, 16-2). This is an important result because some of the controversies regarding absence or presence of premartensitic transition (during thermally induced or stress induced transformations) are most likely related to the uncertainty of the initial conditions (i.e. annealing temperature, residual stress etc.) of this alloy. To study effects of residual stress on the transition temperatures after annealing, each sample was given a 30% cold reduction before annealing. For the near-equiatomic NiTi alloy, it is shown (figure 17) that the premartensitic transformation temperature, T, in alloy A, decreases monotonically up to an annealing temperature of about 600°C, where as the martensitic start temperature, M, increases monotonically up to about 600°C. Thus, a sample annealed at a temperature T≥600°C, martensitic transformation occurs directly from the parent phase (B2) without an intervening premartensitic
change. For a slightly different chemical composition (alloy B), on the other hand, the premartensitic transition persists even for annealing temperatures greater than 600° C (see figure 17). Further, the M_s temperature first decreases up to about 550°C and then increases. For alloy A, premartensitic transformation, under an applied stress, is not expected if the samples are annealed at temperatures greater than or equal to 600° C. But for alloy B, premartensitic transformation will be observed for the same annealing temperature ($\leq 600^{\circ}$ C).

How are these two transformation temperatures T_{R} and M_{S} affected by the annealing temperature and dislocation content? Transmission electron microscopic observations indicate that the microstructure of alloy A at room temperature, (~23°C) consists of parent B2 phase, particles of precipitated NiTi, phase and some needle-like "R-phase". Please, note that M temperature of alloy A is below room temperature. A strain contrast is observed to accompany both the NiTi, precipitates and the R-phase. These results are consistent with those reported by Otsuka and Miyazaki (13). Electron microscopic observation of alloy B shows, in addition to precipitates, a dislocated substructure for sample annealed at 500°C and 600°C (figures 24 (a) and 24 (b)). The 600°C annealing, of deformed B alloy, produces a markedly dislocated substructure and no indication of Rphase. As can be seen from figure 18, the R-phase transition

temperature of B alloy, annealed at 600°C, is below room temperature.

From the results, observed for alloy A (T_R decreases and M_s increases with increasing annealing temperature), it can be speculated that during annealing, dislocation rearrange and some specific dislocation sites become potent embryos for martensite. These potent embryos become martensitic nucleation sites and thus M_s temperature increases. To the contrary, a lack of potent embryonic sites may allow a homogeneous fluctuation to occur in the presense of a thermodynamic driving force. The thermodynamic driving force exists because the M_s temperature is always lower than the "equilibrium" temperature T_0 as shown in figure 32, where ΔG_m^{P-M} and ΔG_m^{M-P} are the nucleation free energies of the forward and reverse transformation, respectively.



Figure 32. Schematic presentation of molar Gibbs free energy, G VS temperature, T, showing T, M and nucleation free energy ΔG_m^{P-M} of parent to martensite and ΔG_m^{M-P} is that for martensite to parent phase.

The initial decrease of M_s with increasing annealing temperature, in alloy B, can be explained by invoking the well known result (66) that M_s is depressed for a very large plastic deformation or a very high dose of radiation damage. A random array of dislocations, lying in the habit plane of the martensite, can impede the propagation of martensite interface in an analogous way that dislocations can hinder slip and produce work hardening. At some higher annealing temperatures, excess random dislocations anneal out and some others assume the configuration necessary for martensitic embryos. There after, M_s increases again with increasing annealing temperature as in alloy A. It is conceivable that impurity atoms in alloy B, hinder dislocation annealing and or rearrangement untill about 550°C annealing temperature is reached.

The role of dislocations, in altering T_R and M_S temperatures, is further demonstrated by the fact that thermal cycling between A_r and M_r systematically lowers M_S temperature in NiTi alloy (65). It has been suggested (65) that each phase reversal introduces some dislocations in the alloy. Either transformation train induced dislocations or misfit (interfacial) dislocations are responsible for this increase in dislocation density.

