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The effect of stress on the transformation in nickel-titanium

Chuen-Hsiung Hsu
Iowa State University

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THE EFFECT OF STRESS ON THE TRANSFORMATION IN NICKEL-TITANIUM

Iowa State University

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The effect of stress on the transformation in nickel-titanium

by

Chuen-Hsiung Hsu

A Dissertation Submitted to the Graduate Faculty in Partial Fulfillment of the Requirements for the Degree of DOCTOR OF PHILOSOPHY

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Ames, Iowa
1982
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I. INTRODUCTION

A. Shape Memory Effect

The intermetallic compound Ni-Ti of nearly equiatomic composition undergoes a reversible thermoelastic transition of martensitic type in the vicinity of ambient temperature\(^1\)-3 and exhibits "shape memory."\(^4\)-9 An Ni-Ti alloy near 50 at.% is metastable in the high temperature phase (austenite) at temperatures below \(M_s\) (martensite start temperature) and undergoes the diffusionless martensitic transformation to form the low temperature phase (martensite). When deformed in the low temperature phase (LTP) and heated to above \(A_s\) (austenite start temperature), the free energy difference between these two phases, the strain energy stored in the lattice (either from the previous transformations or from the externally applied stress), and the energy associated with the defects (twins) initiate a reverse transformation to the high temperature phase (HTP), resulting in the recovery of the original configuration.\(^10\)-13 This shape memory effect induces a fairly large force\(^14\),\(^15\) and considerable work can be done.\(^16\),\(^17\) In the past two decades, the research was mainly on property investigation of this solid-solid phase transformation and on applications of the associated shape memory effect. As a result, a diversity of literature and a complete source manual are available.\(^18\)

One noteworthy application of the shape memory effect is in the heat engine devices that convert low grade heat into useful mechanical work.\(^19\)-\(^21\) In the heat engine devices, the Ni-Ti must perform
satisfactorily after undergoing high numbers of transformation cycles combining variations of temperature and stress (transformation fatigue cycling, TFC). Accordingly, the shape memory transformation behavior under uniaxially applied tensile loads was studied using an Ni-Ti tube of composition 54.7 wt% nickel (49.6 at.% Ni). Equiatomic Ni-Ti wires that received millions of cycles of TFC were also used to study the effects of TFC on the transformation behavior and tensile properties. Measurements of electrical resistivity and strain were made during post-TFC transformation cycles under various deadweight tensile loads for wires in as-received (as-TFC'd) and annealed conditions. Tensile tests were also conducted using the as-received and annealed wires. Many of the experimental results obtained can be rationalized in terms of the generation of dislocations.

B. The Role of Dislocations

It is commonly recognized that the shape memory transformation can be readily affected by composition, prior deformation, and the final heat treatment. The effect of deformation is realized through dislocations and associated stress. A directional deformation can produce a dislocation structure that has an effect on the preferred direction of shear during the transformation. An external force is expected to have a similar ordering effect, provided that it is directionally applied. Khachin and Solovev reported that the ordering effect of the external stress is most effective at the nucleation stage of the martensitic transformation. The ordering effect is expected to increase with the magnitude of the external force or the degree of deformation.
The internal stress (residual stress from prior plastic deformation) can also be produced by repeated transformation. As observed by Sandrock et al., repeated temperature cycling through the transformation temperature range is capable of producing a high density of dislocations. It was pointed out by Wasilewski that the dislocations resulting from the martensitic transformation are formed to accommodate the local strain and not in response to any specific shear stress. The dislocations thus formed are sessile, if the temperature is kept low, and they may be accumulated upon repeated cycling. Dislocations also form to accommodate the distorted interfaces between impinging martensite plates, resulting in the formation of dislocation bands instead of dislocation networks. The subsequent transformation then takes place under the influence of the stress exerted by the previously formed dislocations. The interactions of the high density dislocations (under sufficient stress) can result in a strong work hardening. Wasilewski attributed the unusually high fatigue strength of equiatomic Ni-Ti to the rapid work hardening upon cycling under stress.

C. Premartensitic Effect

In the past, observations have been made of an anomalous resistivity peak associated with the transformation of the Ni-Ti shape memory alloy. Wayman and Cornelis showed that repeated cycling through the transformation temperature range could produce the resistivity peak. Sandrock et al. also indicated that the peak maximum temperature corresponds to the \( M_s \) temperature. Dautovich
and Purdy\textsuperscript{50} observed the resistivity peak and suggested the existence of an intermediate phase of rhombohedral structure before the occurrence of the martensitic transformation on cooling the austenite phase. The resistivity peak is one of the premartensitic phenomena, which also include the appearance of an internal friction peak,\textsuperscript{52-55} a peak in specific heat,\textsuperscript{1,56} the decrease in elastic moduli,\textsuperscript{57,58} additional diffuse reflections in diffraction patterns\textsuperscript{47,50,59,60} and the splitting of the x-ray 110 reflection of the austenite phase.\textsuperscript{50,61}

The structure of the equiatomic Ni-Ti is B2 (CsCl)\textsuperscript{1,3,62-66} in the high temperature phase and is a monoclinic distortion of the orthorhombic B19 structure\textsuperscript{22,67,68} in the low temperature phase (martensite or M). The rhombohedral intermediate phase reported by Dautovich and Purdy\textsuperscript{50} was designated as the R phase by Ling and Kaplow.\textsuperscript{61} The transition of B2 phase to R phase was recently studied by Ling and Kaplow\textsuperscript{61} by using telectrical resistance measurements, x-ray diffraction, and shape memory effects. They observed a rapid increase in electrical resistance during the B2$\rightarrow$R transformation. The B2$\rightarrow$R transformation is of second order and is thermally reversible without hysteresis.\textsuperscript{61} Ling and Kaplow\textsuperscript{61} also suggested that the B2$\rightarrow$R transformation, taking place at a critical temperature $T_R$, can occur before or after the martensitic transformation (B2$\rightarrow$M) and persist to very low temperatures. Thus, three transformations may be involved in the HTP-LTP transition: B2$\rightarrow$R, B2$\rightarrow$M, and R$\rightarrow$M.

In a slightly different hypothesis, Mercier et al.\textsuperscript{69} suggested that the B2$\rightarrow$R transformation occurs in a temperature range much higher than
Mg and $T_R$ (Ling and Kaplow's designation). The B2→R transformation is of second order and is accompanied by a decrease in Young's modulus and the forming of the resistivity curve into a plateau. Between $M_S$ and $T_R$, the "lock-in" of the R phase takes place, which is of first order and is accompanied by an increase in resistivity and the appearance of an internal friction peak. This first order "lock-in" transition was also suggested by Salamon et al. in their work with Ti$_{50}$Ni$_{47}$Fe$_3$.

The rapid increase of the resistivity below $T_R$ may be interpreted by using the charge density wave (CDW) model proposed by Salamon et al., in which they suggested that the increase in resistivity is due to the decrease in the number of charge carriers. The decrease in the number of charge carriers results from the higher number of filled states below an energy gap at the Fermi level. The energy gap is formed as a result of the B2→R transformation. Ling and Kaplow proposed that the resistivity increases continuously due to the formation of R from B2 on cooling. The resistivity decreases rapidly when R→M transformation occurs. Therefore, the shape of the resistivity peak is determined by the temperature difference between $T_R$ and $M_S$.

In this study, the $M_S$ temperature for the transformation fatigue cycled wires is quite low compared to $T_R$ for wires that received millions of cycles of TFC. However, depending on the post-TFC heat treatment, the temperature difference may vary, resulting in different shapes of the resistivity peak. For the TFC'd wires, continuous resistivity curves were recorded simultaneously with strain curves, and the two property changes were correlated with one another.
D. Tensile Properties

The equiatomic Ni-Ti exhibits an unusual ductility during deformation near room temperature.\textsuperscript{71-76} Magnitudes of the elongation ranging from about 15\% to more than 60\% have been reported.\textsuperscript{71-73} The first 8-17\% deformation of a polycrystalline Ni-Ti can be recovered through the shape memory effect upon releasing the stress or heating to above $A_F$ temperature.\textsuperscript{73,74,77} Both the large strain and the recovery are believed to be associated with the stress-induced martensitic transformation and its reverse transformation.\textsuperscript{29,76,78-80} It is commonly agreed that the shape of the stress-strain curve for Ni-Ti is strongly affected by the experimental temperature.\textsuperscript{29,76,80} Generally, the stress-strain curve for an equiatomic Ni-Ti sample at temperatures below $M_d$ (the highest temperature at which the martensitic transformation can be stress induced) shows a multi-stage character similar to that for a FCC single crystal.\textsuperscript{76}

Upon stressing an equiatomic Ni-Ti in high temperature phase (below $M_d$), the formation of martensite can be assisted by the applied stress.\textsuperscript{75,77,80} The first yielding corresponds to the formation of the stress-induced martensite.\textsuperscript{76,79,80} The stress required for the stress-induced formation of martensite increases with increasing temperature.\textsuperscript{75} Upon further stressing, the movements and interactions of dislocations\textsuperscript{76,81} result in the strain hardening of the product martensite, and eventually the fracture. When the tensile test starts with the Ni-Ti in fully martensite, the first yielding is due to the reorientation of martensite by twinning\textsuperscript{78} or the growth of favorably oriented martensite.
at the expense of other less favorably oriented martensite, forming a plateau region. Following the plateau region, there is also a strain hardening region. Different opinions were reported regarding the mechanisms responsible for this strain hardening region. Perkins and Mohamed and Washburn considered this region is the elastic deformation of the martensite produced in the previous stage, while Miyazaki et al. and Melton and Mercier suggested different mechanisms. Miyazaki et al. suggested that this strain hardening region results from the further formation of stress-induced martensite and the movements of martensite or twin boundaries without involvement of dislocation movements. However, Melton and Mercier suggested that the dislocation slip is involved in this region. For the second yielding and the subsequent fracture, the opinions are in agreement that the normal plastic deformation caused by dislocation slip is responsible.
II. EXPERIMENTAL PROCEDURE

A. Arc-Melted and Cast Material

1. Transformation strain measurement

The alloy was arc-melted and cast using high purity electron-beam-melted nickel and titanium as the starting materials. Chemical analyses made with material taken from the cast ingot gave 54.7 wt% Ni, 45.0 wt% Ti, and 0.3 wt% impurities by difference. A length taken from the cast ingot was encapsulated in stainless steel under argon and swaged round at 950°C. The round bar was machined into a rough tube and a hardened steel mandrel was inserted. The Ni-Ti was swaged at 950°C over the mandrel following the encapsulation of the assembly in stainless steel under argon. After swaging, the stainless steel jacket was machined off and the tube was trimmed and mechanically polished to give the final dimensions: 0.31 in (0.79 cm) in outside diameter, 0.26 in (0.66 cm) in inside diameter, and 2.07 in (5.3 cm) in length (Fig. 1). The tube was annealed for 4 hours at 1100°C under 2x10^-5 torr vacuum. The microstructure of the sample tube as examined by room temperature optical microscopy is shown in Fig. 2.