X-ray diffraction studies on thermally induced phase transformation (3, 4), show splitting, broadening and shifting of the (011), peak over a temperature range slightly

above the M temperature. The peak splitting is interpreted in term of a rhombohedral distortion of the B2 unit cell. Salamon, et al (67) suggested that this splitting might be due to a more complex crystallographic change. But present Xray diffraction studies, related to stress-induced transformation, indicated some subtle differences in this alloy compared with the thermally induced phase change. There was a general sharpening and gradual overlapping of the (011) and (011) peaks during the progress of stressinduced transition and phase transition proceeds differently. depending on the deformation temperature. Stress induced transformation above T is from B2 to R-phase to martensite, shows sharpening, overlapping of (011), and (011), peaks followed by a decrease in the intensity of the (011), continuously, until the onset of martensite phase transition. Alternatively, at temperatures below T, a direct conversion to martensite occurs with a sharpening of martensitic reflections followed by a decrease in the intensity of (011) . These two results imply that both stress-assisted Rphase as well as martensite phase transformations occur over an applied stress range. Thus, the R-phase is stable over a stress and temperature range during the stress-induced transformation (akin to its stability over a temperature range during the thermally-induced transformation). It must be noted that this stability range is strongly influenced by the annealing temperature as has been discussed earlier.

Below T_R , R-phase to martensite transformation results in an initial sharpening and shifting of $(011)_R$ and $(0\bar{1}1)_R$, followed by a decrease of intensity of these peaks. Contrary to the fact that there is a shift in the X-ray intensity from $\{hkl\}_R$ to $\{\bar{h}kl\}_R$, it is observed that there is no such shift during deformation above T_R temperature.

One significant difference in X-ray diffraction patterns between thermally induced and stress induced transformation is that the strongest intensity peak is the (111), in the thermally induced phase transformation (23), but the strongest peak is (020) in stress induced phase transformation. There are two possibilities which might explain this difference. First, it might be that the atom positions within the unit cell of the stress-induced martensite is different from those proposed by Otsuka, et al (23) for the thermally-induced martensite. It was reported that the atomic arrangement in the unit cell proposed by Otsuka, et al might not be correct since a forbidden reflexion, (001), for the proposed structure was observed in the X-ray diffraction patterns (1). A second, and more likely explanaion is that a texture develops during stress-induced transformation, since a selected number of martensite variants are present. During the thermally-induced transformation, all 24 variants of the martensite are equally probable. However, during stress-induced transformation, only those habit planes which are favorably oriented with respect

to the stress-axis are activated.

The macroscopic mechanical response of shape memory alloy, such as the NiTi, is dominated by the martensitic transformation. The nature of this deformation behavior, in tension, is schematically shown in figure 33.



Figure 33. Schematic diagram showing the stress-strain response of NiTi (equiatomic) alloys.

The region A (in figure 33) is the elastic region. In the vicinity of B an "yielding" occurs. However, this yielding must not be confused with the plastic yielding in normal alloys. In fact at $\sigma_{_{\rm H}}$, a stress induced martensitic transformation occurs (without generating dislocations). The region B to C is associated with transformation strain $\epsilon_{_{\rm T}}$ which is fully recoverable upon heating to a temperature T>A_f. The region CDE is the normal plastic deformation (dislocation generation and motion) with a plastic yield stress $\sigma_{_{\rm V}}$, an ultimate tensile strength $\sigma_{_{\rm HT}}$ and finally at

point E a fracture occurs. Thus, the region of interest to us is OABC.

Somewhere near the point B, stress induced martensitic transformation occurs. If an applied stress (under certain conditions of thermal and mechanical histories) can also induce the R-phase prior to the martensitic transformation, then an observable discontinuity or a change of slope may be expected in region. Mukherjee, et al (18) have recently shown a detectable change in temperature rise during stress-induced transformation in a NiTi alloy. They have concluded the existance of a premartensitic phase during deformation induced transformation. Actual discontinuities in σ VS ϵ plot of NiTi alloys have also been reported by Otsuka, et al (13).

Our observations indicate, once again, that the annealing temperature has a marked effect on the stressstrain diagrams as shown in figures 27, 29 and 30. It is found that within the limit of experimental resolution, no detective discontinuity or change of slope, identificable with premartensitic transformation, exists in alloy A. A detectable change of slope, however, is found in this alloy after thermal cycling between 373° K and 77° K (see figure 28). It must be noted that such a thermal cycling depresses the M_s temperature and thus enhances the R-phase (or premartensitic phase) transition.

Unlike alloy A, alloy B shows a number of discontinuities in the stress-strain diagrams as shown in figures 29 and 30. These discontinuities are reminiscent of repeated yielding or yielding by Lüders band formation in some alloys (1). The fact that indeed a discontinuous "yielding" by a localized bursts of martensitic transformation occurs in this alloy is evidenced by the banded surface markings shown in figure 31. It can be seen (figures 29 and 30) that before the actual plastic deformation occurs in alloy B, there exists a small but detectable yield drop. These behaviors are indicative of a strong interaction between inpurities and dislocation. Such an interaction undoubtedly affects the kinetics, if not the thermodynamics of the martensitic transformation. Thus, an impurity-dislocation interaction can modify the nature of stress-induced martensitic transformation in the NiTi alloys.