The purpose of the experiment was to measure the strain variations during the phase transformation, while the sample tube was temperature cycled through the transformation temperature range under various deadweight tensile stresses. After the loading of a deadweight at a temperature above 100°C, the sample was cooled to about -20°C and then reheated to about 100°C, at which the deadweight load was unloaded. The
Fig. 1. Photograph of the Ni-Ti tube, 54.7 wt% Ni
Fig. 2. Differential interference contrast photomicrograph of polished and etched (4% HNO₃, 2% HF, and 94% H₂O) longitudinal section of Ni-Ti tube, showing the microstructure
transformation strain was measured by foil-type resistance strain gages bonded to the outside surface of the tube. A copper-constantan thermocouple was also cemented on the tube surface for temperature measurement. The Ni-Ti tube was assembled with two grips on the ends and then vertically mounted on a test stand. The grips were designed to allow fluid to flow through while the lower grip was connected to a deadweight holder. The strain in units of microstrain was recorded as a function of temperature by using a digital data logging system. The sample temperature was controlled by circulating preheated or precooled low viscosity silicone liquid through the grips and the tube. The heating or cooling rate was about 2-3°C/min with the liquid circulating at a speed of about 3-5 liters/min.

2. **Transformation volume change measurement**

The purpose of the experiment was to weigh a Ni-Ti sample in a liquid of known density over a temperature range within which the Ni-Ti undergoes phase transformation. According to Archimedes' Law, the apparent weight loss of Ni-Ti in liquid is the weight of liquid displaced by the Ni-Ti. The volume of Ni-Ti at temperature T can be calculated from the measured weight change due to liquid buoyancy and the density of the liquid at the same temperature. The liquid used in this measurement was methylene iodide (CH₂I₂).

The density of the CH₂I₂ liquid as a function of temperature between 100 and 20°C was determined by the weighings of a Ni standard of predetermined mass and volume in the same liquid bath and the same
temperature range. The mass and volume of the Ni standard at ambient
temperature were determined by comparative weighings with a Si standard
of known density and thermal expansion coefficient in air and in a
fluorocarbon liquid ($C_{8}F_{16}O$).\textsuperscript{83}

The Ni-Ti sample used was the same tube as that used in the trans­
formation strain measurements except the tube was about 3 mm shorter
and was electropolished as a final treatment to remove the surface
roughness. The pure Ni standard was a cylinder of 9.5 mm in diameter
and 32 mm in length while the Si standard was a cube of about 16 mm on
each side. The Ni-Ti sample, Ni standard, and the Si standard are shown
in Fig. 3. A photomicrograph showing the grain structure is given in
Fig. 4. Optical microscopic examination made on the samples taken from
longitudinal and cross sections indicated that there was no significant
difference between the grain sizes (average grain diameter ~150 μm) in
these two directions. The Si standard had a density of 2.32912 gm/cm$^3$
and a linear thermal expansion coefficient of $2.56 \times 10^{-6}$ °C$^{-1}$ at 20°C as
determined at the National Bureau of Standards.\textsuperscript{84} The methylene iodide
liquid was selected for the measurements because of its unusually high
density (approximately 3.3 gm/cm$^3$ at room temperature).

A two-pan balance located in a glass case and a liquid bath cell
in a chamber below the glass case were used for the measurements. A
hole was drilled in one of the pans of the balance and the case floor
below the pan. A light chain attached to the pan carrying hook passed
through the holes and extended down into the chamber below the glass
case. A cradle for sample holding was attached to the lower end of the
Fig. 3. Photograph of the Si and Ni standard samples and the Ni-Ti tube.
Fig. 4. Bright field photomicrograph of polished and etched longitudinal section of Ni-Ti tube, showing grain structure
chain by a fine copper wire (0.1 mm in diameter) and a hook. The weighings in air or in liquid (held in a special cell) were carried out in the chamber. The cell contained a copper enclosure, along with heater winding and thermal insulator, and was built inside a Dewar flask, as shown in Fig. 5. Thermocouples were attached to the inside wall of the enclosure to measure its temperature. Thermocouples were also immersed in the liquid to measure the temperature gradients in the radial and vertical directions. The enclosures served to warm up the liquid bath to a desired temperature and provide a low cooling rate to minimize the convection currents in the liquid. Other apparatus used included a power supply and digital temperature indicators.

The experimental procedure consisted of:

(a) Determination of the mass and volume of the Ni standard at 22°C by comparative weighings with the Si standard in air and in fluorocarbon liquid.

(b) Determination of the volume and mass of the Ni-Ti sample at 22°C by weighings in air and in fluorocarbon liquid.

(c) Determination of the methylene iodide liquid density as a function of temperature by weighings of the Ni standard in the liquid over the desired temperature range (100 to 20°C).

(d) Determination of the volume of the Ni-Ti sample as a function of temperature by weighings in the methylene iodide liquid over the desired temperature range (100 to 20°C).

For all the weighings in air and in liquid, the sample holder was weighed alone and with the sample. The difference was taken as the net
Fig. 5. Diagram of cell for weighing in liquid as a function of temperature.
weight of the sample. The variation of air density was also considered to correct the air weighings for air buoyancy.

The transformation volume change obtained by hydrostatic weighing was compared with that deduced from strains measured using strain gages. In the strain gage measurements, a two-gage (90-degree) rosette was bonded to the outside surface of the tube with the gages oriented in axial and circumferential directions. The gages and the sample tube were fired at 130-160°C as required for the curing of the bonding adhesive and a protective coating was applied as a final preparation. The strain as a function of temperature was indicated by a digital strain indicator and recorded by a data logging system. The system was adjusted for zero strain at 100°C.

In step (d) of the hydrostatic weighing and in the following strain gage measurements, the sample was heated to 130-150°C before being transferred to the preheated liquid bath at 100°C in the special cell (Fig. 5). The only difference is that the liquid bath was methylene iodide for the hydrostatic weighings, while it was silicone liquid for the strain gage measurements.

B. Transformation Fatigue Cycled Wires

1. Material characterization

The Ni-Ti wire used in this investigation originated from Timet heat V4609. Sample wire lengths from this heat were TFC'd in uniaxial tension at Lawrence Berkeley Laboratory using several shape memory heat engine devices. The working conditions comprised a length change of about 3
percent between 20°C and 50°C at a frequency of 50-100 cycles per minute. The wires investigated included an uncycled wire and four cycled wires given 1.0, 2.7, 3.7, and 5.3 million such transformation fatigue cycles. The uncycled wire was vacuum annealed for 24 hours at 700°C. The diameter of the wires was about 20 mil (0.5 mm).

The composition of the Ni-Ti wires was determined by wet chemistry analyses to be 54.92 wt% Ni, 44.93 wt% Ti, and 0.15 wt% trace impurities by difference. The trace impurities were determined by spark source mass spectroscopy and vacuum fusion techniques. The trace impurities of higher concentrations are listed in Table 1. The oxygen and carbon of concentration 420 and 225 wt ppm, respectively, were the major impurities.

Table 1. Composition of Ni-Ti wire

<table>
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<th>Trace impurities</th>
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<tr>
<td>Wet chemistry: 54.92 wt% Ni, 44.93 wt% Ti</td>
<td>Mass spectroscopy, wt ppm</td>
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<tr>
<td></td>
<td>C 225</td>
</tr>
<tr>
<td></td>
<td>Co 133</td>
</tr>
<tr>
<td></td>
<td>Fe 126</td>
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<tr>
<td></td>
<td>S 48</td>
</tr>
<tr>
<td></td>
<td>Cu 43</td>
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<tr>
<td></td>
<td>Mo 18</td>
</tr>
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<td></td>
<td>Bi 12</td>
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Vacuum fusion, wt ppm

| O 420 |
| N 45 |
Figs. 6 and 7 show the microstructure of the Timet wire as examined by room temperature optical microscopy. This same microstructure was observed for all of the wires regardless of the amount of TFC. The cross section (Fig. 6) shows numerous dark spots, which have been analyzed to be about 1 μm in diameter and to have a density of about 8×10^6 cm^-2. The longitudinal section (Fig. 7) shows that the feature is elongated in the drawing direction of the wire (wire axis). Further optical examination at higher magnification was carried out using differential interference contrast. The photomicrograph in Fig. 8 is for a wire that was polished and etched with nitric-hydrofluoric acid solution (4% HNO₃, 2% HF, and 94% H₂O). It shows that the features are primarily elongated cavities containing precipitate particles as shown at A. Some banded structure characteristic of twinned martensite is also shown at B in Fig. 8. A transmission electron micrograph showing this twinned structure within a martensite variant is shown in Fig. 9.

The precipitate particles trapped in the elongated cavities (Fig. 8) probably are a complex oxide or nitride phase resulting from the contamination of starting materials. The elongated holes probably are formed either by the tearing of the matrix by the precipitate particles during the drawing action of the wire or as the result of the extraction of precipitate particles during polishing and etching. The fact that the oxygen concentration is high (vacuum fusion analysis result, Table 1) and the titanium oxide (on the starting material) is stable leads to the suggestion of an oxide phase. Similar precipitates were observed by other investigators. Michal et al. suggested that the
Fig. 6. Photomicrograph of polished and etched cross section of Timet V4609 Ni-Ti wire

Fig. 7. Photomicrograph of polished and etched longitudinal section of Timet V4609 Ni-Ti wire
Fig. 8. Timet V4609 Ni-Ti wire, polished and etched (4% HNO₃, 2% HF, and 94% H₂O). Observed at 1000x by differential interference contrast (after Ref. 86)
Fig. 9. Bright field TEM micrograph showing the twinned martensite (after Ref. 86)
precipitates could be Ti$_4$Ni$_2$O$_x$, while Rozner et al.\textsuperscript{91} suggested Ti$_4$Ni$_2$O. Electron microprobe and Auger spectrum analyses indicated that this precipitate was most likely Ti$_4$Ni$_2$O.\textsuperscript{86} The structure of this Ti$_4$Ni$_2$O is f.c.c., as determined by Mueller and Knott.\textsuperscript{87}

2. \textbf{Resistivity and strain measurements}

The Ni-Ti wires were studied in the following conditions: (I) as-received, (II) after 1 hr anneal at 400°C, and (III) the same as II plus an additional 1 hr anneal at 600°C. The resistivity and strain changes during transformation were measured under various uniaxial tensile stresses. The stresses were produced by deadweights using a simple tensioning device, as shown in Fig. 10. The stress levels used in the study were 284, 1150, 3450, 5750, and 8130 psi (1.9, 7.9, 23.8, 39.6, and 56.1 MPa, respectively). Since the wire had to be taut to support the extensometer, no measurements were made under zero stress condition. Nevertheless, the 284 or 1150 psi stresses are believed to give reasonable approximations to the zero stress condition.

For the resistivity measurements, the standard four-point method was used. The voltage contacts were spot welded to the sample wire between the current contacts that were fastened to the sample holder by screws (Fig. 10). The sample wire was connected in series with a 0.1 Ω standard resistor and a constant DC current supply operating at 90 milliamps. The voltage across the standard resistor was regularly checked to verify the current constancy. The voltage across the sample voltage contacts was indicated on a digital voltmeter and fed to a X-$Y_1$-$Y_2$ recorder. The electrical resistance between the voltage
Fig. 10. Tensioning device used to produce deadweight tensile stresses during simultaneous resistivity and strain measurements as a function of temperature.
contacts were determined from the measured sample voltage and the constant current.

The strain was measured by using a modified extensometer in which the arms were insulated from the sample support knife edges. The coil springs in the sample clamps were also replaced to provide the spring loaded plunger with a suitable force for the clamping to wire samples. The extensometer was precalibrated using an extensometer calibrator and a constant voltage power supply such that the output from the extensometer could be converted to length change (or strain). The same power supply with the setting for the output unchanged was used in the subsequent strain measurements. In the strain measurements, the extensometer output was fed through a digital voltmeter and a low pass filter to the X-Y-Y recorder.

The simultaneous measurements of sample resistivity and strain as a function of temperature were carried out with the sample immersed in a silicone liquid bath. The liquid bath was heated by an immersion heater and cooled by liquid nitrogen flowing through cooling coils that were also immersed in the liquid. A motor-driven stirrer was used to stir the bath constantly to reduce the temperature gradient. A copper-constantan thermocouple was placed adjacent to the wire sample to measure the temperature. The thermocouple was connected to a digital temperature indicator and to the X-Y-Y recorder.

The voltage outputs from the thermocouple, extensometer and sample voltage contacts were fed to the X, Y, and Y inputs, respectively, on the X-Y-Y recorder. The sample wire was heated to 100°C under the
lowest stress (284 or 1150 psi), an additional load was added (if necessary) to produce the desired stress level, and the temperature cycling began on cooling. The wire was cooled to about −50°C and subsequently, without interruption, heated back to 100°C to end a temperature cycle. The cooling and heating were controlled to a rate of about 2°C per minute. Continuous curves for electrical resistance and strain change versus temperature were plotted simultaneously on the X-Y₁-Y₂ recorder.

Following the completion of the measurements for wires in the as-received condition, the wires were cleaned, wrapped in tantalum sheet, and vacuum annealed (10⁻³ torr) for one hour at 400°C. The wires were furnace cooled. Resistivity and strain measurements were performed using the same stress levels (1150, 3450, 5750, and 8130 psi, in that order) within the same temperature range (100 to −50°C) after the 400°C anneal. In some cases, a fifth run at the lowest stress (1150 psi) was repeated to study the possible effect of previous four cycles. A second anneal was performed after the measurements in the 400°C-annealed condition. The second anneal also lasted for 1 hr, but at 600°C under 10⁻⁵ torr vacuum. The measurements after the 600°C anneal were generally the same as that for the previous work except that the first and the last runs were under a stress of 284 psi in addition to the four stress levels used before.

3. Tensile tests

Tensile tests were conducted to investigate the effects of prior TFC on the strength and ductility of the wires. The tests included the
sample wires in as-received (as-TFC'd) condition and in annealed condition. The as-received samples included one uncycled wire and wires given 1.0, 2.7, 3.7, and 5.3 million cycles of TFC. The anneal consisted of two separate one hour heatings of the sample wires at 400°C and 600°C under vacuum.

The key characteristic temperatures of the samples had been determined by the electrical resistance and strain measurements prior to the tensile tests. The measurements indicated that, depending on the history, the $M_S$ temperature was between 12°C and 28°C, the $M_F$ at about -20°C, the $A_S$ between 23°C and 50°C, and the $A_F$ at about 60°C. Accordingly, the tests with the samples initially in the high temperature phase were performed at 78°C while tests with samples initially in the low temperature phase were performed at 21°C.

The tests at 78°C were conducted with sample wires immersed in a silicone liquid bath, which was controlled by an immersion heater at 78°C to within ±1°C. At the beginning, the sample together with grips were mounted to the pulling rods and the liquid bath held in a large insulated beaker sitting on a platform was raised to immerse the sample. The liquid bath was then heated up to 78°C, while the sample was subjected to a small load (weight of the lower grip, 0.326 lb or 148 gm). For the tests performed at 21°C, the sample was chilled to the liquid nitrogen temperature and was always kept below ambient temperature (21°C) to ensure that the sample was fully in the low temperature phase before tests. The tests at 21°C were conducted in air.

The grips used in the tests had serrated surfaces in contact with
samples. The gage length was 0.85 cm and the strain rate was $1.1 \times 10^{-4}$ sec$^{-1}$ for tests at 78°C and $0.9 \times 10^{-4}$ sec$^{-1}$ for tests at 21°C. The strain rate was calculated from the crosshead motion, and the strain was calculated from the strain rate and the recorder chart speed.
III. RESULTS AND DISCUSSION

A. Arc-Melted and Cast Material

1. Transformation strain

In this experiment, the sample tube was temperature cycled under various deadweight tensile stresses. Six stress levels ranging from zero stress to 9910 psi were employed. A repeated run was performed at 7670 psi. Before the test, the sample was given 35 transformation cycles. A summary plot of the strain changes in the axial direction during the temperature cycles under tensile stresses is shown in Fig. 11. In the figure, the asterisk and the cross symbols indicate the starting point and finishing point, respectively. The vertical arrows indicate the strain change on loading (open symbols) or unloading (closed symbols). To deduce information from Fig. 11, the characteristic temperatures and strains are defined in Fig. 12. The transformation strain ($\varepsilon_\text{T}$) is given by the average of the strain change on cooling ($\Delta\varepsilon_\text{C}$) and on heating ($\Delta\varepsilon_\text{H}$).

As shown in Fig. 11, the magnitude of the axial transformation strains increases with increasing applied tensile stress. A careful calculation indicates that the transformation strain on cooling ($\Delta\varepsilon_\text{C}$) is larger than the strain recovery ($\Delta\varepsilon_\text{H}$) on heating under the same tensile stress. The magnitude of the unrecovered strain also increases with increasing stress. The average transformation strain as a function of tensile stress is shown in Fig. 13.

In this experiment, the deadweights were applied at a temperature slightly above $A_F$ (austenite finish temperature), which is below $M_d$ (the
Axial strain versus temperature for transformation cycling at various applied tensile stresses for Ni-TI tube, 54.7 wt% Ni. Cooling, open symbols; heating, closed symbols.
Fig. 12. Schematic axial strain versus temperature curves upon cooling and heating.
Fig. 13. Axial transformation strains versus applied tensile stress

\[ \varepsilon_t = \frac{\Delta \varepsilon_C + \Delta \varepsilon_H}{2} \]
highest temperature that the martensite formation can be induced by
stress). The loading temperature was lower (but still above \( M_s \)) for
smaller loads, and increased with increasing load. Therefore, it is
believed that the loadings might introduce a small amount of stress-
induced martensite. This may be confirmed by the comparison between
the fifth and the sixth run. In the fifth run, a 7670 psi tensile
stress was applied at 110°C, while the same stress was applied at 116°C
in the sixth run. Nevertheless, the 7670 psi stress induced a larger
strain upon loading in the fifth run than in the sixth run by a strain
difference of about 0.05%. The difference is believed to be caused by
the larger amount of martensite induced by the stress at a temperature
closer to \( M_s \).