7 REFERENCES

- 1) Z. Nishiyama, Martensitic Transformation, Academic Press (1978)
- 2) H. Livingston and K. Mukherjee, J. Appl. Phys., <u>43</u>, 4944 (1972)
- 3) K. Mukherjee, M. Chandrasekran and F. Milillo, "Shape memory effects in alloys" Plenum Press, Jeff Perkin, Ed., 177 (1975)
- 4) Hung C. Ling and Roy Kaplow, Metallurgical Transactions, Vol. 12A, 2101 (1981)
- 5) R. R. Hasiguti and K. Iwusaki, J. Appl. Phys, <u>39</u>, 2182 (1968)
- 6) F. E. Hwang, W. J. Buehler and S. J. Pickart, J. Appl. Phys., <u>36</u>, 3232 (1965)
- 7) D. P. Dautovich and G. R. Purdy, Can. Metall. Q.,<u>4</u>, 129 (1965)
- 8) V. N. Khachin, Y. I. Paskal, V. E. Gunter, A. A. Monasevich and V. P. Sivokha, Phys. Metal Metallog., Vol. 46, 49 (1978)
- 9) V. N. Khachin, V. E. Gunter, V. P. Sivokha and A. S. Savvinov, Proc. of ICOMAT-79, International Conference on Martensitic Ttansformation, Boston, MA., 474 (1979)
- 10) H. C. Ling and R. Kaplow, Metall. Trans., Vol. 11A, 77 (1980)
- 11) C. M. Hwang, M. Meichle, M. B. Salamon and C. M. Wayman, Phil. Mag., <u>A47</u>, 31 (1983)
- 12) M. B. Salamon, M. Meichle, C. M. Wayman, C. M. Hwang and S. M. Shapiro, American Institute of Physics, 223 (1979)
- 13) S. Miyazaki and K. Otsuka, Metallurgical Transactions,<u>17A</u>, 53 (1986)
- 14) S. Miyazaki and K. Otsuka, Philo. Mag. A, Vol.<u>50</u>, 393 (1984)
- 15) G. Thomas, Diffraction and Imaging "Techniques in Materials Science" North-Holland Publishing Company,

S. Amelinckx, R. Gevers and J. Van Landuyt, Ed., 217 (1978)

- 16) L. A. Middleton, N. F. Kennon and D. P. Dunne, Metallography, <u>17</u>, 51 (1985)
- 17) K. Otsuka, T. Sawamura, K. Shimizu and C. M. Wayman, Metallurgical Transactions, Vol.2, 2583 (1971)
- 18) K. Mukherjee, S. Sircar and N. B. Dahotre, Materials Science and Engineering, <u>74</u>, 75 (1985)
- 19) S. Miyazaki, Y. Ohmi, K. Otsuka and Y. Suzuki, Journal De Physique, Dec., C4-255 (1985)
- 20) K. Chandra and G.R.Purdy, J. Appl. Phys., <u>39</u>, 2176 (1968)
- 21) A. Nagasawa, T. Maki and J. Kakinoki, J. Phys. Soc. Japan, <u>26</u>, 1560 (1969)
- 22) S. P. Gupta, A. A. Johnson and K. Mukherjee, Materials Science and Engineering, <u>11</u>, 29 (1973)
- 23) K. Otsuka, T. Sawamura and K. Shimizu, Phys. Status Solidi, a5, 457 (1971)
- 24) R. F. Hehemann and G. D. Sandrock, Scripta Met., <u>5</u>, 801 (1971)
- 25) G. M. Michal and R. Sinclair, Acta Cryst., <u>B37</u>, 1803 (1981)
- 26) T. Saburi and S. Nenno, Scripta Met. Trans., <u>7A</u>, 569 (1976)
- 27) G. M. Michal, P. Moine and R. Sinclair, Acta Metallurgica, Vol. 30, 125 (1985)
- 28) K. M. Knowles and D. A. Smith, Acta Metallurgica, Vol. 29, 101 (1981)
- 29) F. E. Wang, B. F. DeSavaga, W. J. Buehler and W. R. Hosler, Journal of Applied Physics, <u>39</u>, 2166 (1968)
- 30) G. P. Sandrock, A. J. Perkins and R. F. Hehemann, Metall. Trans., <u>2</u>, 2769 (1971)
- 31) C. M. Wayman, I. Cornelis and K. Shimizu, Scripta Met., <u>6</u>, 115 (1972)