Ideally, the 24 crystallographically equivalent martensite variants
nucleate with equal probability under zero stress. However, under a
directional stress, a fraction of the martensite nucleates and grows with
an orientation compatible with the stress at the expense of those with
less favorable orientations. This results in a local strain in the
direction of stress. The amount of martensite thus formed increases with
increasing applied stress. Besides, during the transformation, more ex­
isting martensite of less favorable orientations is reoriented in response
to the stress. The strain produced by the abovementioned mechanisms in­
increases with increasing stress. The resulting strains plus the possible
growth of twins and the movement of stacking faults result in an
increasing macroscopic strain with increasing applied stress, as shown in
Fig. 13. It was also pointed out by Pops that the volume change caused
by the transformation may produce internal stresses, which may act together with the externally applied stress. However, the internal stresses may be small due to the small volume change accompanying the transformation in Ni-Ti.

Fig. 11 also shows that the magnitude of the unrecovered strain upon heating increases with increasing applied stress. This might be a result of the possible dislocation movements when the applied stress is larger than a certain value, as suggested by Bolling and Richman. The incomplete recovery of the transformation strain was also observed by Khachin and Solov'ev. They suggested that the unrecovered strain is produced by dislocation glide, which is caused by external force during the previous transformation on cooling. A strain resulting from the movements of dislocations could be unrecoverable. The number of the dislocations that move under stress may increase with increasing stress, resulting in the increasing unrecoverable strain.

Normally, under a directionally applied stress there is always a favored orientation for the martensite to form (HTP→LTP) due to the high symmetry in the structure of the high temperature phase. As the applied stress may contribute to the driving force for the transformation, the $M_S$ temperature may increase with increasing stress since a smaller undercooling is needed. Nevertheless, the increase in $M_S$ temperature was not observed except at very low stresses (1690 and 3370 psi) in this experiment (Fig. 14). Since the sample was given 35 transformation cycles before this experiment, it was expected to have a high density of dislocations. The dislocations might have hindered the
Fig. 14. Martensite start temperature versus applied tensile stress
formation of martensite phase, resulting in the decrease in $M_S$ temperature for a higher driving force. However, the decrease of $M_S$ was observed only for stresses above about 3400 psi (Fig. 14). This would suggest that the generation of dislocations during transformation under stress might become significant when the stress increases to above a certain value. The dislocations thus produced will affect the subsequent transformation.

Upon heating, the reverse transformation of the martensite formed under the directionally applied stress will be opposed by the same stress. Therefore, the reverse transformation needs to start at a temperature above the normal $A_S$. The increase in $A_S$ with increasing applied stress is shown in Fig. 15. In Fig. 12, the width of the transformation hysteresis loop is shown as $\Delta T = T_H - T_C$, where $T_H$ and $T_C$ are the temperatures at which 50% of the transformation strain is produced on heating and on cooling, respectively. It appears (Fig. 16) that the width of the transformation hysteresis loop decreases at very low stress (from 26.5°C to 25.5°C) and then increases steadily (from 25.5°C to 29.5°C) with increasing stress. According to Wasilewski, a high density of dislocations can cause the transformation hysteresis loop to broaden by lowering the $M_S$ temperature. In this experiment, however, the broadening of the transformation hysteresis loop was further enhanced by the increase of $A_S$ temperature.
Fig. 15. Austenite start temperature versus applied tensile stress
Fig. 16. Width of transformation hysteresis loop versus applied tensile stress
2. Transformation volume change

a. Mass and volume of the Ni standard  The mass and volume of the Ni standard at 22°C were determined by comparative weighings with the Si standard in air and in the fluorocarbon liquid. The density of the Si standard at 22°C was calculated to be $(2329084 \pm 2) \times 10^{-6}$ gm/cm³ from its density at 20°C, $(2329120 \pm 2) \times 10^{-6}$ gm/cm³, using a linear thermal expansion coefficient of $2.56 \times 10^{-6}$ °K⁻¹. The density and the linear thermal expansion coefficient were previously determined at the National Bureau of Standards (NBS).°

The mass of the Si standard was measured in air and calculated to be $10.00565 \pm 0.00014$ gm using

$$M(Si) = \frac{1 - \frac{d(A)}{d(W)}}{1 - \frac{d(A)}{d(Si)}} M(W, Si)$$

(1)

in which $d(A)$, $d(W)$, and $d(Si)$ are the densities of air, balance weights, and Si standard, respectively, and $M(W, Si)$ is the mass of the balance weights. The derivation of Eq. 1 and the calculation for $d(A)$ are shown in Appendix A. The balance weights were calibrated at NBS and the density of the balance weights was obtained from the NBS calibration.

The volume of the Si standard at 22°C was then calculated to be $4.29596 \pm 0.00006$ cm³ from $V(Si) = M(Si)/d(Si)$. In the calculations, the error involved for $C \pm \Delta C = (A \pm \Delta A) \pm (B \pm \Delta B)$ is estimated as $\Delta C = [(\Delta A)^2 + (\Delta B)^2]^{1/2}$; the error for $C \pm \Delta C = (A \pm \Delta A)/(B \pm \Delta B)$ or $C \pm \Delta C = (A \pm \Delta A)/B \pm \Delta B$ is estimated as $\Delta C = [(\Delta A/A)^2 + (\Delta B/B)^2]^{1/2}$.

For the weighing of the Si standard in air,
and in the fluorocarbon liquid (called LI for convenience)

$$W_{L1}(Si) = M(Si) - d(LI) V(Si)$$

(3)

whereby from Eqs. 2 and 3

$$W_A(Si) - W_{L1}(Si) = [d(LI) - d(A)] V(Si)$$

(4)

Similarly, for the weighings of the Ni standard

$$W_A(Ni) - W_{L1}(Ni) = [d(LI) - d(A)] V(Ni)$$

(5)

Division of Eq. 4 by 5 gives

$$V(Ni) = \frac{W_A(Ni) - W_{L1}(Ni)}{W_A(Si) - W_{L1}(Si)} V(Si)$$

(6)

which gives

$$V(Ni) = 2.97968 \pm 0.00014 \text{ cm}^3 \text{ at } 22^\circ \text{C}.$$  

The mass of the Ni standard is then given by

$$M(Ni) = W_A(Ni) + d(A) V(Ni) = 26.54594 \pm 0.00014 \text{ gm}$$

and the density is given by $$M(Ni)/V(Ni) = 8.9090 \pm 0.0002 \text{ gm/cm}^3.$$ A value of $$8.9081 \pm 0.0002 \text{ gm/cm}^3$$ at 23°C was reported by Kayser et al. from their hydrostatic weighing experiments. Their value becomes $$8.9084 \pm 0.0002 \text{ gm/cm}^3$$ after correction to 22°C using the thermal expansion information reported by Kirby et al. The linear thermal expansion coefficient of Ni
\[ \alpha = \frac{1}{293} \frac{d\ell}{dT} = \beta_0 + \beta_1 T \]  

(7)

in which \( \beta_0 = 9.24 \times 10^{-6} \, \text{K}^{-1} \) and \( \beta_1 = 0.0122 \times 10^{-6} \, \text{K}^{-2} \) were obtained from the least-squares fit to the experimental data between 293-400\textdegree K (20-127\textdegree C), as shown in Fig. 17. Kayser et al. also gave a value of 8.9078 \pm 0.0015 \text{gm/cm}^3 from their x-ray work. Another theoretical value of 8.908 \pm 0.005 \text{gm/cm}^3 at 22\textdegree C can be deduced from the lattice parameter of Ni at 20\textdegree C, \( a_0 = 3.5241 \pm 0.0007 \text{\AA} \) by Donohue,\textsuperscript{97} which is an average value of some 44 determinations.

The density of the fluorocarbon liquid at 22\textdegree C was determined as 1.772 \text{gm/cm}^3 by using Eq. 3. The manufacturer's value is 1.766 \text{gm/cm}^3.\textsuperscript{83}

b. \textbf{Mass and volume of the Ni-Ti}  
The mass and volume of the Ni-Ti sample at 22\textdegree C were also determined by weighings in air and in the fluorocarbon liquid. An equation similar to Eq. 4 for Ni-Ti gives the volume as

\[ V(\text{Ni-Ti}) = \frac{W_A(\text{Ni-Ti}) - W_L(\text{Ni-Ti})}{d(L_1) - d(A)} = 0.59794 \pm 0.00012 \text{ cm}^3 \]

whereby the mass \( M(\text{Ni-Ti}) = W_A(\text{Ni-Ti}) + d(A) V(\text{Ni-Ti}) = 3.84143 \pm 0.00014 \text{ gm} \) and the density \( d(\text{Ni-Ti}) = M(\text{Ni-Ti})/V(\text{Ni-Ti}) = 6.4244 \pm 0.0013 \text{ gm/cm}^3 \).

c. \textbf{Density of the methylene iodide liquid}  
To determine the volume change upon transformation, the Ni-Ti sample was weighed in the methylene iodide liquid (called L2 for convenience) as a function of temperature between 100 and 20\textdegree C, on cooling. For this purpose, the density of the methylene iodide liquid as a function of temperature was
Fig. 17. Linear thermal expansion coefficient of pure nickel as a function of temperature (AIP Handbook, 3rd edition)
determined by weighings of the Ni standard within the same temperature range. The density of the methylene iodide (L2) at temperature T is given by

\[ d(L2, T) = \frac{M(Ni) - W_{L2}(Ni, T)}{V(Ni, T)} \]

in which \( W_{L2}(Ni, T) \) is the apparent weight of Ni in L2 liquid at T and \( V(Ni, T) \) is the volume of Ni at T calculated from the previously determined volume at 22°C using the thermal expansion coefficient given by Eq. 7. The density of the methylene iodide liquid as a function of temperature as determined from the continuous cooling measurements is shown in Fig. 18. Other data by Griffing et al.\(^8\) and Timmermans\(^9\) are also given in Fig. 18 for comparison. The result of the present work and the reference data are in reasonably good agreement.

d. **Transformation volume change of Ni-Ti** For the determination of the Ni-Ti volume change within 100 and 20°C, the apparent weight of the Ni-Ti sample in methylene iodide liquid was measured versus temperature on cooling from 100°C to 27°C. The measured apparent weight versus temperature is shown in Fig. 19. The deviation at about 70°C from the linear decrease of apparent weight is caused by the change in liquid buoyancy resulting from the volume change of the Ni-Ti sample upon phase transformation. A least-squares linear fit was determined for the apparent weights between 100 and 80°C. Fig. 20 shows the deviation of the measured apparent weight from the least-squares fit line, \( \Delta W = W - W_{LS} \), as a function of temperature. The standard deviation from the least-squares fit line between 100 and 80°C is about ±0.083 mg.

An equation similar to Eq. 8 was used to calculate the volume of the
Fig. 18. Density of methylene iodide (CH$_2$I$_2$) versus temperature
Fig. 19. Apparent weight versus temperature of the Ni-Ti tube on cooling in the CH₂I₂ (L₂) liquid.
Fig. 20. Deviation of the apparent weight of the Ni-Ti tube from the least squares straight line fit to data for 80-100°C

\[ \Delta W = W - W_{LS}, \text{mg} \]

\[ W = \text{APPARENT WEIGHT OF Ni-Ti IN CH}_2\text{I}_2 \]

\[ W_{LS} = \text{LEAST-SQUARES FIT FOR 80-100°C} \]

Ni-Ti IN CH\textsubscript{2}I\textsubscript{2}, COOLING

\[ \text{T Temperature, } ^\circ\text{C} \]
Ni-Ti sample at temperature T, which gives

\[ V(Ni-Ti, T) = \frac{M(Ni-Ti) - W_{L2}(Ni-Ti, T)}{d(L2, T)} \]  

(9)

where \(M(Ni-Ti)\) and \(d(L2, T)\) are previously determined and \(W_{L2}(Ni-Ti, T)\), the apparent weight of Ni-Ti in L2 liquid at T, is obtained from the measurements.

The volume of the Ni-Ti sample versus temperature is shown in Fig. 21. It appears that the Ni-Ti contracted upon cooling from 100°C to about 75°C, at which the phase transformation took place causing a volume change in the opposite direction (expansion). The linear thermal expansion coefficient of Ni-Ti between 100 and 80°C may be roughly estimated from a least-squares fit line, which gives

\[ \alpha_{HTP} = \frac{1}{3} \frac{\Delta V}{\Delta T} \frac{1}{V(100°C)} = 1.49 \times 10^{-5} \text{ (°C)}^{-1} \]

The value reported by Wasilewski et al. for their 50.2 at% Ti sample (49.8 at% Ni or 54.9wt% Ni, assuming negligible impurities) is \(1.1 \times 10^{-5}\) (°C)\(^{-1}\) for temperatures up to 800°C. The volume change upon transformation on cooling is estimated as

\[ \frac{\Delta V}{V} = \frac{V(Ni-Ti, 54°C) - V(Ni-Ti, 77°C)}{V(Ni-Ti, 77°C)} = 0.0019 \]

The positive value indicates a volume increase resulting from the phase transformation on cooling.

e. **Volume change by strain gage measurements**  
The transformation volume change was also estimated from the axial and circumferential strains measured by strain gages. The strain values recorded by the
Fig. 21. Volume of the Ni-Ti tube versus temperature
data logging system were corrected for several adjustments to obtain higher accuracy. The initial corrections were made for the temperature induced apparent strain and the temperature dependence of the gage factor. Both corrections were based on the engineering data sheet provided with the strain gages by the manufacturer. The correction of the temperature induced apparent strain was about 60 microstrain units at 100°C, decreasing to a negligible value below about 65°C, while the correction for the temperature variation of the gage factor was always below one percent. The gage factor is the fractional resistance change per unit microstrain for the strain gage. A correction was also made for the difference between the gage factor (2.0) on which the manufacturer's data sheet was based and the actual gage factors for the gages used (2.08 and 2.12 for the axial and circumferential strain gages, respectively).

An additional correction for the effect of sample surface curvature was made for the circumferential strain values. This correction was based on an expression supplied by the manufacturer and was for the radius of curvature of the sample tube, thickness of bonding adhesive and gage backing, temperature difference from the reference temperature (100°C), and other variables. This correction was only about 1 microstrain unit per degree difference from the reference temperature. The last correction was made for the transverse sensitivity. The magnitude of this correction was about 20 microstrain units in the axial direction and about 10 microstrain units in the circumferential direction at 22°C (reference temperature = 100°C).

The strains as a function of temperature are shown in Fig. 22, after
making the corrections described above. On the assumption that the radial strain is the average of the axial and circumferential strains, the volume estimated as the sum of the strains in the three principal directions is shown as a function of temperature in Fig. 23. The strain gage measurements also indicate a relative volume increase upon transformation on cooling. The relative volume change of 0.0022 as estimated from Fig. 23 is not very different from the value of 0.0019 obtained from the hydrostatic weighings.

The volume change for the transformation from the austenite (A) B2 structure to the martensite (M) monoclinic distortion of B19 structure may be deduced from the lattice parameters for austenite and martensite. Philip and Beck\textsuperscript{102} reported the lattice parameter (a\textsubscript{0}) for B2 structure; Otsuka et al.,\textsuperscript{103} Hehemann and Sandrock,\textsuperscript{104} and Michal and Sinclair\textsuperscript{105} reported the lattice parameters (a, b, and c) and the monoclinic angle (θ) for the distorted B19 structure from their x-ray diffraction work. The reported values are listed in Table 2. Also listed are the volume per atom given by \( V_A = \frac{1}{2} a_o^3 \) for B2 structure and \( V_M = \frac{1}{4} a b c \sin θ \) for the distorted B19 structure, and the relative volume change given by \( \frac{ΔV}{V} = \frac{V_M - V_A}{V_A} \). Of the authors mentioned, only Otsuka et al.\textsuperscript{103} give a clear indication of their experimental temperature.

It appears (Table 2) that the volume change upon phase transformation specifically for the B2 to distorted B19 structure change is negative (volume contraction). The relative volume change calculated from the reported lattice parameters are -0.0034±0.0049, -0.006±0.0030, and -0.0048±0.0028, with an average of -0.0047, whereas the present
Fig. 22. Strain versus temperature from the strain gage measurements
Fig. 23. Sum of strains in three principal directions versus temperature. \( \varepsilon_a \), axial strain; \( \varepsilon_c \), circumferential strain
Table 2. Lattice parameters for B2 A phase and distorted B19 M phase and relative volume change for the HTP+LTP transition

<table>
<thead>
<tr>
<th>Reference no.</th>
<th>PB 102</th>
<th>OSS 103</th>
<th>HS 104</th>
<th>MS 105</th>
</tr>
</thead>
<tbody>
<tr>
<td>( a_0 (\text{Å}) )</td>
<td>3.015±0.001</td>
<td>2.889±0.005</td>
<td>2.882±0.004</td>
<td>2.885±0.004</td>
</tr>
<tr>
<td>( a (\text{Å}) )</td>
<td></td>
<td>4.120±0.012</td>
<td>4.623±0.005</td>
<td>4.622±0.005</td>
</tr>
<tr>
<td>( b (\text{Å}) )</td>
<td></td>
<td></td>
<td>4.622±0.016</td>
<td>4.117±0.005</td>
</tr>
<tr>
<td>( c (\text{Å}) )</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>( \theta ) (degrees)</td>
<td>96.8 ±0.32</td>
<td>96.8 ±1.0</td>
<td>96.8 ±1.0</td>
<td></td>
</tr>
<tr>
<td>( V_M = \frac{1}{4} abc \sin \theta (\text{Å}^3) )</td>
<td>13.657±0.067</td>
<td>13.622±0.041</td>
<td>13.638±0.037</td>
<td></td>
</tr>
<tr>
<td>( V_A = \frac{1}{2} a_0^3 (\text{Å}^3) )</td>
<td>13.7035±0.0079</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>( \Delta V/V = \frac{V_M}{V_A} - 1 )</td>
<td>-0.0034±0.0049</td>
<td>-0.0060±0.0030</td>
<td>-0.0048±0.0028</td>
<td></td>
</tr>
</tbody>
</table>
hydrostatic weighing and strain gage measurements indicate a volume increase of about 0.0019 and 0.0022, respectively. The hydrostatic weighings are thought to be straightforward since the weighings are essentially a direct measurement of the bulk property. While the hydrostatic weighings are continuously performed over a temperature range, the volume change resulting from the premartensite effects as well as the martensitic transformation are directly measured. The measurements by strain gages apparently are limited to the surface area covered by the gage grids which may not be a good representative of the whole sample. The surface area covered by the gage grid is about 0.32x0.42 cm, which covers about several hundred grains.