32) D. J. Bradley, Acous. Soc. Am., <u>37</u>, 700 (1965) 33) R. J. Wasilewski, Trans. TMS-AIME, 233, 1691 (1965) 34) D. P. Dautovich, Z. Melkvi, G. R. Purdy and C. V. Stager, J. Appl. Phys., <u>37</u>, 2513 (1966) 35) R. J. Wasilewski, S. R. Butler, J. E. Hanlson, Met. Sci. J., <u>1</u>, 136 (1971) 36) H. Warlimont, Materials Science and Engineering, 25, 139 (1976) 37) C. M. Wayman, Mat. Res. Soc. Symp. Proc., Vol. 21, 657 (1984) 38) J. Perkins, Mat. Sci. and Eng., <u>51</u>, 181 (1981) 39) H. Warlimont and L. Delaey, Prog. Mater. Sci., Vol. 18, 113 (1974) 40) C. M. Wayman and K. Shimizu, Met. Sci. J., Vol. 6, 175 (1972) 41) R. J. Wasilewski, Metall. Trans. Vol. 2, 2973 (1971) 42) J. Perkins, Scri. Metall., Vol. 8, 1469 (1974) 43) H. A. Mohamed and J. Washburn, J. Mater. Sci., Vol. 12, 469 (1977) 44) R. J. Wasilewski, S. R. Butler, J. E. Hanlon and D. Worden, Metallurgical Transactions, Vol. 2, 229 (1971) 45) K. H. Eckelmeyer, Scripta Metallurgica, Vol. 10, 667 (1976) 46) K. Melton and O. Merciev, Acta Met., Vol. 29, 393 (1981) 47) H. C. Ling and R. Kaplow, Mat. Sci. and Eng., <u>48</u>, 241 (1981) 48) T. Saburi, M. Yoshida and S. Nenno, Scripta Met., Vol. 18, 363 (1984)

- 49) W. B. Cross, NASA. Spec. Publ., 5110 (1972)
- 50) J. E. Anlon, S. R. Butler and R. J. Wasilewski, Trans. TMS-AIME, <u>239</u>, 1323 (1967)
- 51) W. B. Cross, A. H. Kariotis and F. J. Stimler, NASA CR, 1433, Sep. 1969
- 52) T. Saburi, T. Tatsumi and S. Nenno, Journal De Physique, Vol. 43, C4-261 (1982)
- 53) M. Matsumoto and T. Honma, New Asp. of Mart. Tran., 1st JIM Int. Symp. on MART., Kobe, Japan, 199 (1976)
- 54) K. Mukherjee, Scripta Metallurgica, Vol. 14, 405 (1980)
- 55) D. P. Dautovich, Z. Melkvi, G. R. Purdy and C. V. Stager, J. Appl. Phys., Vol. 37, 2513 (1966)
- 56) R. J. Wasilewski, Met. Sci. J., Vol. 1, 104 (1967)
- 57) W. A. Jonson, J. A. Domingue and S. H. Reichman, Journal De Physique, Dec., C4-285 (1982)
- 58) D. Goldstein, L. Kabacoff and J. Tydings, J. of Metals, March, 19 (1987)
- 59) H. C. Ling and R. Kaplow, Rev. Sci. Instrum, Vol. 51, 1335 (1980)
- 60) C. M. Wayman and I. Cornelis, Scripta Met., Vol. 6, 115 (1972)
- 61) W. J. Buehler and F. E. Wang, Ocean Eng., Vol. 1, 105 (1969)
- 62) J. Perkins, Mat. Res. Soc. Symp. Proc., Vol. 21, 669 (1984)
- 63) K. Mukherjee, F. Milillo and M. Chandrasekaran, Materials Science and Engineering, <u>14</u>, 143 (1974)
- 64) C. M. Hwang, M. Meichle, M. B. Salamon and C. M. Wayman, Res. Mechanica, <u>10</u>, 1 (1984)
- 65) P. Moine, G. M. Michal and R. Sinclair, Acta Metallurgica, Vol. 30, 109 (1982)

- 66) K. Mukherjee, J. Sci. and Indus. Research, <u>32</u>, No 10, 512 (1973)
- 67) M. B. Salamon, M. Meichle, C. M. Wayman, C. M. Hwang and S. M. Shapiro, Int. Conf. on Modulated Structures, Kona, Hawaii, AIP Conf. Proc. No.53, p.223, American Institute of Physics, New York, 1979

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