Repeated measurements with strain gages bonded at different positions on the sample surface indicated that the strain measured in a given direction might vary by a factor of 2; nevertheless, the sum of the strains in three principal directions always gave a positive value between 0.002 and 0.004. A similar measurement made earlier indicated that the strains in the axial and circumferential directions could even have opposite signs (Fig. 24), but the sum of strains (assuming radial strain and circumferential strains are equal) gave a volume increase of about 0.0035.106

One of the characteristics associated with the thermoelastic phase transformation is a small volume change.68,107 The relative volume changes calculated from the lattice parameters (Table 2) and the hydrostatic weighings do show the small volume change (absolute magnitude smaller than 0.006). Otsuka et al.68 estimated the volume change to be 0.16% using data from their earlier lattice parameter measurements.103
Fig. 24. Axial and circumferential strains versus temperature at zero applied tensile stress for Ni-Ti tube, 54.7 wt% Ni
Since they did not indicate the direction of the volume change, an attempt was made to calculate the volume change from their data. The $M_S$ temperature for their sample was between -40 and -50°C, while the x-ray diffraction work was performed at -192°C. Assuming the transformation takes place at -45°C, the volumes per atom for B2 phase and martensite were corrected to -45°C from room temperature and -192°C, respectively. The thermal expansion coefficients used for B2 phase and martensite were $1.1 \times 10^{-5}$ °C$^{-1}$ and $0.66 \times 10^{-5}$ °C$^{-1}$, respectively, as reported by Wasilewski et al. The volume corrections were done by using the following equation for the corrections of lattice parameters:

$$
\varepsilon = \varepsilon (25°C)[1 + \alpha(T - 25°C)]
$$

where $\varepsilon = a_o, a, b, c$ and $\alpha$ is the thermal expansion coefficient.

The volumes per atom at $M_S$ (-45°C) for martensite and B2 phase were 13.697 (Å)$^3$ and 13.672 (Å)$^3$, respectively, indicating a volume increase on cooling of 0.18%. The value of 0.18% calculated here is slightly larger than the value of 0.16% calculated by Otsuka et al., but it happens to be very close to the result (0.19%) from the present hydrostatic weighings. In any case, the relative volume change is so small that a precise determination is difficult for any of the methods.

B. Transformation Fatigue Cycled Wires

1. Resistivity behavior

The electrical resistance of the sample wires was recorded continuously as a function of temperature on a X-Y$_1$-Y$_2$ recorder. The resistivity
was then calculated from the recorded resistance and the form factor. The form factor, which is the cross-sectional area divided by the gage length, was corrected for the axial strain on the assumption of negligible volume change. The change in volume upon transformation is about -0.5% (contraction) deduced from the lattice parameter measurements or is about 0.2% (expansion) from the hydrostatic weighings, as described above. Although results from the two methods differ, the magnitudes of the transformation volume change as well as the normal thermal expansion or contraction within the experimental temperature range (100 to -50°C) are sufficiently small to be neglected for the purpose of the resistivity calculation. Another term, "nominal resistivity", appears in the following. The nominal resistivity is calculated from the recorded electrical resistance and the form factor at 100°C without correction for the changes in length with temperature.

Different shapes of the resistivity peak were observed. Some typical curves are shown in Figs. 25 and 26 for the uncycled and the 5.3 million cycled wires in the following conditions: (I) as-received, (II) after 1 hr at 400°C, and (III) after II plus 1 hr at 600°C. Generally, the resistivity decreases fairly linearly upon cooling from 100°C. The resistivity starts to deviate from the linear decrease at \( T_R \) and continues to decrease with a lower slope until \( T_{R_1} \) is reached. In this study, \( T_R \) is defined as the temperature at which the resistivity departs from the linear decrease, while \( T_{R_1} \) is the temperature at which the resistivity starts to increase rapidly. However, \( T_R \) cannot be firmly assigned in this study since it is difficult to tell where the linear
Fig. 25. Resistivity versus temperature at 1150 psi (7.9 MPa) for uncycled wire. The resistivity anomaly peaks and the key characteristic temperatures are shown.
Fig. 26. Resistivity versus temperature at 1150 psi (7.9 MPa) for 5.3 million cycled wire. The resistivity anomaly peaks and the key characteristic temperatures are shown.
decrease in resistivity on cooling ends. The temperature range for this low-slope region (between $T_R$ and $T_R'$) varies with prior treatments. This low-slope region might be a part of the resistivity "plateau" described by Mercier et al. 69

Upon cooling to below $T_R$ (Fig. 25), the resistivity starts to increase rapidly to a maximum at $M_S$. The rapid increase in resistivity in this region was described as an attendant effect of the B2-R transformation by Ling and Kaplow, 61 but Mercier et al. 69 connected it to the "lock-in" of the R phase, while the R phase itself occurs at a much higher temperature. At $M_S$ (Fig. 25), the transformation to martensite takes place and the resistivity starts to decrease sharply. The decrease in resistivity continues with further cooling to $M_F$, at which the transformation ends and the resistivity resumes a linear decrease. Upon heating from below $M_F$, the resistivity rises with a constant slope, which is the temperature coefficient of the low temperature phase, and reaches a maximum value at $A_S$, whereupon the transformation to B2 starts. Above $A_S$, the resistivity drops to near the value on cooling at $A_1$ and merges with the cooling curve upon further heating. The resistivity starts to increase linearly upon heating to above $A_F$. In all cases, $A_F$ appeared to be very close to $T_R$ (Figs. 25 and 26). Nevertheless, as described by Ling and Kaplow, 61 the shape of the resistivity peak is governed by the relative temperature difference between $T_R$, and $M_S$, which depends largely on the prior mechanical and heat treatments. 104,108

a. As-received condition The most evident effects of the prior TFC on the resistivity behavior are to cause the resistivity curves to
show the multi-stage character of strain change and to broaden the resistivity peaks, as shown in column I, Fig. 27. Although the as-received uncycled wire underwent a two-stage strain change on cooling (Fig. 28B), this two-stage character was not shown in the resistivity curve (Fig. 28A). The multi-stage character of the 5.3 million cycled wire was clearly exhibited by a slope change at \( \text{M}_1 \) (Fig. 28C), which was correlated with a sharp increase in length on cooling (Fig. 28D), and a double bend between \( \text{A}_S \) and \( \text{A}_t \) on heating. This double bend also could be correlated with the two-stage change in strain during transformation on heating. Much of the broadening of the resistivity peaks resulting from the high-level TFC was due to the upward shift of the low-slope region (thus the \( \text{T}_{R_1} \)) and the occurrence of the second stage transformation at a lower temperature on cooling.

Another effect of the TFC is to decrease the transformation start temperatures (\( \text{M}_S \) and \( \text{A}_S \)). The comparison of the \( \text{M}_S \) and \( \text{A}_S \) temperatures (deduced from the resistivity peak temperatures on cooling and on heating, respectively) for the as-received uncycled and 5.3 million cycled wire is shown in Figs. 29(1) and 30(1), respectively. The decrease in the martensite start temperature (\( \text{M}_S \)) due to the TFC is probably due to the high density of dislocations that act as barriers against the nucleation of the martensite phase. Therefore, a higher driving force (further undercooling or lower \( \text{M}_S \)) is required for the occurrence of the transformation on cooling. However, the strain energy stored in the martensite may assist the reverse transformation on heating, resulting in a lower austenite start temperature (\( \text{A}_S \)), as shown in Fig. 30(1). Also
Fig. 27. Summary figure. Nominal resistivity versus temperature at constant stresses as follows: Run (0), 284 psi; Run (1), 1150 psi; Run (2), 3450 psi; Run (3), 5750 psi; Run (4), 8130 psi; and Run (5), repeated run at the lowest stress (shown dashed).
Fig. 28. Resistivity and strain versus temperature for as-received uncycled wire (A and B, respectively) and for as-received 5.3 million cycled wire (C and D, respectively). Each pair of resistivity and strain measurements was made simultaneously at a stress of 1150 psi (7.9 MPa)
Fig. 29. $M_s$ (deduced from resistivity curves) versus stress
Fig. 30. $A_s$ (deduced from resistivity curves) versus stress
observed is the smaller stress dependences of $M_S$ and $A_S$ temperatures for
the TFC'd wires than the uncycled wire (Fig. 29(I) and 30(I), respectively).
The difference in the stress dependence may be rationalized in terms
of the competition between the effectiveness of the applied stress and the
dislocations. For the 5.3 million cycled wire, at least part of the ap-
plied stress was used to overcome the effects of the dislocations, causing
a decrease in the effectiveness of the applied stress.

The difference in the stress dependence of $M_S$ for the uncycled and
the TFC'd wires also resulted in a more significant change in the shape
of the resistivity peak under higher stresses. The relative tempera-
ture difference between $M_S$ and $T_R$, became smaller for the uncycled wire
when $M_S$ increased with increasing stress, while $T_R$, remained largely
unchanged, resulting in a narrower and somewhat pointed resistivity
peak, as shown in Fig. 31A. The resistivity peaks of the 5.3 million
cycled wire, however, did not change much with increasing stress, as
shown in Fig. 32A. It is noted that the TFC'd wires exhibited higher
electrical resistivities, particularly in the low temperature phase.

The higher resistivities of the TFC'd wires might be due to higher densi-
ties of point defects produced by dislocation reactions during the prior
TFC. Nevertheless, the significantly higher resistivities in the low
temperature phase exhibited by the TFC'd wires is proposed to be due
to a large amount of retained R phase. Ling and Kaplow\textsuperscript{61} have reported
that the B2+R can persist to very low temperatures. They also suggested
the possible stabilization of the high temperature phase (including R
phase) relative to martensite when the R distortion reaches a certain
value. For a TFC'd wire, it is possible that a larger amount of R phase may be easily retained under the same stress, while further retention of R phase requires a higher stress than for the uncycled wire, resulting in the small dependence of the low temperature phase resistivity on stress.

b. After one hour anneal at 400°C The nominal resistivity curves for the wires after one hour anneal at 400°C are shown in column II, Fig. 27. After the 400°C anneal, the resistivity low-slope region became smaller and the critical temperature $T_R$, increased to a higher temperature (from below 40°C to about 50°C). The $M_S$ temperatures for the TFC'd wires remained unchanged (between -2°C and 2°C) under lower stresses (1150 and 3750 psi), but shifted to higher temperatures (between 18°C and 22°C) under higher stresses (5750 and 8130 psi). Therefore, the relative temperature difference was larger under lower stresses. The resulting resistivity peaks were then broader and flatter on top under lower stresses and much narrower under higher stresses (Fig. 27II(b)-(e)). However, the $M_S$ for the uncycled wire increased to a higher temperature (between 22°C and 31°C), resulting in a smaller temperature difference than that of TFC'd wires between $M_S$ and $T_R$. Therefore, the resistivity peak of the uncycled wire was narrower than that of TFC'd wires under the same stress level (Fig. 27II(a)) as compared to Fig. 27II(b)-(e).

Figs. 29(II) and 30(II) show that $M_S$ and $A_S$, respectively, increase upon annealing at 400°C for both wires. While the stress dependences of the $M_S$ and $A_S$ temperatures for the uncycled wire remained unchanged,
Fig. 31. Resistivity versus temperature curves as a function of applied stress for uncycled wire. Dashed curve refers to a final run at the lowest stress (Run 5)
Fig. 32. Resistivity versus temperature curves as a function of applied stress for 5.3 million cycled wire. Dashed curve refers to a final run at the lowest stress (Run 5).
that for the TFC'd wires increased dramatically, as shown in Figs. 29(II) and 30(II), respectively. The abovementioned changes in the transformation behavior indicate a decrease in the effects of prior TFC after the one hour anneal at 400°C.

A comparison of the resistivity values for the uncycled and TFC'd wires indicated that the 400°C anneal caused the resistivities to decrease to a similar level in the high temperature phase or the low temperature phase. However, the stress dependences of the low temperature resistivities for the TFC'd wires (Fig. 27II(b)-(e)) were larger than that for the uncycled wire (Fig. 27II(a)). In most cases (except II(e)), a fifth run (dashed curve) repeating at the lowest stress (1150 psi) was conducted. The repeated runs indicated that the resistivity curves were fairly reproducible even after four continuous runs under stresses, although the low temperature phase resistivities were slightly higher in the fifth runs than in the first runs (Fig. 27II(a)-(d)).

c. After an additional one hour anneal at 600°C As shown in column III, Fig. 27, the $T_{R'}$ temperatures decreased (from about 40°C to about 20°C), while the $M_S$ temperatures either increased or decreased (depending on the stress level) to an average temperature of about 16°C. Because of the small difference between $M_S$ and $T_{R'}$, the resistivity of the uncycled wire decreased sharply in a single step upon cooling to below $M_S$ under lower stresses (284, 1150, and 3750 psi), the resistivities of the TFC'd wires decreased in more than one step, forming a double bend (Fig. 27, column III). A repeated run (dashed curve) under the lowest stress (284 psi) showed a higher and broader resistivity peak
and higher resistivity than the first run under the same stress. The shape of the repeated run is similar to that of the uncycled wire under a higher stress (1150 psi) in as-received condition (Fig. 27I(a)). After the anneals at 400°C and 600°C, the resistivities in the low temperature phase (at -40°C) for the uncycled and the 5.3 million cycled wire are of similar values and have similar stress dependences, as shown in Fig. 33.

The characteristic temperatures deduced from the resistivity curves indicated that the $M_S$ temperatures for the uncycled and TFC'd wires decreased to similar values and had similar stress dependences following annealing at 600°C, as shown in Fig. 29(III). Similar changes were also observed for $A_S$ temperatures except that the $A_S$ temperatures had larger dependences on stress than $M_S$ temperatures (Fig. 30(III)). In general, the anneal at 600°C restored the wires to a similar condition.

2. Strain behavior

All the sample wires were originally from the same heat (Timet V4609) and may be assumed to have had the same diameter. Upon transformation fatigue cycling, the diameters of the wires were found to decrease progressively (from 19.6 to 18.7 mils or from 0.498 to 0.475 mm) with increasing numbers of prior TFC, as shown in Fig. 34. On the assumption of constant volume, the decrease in diameter indicates an increasing unrecovered axial strain with increasing number of TFC. This is consistent with the observation that the wires in the Lawrence Berkeley Laboratory engine devices required occasional tensioning during the course of the repeated TFC. The decrease in diameter is most pronounced at lower TFC cycles and levels off with increasing number of TFC.
Fig. 33. Electrical resistivity at -40°C for uncycled wire and 5.3 million cycled wire. Open symbols, as-received condition; closed symbols, after 1 hr anneals at 400°C and 600°C.
Fig. 34. Diameter versus number of cycles of transformation fatigue cycling (TFC)
The continuous strain changes were recorded simultaneously with the electrical resistance as a function of temperature. The simultaneous recording provided a ready correlation of the strain change with the resistivity behavior. The strain change and the nominal resistivity recorded as a function of temperature for each wire (5 wires) in different treatment conditions (3 conditions) are collected in Appendix B. Most of the strain versus temperature curves are summarized in Fig. 35. The effects of the prior TFC, applied tensile stress, and heat treatment on the transformation strain behavior are deduced from the individual curves and the summary figure (Fig. 35). The characteristic temperatures used in the following are defined in Fig. 36.

a. As-received condition The strain change of the as-received sample wires during transformation under deadweight tensile stresses is shown in column I, Fig. 35. It is evident that the major effect of prior TFC is to cause the transformation to take place in more than one step. The multi-stage transformation process becomes more distinct with increasing number of TFC. The 5.3 million cycled sample, which was given the highest number of TFC cycles and may be taken as the representative of the TFC'd samples, distinctly shows the two-stage transformation both on cooling and on heating (Fig. 35I(e)). Upon cooling, the first length change takes place at \(M_{S1}\) (Fig. 36), while the second stage takes place around \(M_{S2}\). The first stage usually proceeds fairly quickly within a temperature range of about 3°C, while the second stage proceeds more gradually and persists to much lower temperatures. A positive strain (length increase) was registered for both stages on cooling. During
Fig. 35. Summary figure. Axial strain versus temperature at constant stresses as follows: Run (1), 1150 psi; Run (2), 3450 psi; Run (3), 5750 psi; Run (4), 8130 psi
Fig. 36. Schematic axial strain versus temperature curves, showing the starting temperatures for each stage
heating, the first stage starts at $A_{S1}$, which is higher than $M_{S1}$, while the second stage starts at $A_{S2}$. A negative strain (length decrease) was recorded for both stages on cooling. Although the unycled sample (Fig. 351(a)) also exhibits a slight two-stage transformation on cooling, the transformation on heating is continuous in a single step.

Due to the lack of further information, it is difficult to make firm assignments of particular transitions to these stages. However, a similar two-stage transformation behavior also was observed recently by Ling and Kaplow by suppressing the $M_s$ temperature of their samples. Based on the observations of x-ray peak intensities and peak widths, they assigned a $B2\rightarrow R$ transformation to the first stage, which is accompanied by an increase in resistivity and a decrease in length, and a $R\rightarrow M$ transformation to the second stage, which was accompanied by a decrease in resistivity and an increase in length. They also observed that $(\Delta V/V)_{R\rightarrow M}$ was larger than $(\Delta V/V)_{B2\rightarrow M}$ and suggested that the $R\rightarrow M$ transformation should take place at a lower temperature than the $B2\rightarrow M$ temperature.

Based on their observations and present correlated resistivity and strain curves, the transformations during cooling for the TFC'd samples are proposed to proceed in the following sequence:

$$
\begin{align*}
B2 \xrightarrow{(1)} & \quad M_{S1} < T < T_R \xrightarrow{(2)} B2+R \xrightarrow{(3)} M+R \xrightarrow{(3)} M+R \text{(retained)} \\
T = M_{S1} & \quad T < M_{S1}
\end{align*}
$$

Transition (1), $B2\rightarrow R$, is not visible in all the strain curves obtained from the as-received samples but can be seen as a small step at $\sim 40\degree C$ in the curves for samples after a $400\degree C$ anneal. Transition (2), $B2\rightarrow M$, starts and ends within a very narrow temperature range probably due
to the internal stress resulting from the prior TFC. During the course of TFC, the wires were transformed under stress producing a strain of about 3%, which was partially due to the forming of stress-induced martensite. Wasilewski\textsuperscript{29} has pointed out that the stress exerted by the high dislocation density at the transformation interfaces governs the following transformation. After millions of cycles of TFC, it is reasonable to expect that the internal stress associated with the dislocations could develop into a pattern such that the transformation is ordered\textsuperscript{3} (preferred martensite variants), both on cooling and on heating. The internal stress thus could promote rapid transformation the moment sufficient driving force needed for the B2+M transformation is acquired while the temperature drops. Upon further cooling, the R+M (transition (3)) becomes operative, first gradually (between $M_{S1}$ and $M_{S2}$) but later at a higher rate (at $M_{S2}$) when the transformation is thermodynamically favored. Transition (3) becomes sluggish when available R phase becomes exhausted, but it persists to lower temperatures (along with B2+R transformation) forming the bend shape of the second stage (Fig. 35I(a)-(e)). The attendant resistivity change is small when R+M transformation proceeds slowly (between $M_{S1}$ and $M_{S2}$), while the resistivity decrease is sharp below $M_{S2}$ when R+M transformation occurs at a higher rate. These behaviors are constant with Ling and Kaplow's observation.\textsuperscript{61,109}

Upon heating, the sequence of transformation is then

$$M+R(\text{retained}) \xrightarrow{T=A_{S1}} B2+M+R \xrightarrow{A_{S1}<T<T_R} B2+R \xrightarrow{T_R<T} B2$$
The transition (1) on heating could be complicated by the fact that more than one transformation may participate, namely \( R(\text{retained}) \rightarrow B2 \) and \( M \rightarrow R + B2 \). The latter transformation may proceed in two steps at different temperatures. This would provide some \( R \) phase for the transition (3), \( R \rightarrow B2 \), consistent with Ling and Kaplow's observation that \( R \rightarrow B2 \) is thermally reversible without hysteresis. Transition (2), \( M \rightarrow B2 \), would be the reverse transformation of transition (2) on cooling.

When the samples were temperature cycled under increasingly higher constant tensile stress, it was found that the onset temperature for each stage, Figs. 37(I) and 38(I), and the total transformation strain, Figs. 39(I) and 40(I), increase with increasing stress. The increase in the transformation start temperature is probably due to the effect from the applied stress. A comparison of the strains generated in these stages reveals that the strains produced in the first stage on cooling and the second stage on heating increase very slowly with increasing stress (low stress dependence), while the strains produced in the second stage of cooling and the first stage on heating have similar higher stress dependences (Fig. 41). This might suggest that the participating transformations for stages that have similar stress dependence might be of the same type, but one is a reverse transformation of the other. This is consistent with the sequence of transformations proposed above.

It is also noted that the stress dependence of the total transformation strain decreases with increasing number of TFC, as shown in Figs. 39(I) and 40(I). This decrease in stress dependence may be rationalized in terms of the dislocation density. It is thought the internal stress
Fig. 37. $M_s$ (deduced from strain curves) versus stress
Fig. 38. $A_s$ (deduced from strain curves) versus stress
Fig. 39. Total axial transformation strain (cooling) versus applied tensile stress
Fig. 40. Total axial transformation strain (heating) versus applied tensile stress
Fig. 41. Axial strain versus stress for each stage on cooling and on heating.
associated with the dislocations may have an ordering effect on the preferred direction of shear during the transformation. Nevertheless, other mechanisms like growth and reorientation of martensite variants that are usually responsible for high strains may be retarded by dislocations. The TFC'd samples having higher dislocation densities would have lower stress dependence for the transformation strain. The existence of the high dislocation density may be further supported by the observation that the $M_S$ temperatures ($M_{S1}$ and $M_{S2}$) are lower for TFC'd samples than for the uncycled sample, as shown in Fig. 37(I). A similar relation is also observed for $A_S$ temperature (Fig. 38(I)). The stress dependences of all the transformation start temperatures of these stages for TFC'd samples are observed to be much smaller than for the uncycled sample (Figs. 37(I) and 38(I)) for the same reason.

b. After one hour anneal at 400°C The strain versus temperature curves for samples at the same stress levels but in the 400°C-annealed condition are summarized in column II, Fig. 35. It appears that the multi-stage character has subsided substantially after anneal. Although a very small stage can be observed on cooling, it is not seen on heating. The small stage observed is thought to be the transition (1) on cooling as proposed above for wires in the as-received condition. The negative strain change (contraction) was observed to take place at the lowest stress level (1150 psi or 7.9 MPa) and at about the same temperature where the resistivity increased rapidly, as shown in Fig. 42. The correlated resistivity increase and the length decrease at $T_R$, are consistent with Ling and Kaplow's observations on their Ni-Ti wire.
Fig. 42. A pair of resistivity and strain curves, showing the correlated characteristic temperatures. Stress: 1150 psi.
Nevertheless, the direction of the length change accompanying the B2→R transformation changed to an opposite direction at a temperature a few degrees lower under higher tensile stresses, as shown in Fig. 35II(e). Ling and Kaplow\textsuperscript{110} also observed a contraction for R→B2 transformation on heating a prestrained Ni-Ti wire sample containing a large amount of R phase. The negative strain recovery indicates that during straining, the R phase can be strained to produce a positive strain (elongation) under sufficient tensile stress if $M_s < T_R$. This stress-induced change is rationalized\textsuperscript{110} in terms of the difference in d-spacings and multiplicity factors between $\{111\}_R$ when $<111>_{B2}$ directions are converted to $<111>_R$ or $<\overline{1}11>_R$ in the B2→R transformation (an elongation along a $<111>$ in B2). This mechanism might be the one causing the small stage of strain change on cooling.

From the data deduced from the curves shown in column II, Fig. 35, the stress dependence of the total transformation strain ($\Delta \varepsilon_c$ and $\Delta \varepsilon_h$) for TFC'd samples has recovered to that similar to what was observed for the uncycled sample, but the strains produced under the same stress are still smaller for the TFC'd samples, as shown in Figs. 39(II) and 40(II). Also observed is that the stress dependence for the transformation start temperatures (except $M_s$ for TFC'd samples at lower stress levels) increases after the 400°C-anneal, as shown in Figs. 37(II) and 38(II). The increase in the stress dependence for the transformation start temperatures and the transformation strains is an indication of the significant reduction in dislocation density.
c. After an additional one hour anneal at 600°C

It appears that the two-stage character of the transformation is completely wiped out, as shown in column III, Fig. 35. The stress dependence of the transformation strains (\(\Delta e_C\) and \(\Delta e_H\)) for all the annealed samples becomes similar regardless of their prior histories, as shown in Figs. 39(III) and 40(III). The transformation start temperatures (\(M_S\) and \(A_S\)) have similar values at the same stress levels and increase with increasing stress at a similar rate, although the rate for \(A_S\) is higher, as shown in Figs. 37(III) and 38(III).

3. Tensile tests

The stress-strain curves of the wires at 78°C in as-received condition are shown in a summary plot, Fig. 43. All the wires exhibited a typical multi-stage \(\sigma\) vs. \(\varepsilon\) curve of a metastable alloy that is capable of stress-assisted martensitic transformation at a temperature between \(M_S\) and \(M_d\). The curve consists of a linear elongation region, a first yielding followed by a plateau stage, and then a second yielding followed by the fracture of the sample. Similar \(\sigma\) vs. \(\varepsilon\) curves for near equiatomic polycrystalline Ni-Ti samples also have been observed by other investigators.\(^{13,54,64,74,81}\)

The curves in Fig. 43 show that the first apparent yielding of the TFC'd samples occurs at a stress level of about 80 ksi (552 MPa), while the uncycled sample yields at -65 ksi (449 MPa). The 0.2% yield stress of the TFC'd samples is about 66 ksi (455 MPa), while that of the uncycled sample is only 49.5 ksi (342 MPa). The 0.2% yield stress is
Fig. 43. Engineering stress-strain curves for an uncycled wire and for wires given 1.0, 2.7, 3.7, and 5.3 million transformation fatigue cycles. As-received condition. Strain rate: $1.1 \times 10^{-4}$ sec$^{-1}$. AS RECEIVED, 78°C
plotted as a function of the number of prior TFC in Fig. 44.

Upon stressing the Ni-Ti sample in the high temperature phase, the initial elongation is elastic as indicated by the linear region of the $\sigma$ vs. $\varepsilon$ curve. When the applied stress reaches a certain value by which the formation of martensite can be stress-assisted, the first yielding takes place. The degree of ease that the transformation can be stress-induced may be affected by the same factors that affect the martensitic transformation in the stress-free condition. For the TFC'd samples used in the present study, the predominant factor is the high density of dislocations resulting from prior TFC. The formation of martensite is hindered by the dislocations; therefore, a higher stress is required to assist the transformation. The transformation continues at a fairly constant stress level, forming a "plateau" region on the $\sigma$ vs. $\varepsilon$ curve. This would suggest that the assisted transformation for the wire given a higher number of prior TFC will occur at a stress level higher than that of the wire given a smaller number of TFC. Generally this is true as indicated in Fig. 43; the plateau region of the 5.3 million cycled wire occurs at a slightly higher stress than the 2.7 and 1.0 million cycled wires, in that order, except for the 3.7 million cycled wire, which is out of the order. Nevertheless, the yield stress of the TFC'd samples obviously is higher than that for the uncycled sample by about 30%.

Following the formation of the stress-induced martensite is a work hardening region before the fracture occurs at a higher stress level. It appears (Fig. 43) that the TFC'd samples have a similar rate of work
Fig. 44. The 0.2% yield stress at 78°C for wires in as-received and annealed (one hour anneals at 400°C and 600°C) conditions.
hardening, which is significantly higher than that for the uncycled sample. Sastri et al. have reported their TEM work on the stress-induced martensite that the martensite thus formed has a complex structure consisting of either alternating fine lamellae of B2 phase and martensite or two distinct martensites. The numerous interfaces serve as obstacles to slip, making further deformation more difficult. Bensmann et al. also attributed the strengthening of this stage to the dislocation activities like the dislocation reactions due to short glide path and the locking of dislocations. In such a way, the yield stress becomes higher due to increasingly higher density of the locked dislocations resulting from further deformation. It is believed that the TFC'd samples contained a higher density of dislocations, which caused the individual martensite variant to form in a smaller size, resulting in a larger number of interfaces and thus a higher stress for further deformation. When the stress reached a certain value, the screw dislocations cross slipped and became mobile, through which the work hardening rate decreased and the curve became flatter until fracture occurred, as suggested by Bensmann et al.

With increasing stress, the TFC'd samples fractured at a stress level of about 145 ksi (1000 MPa), while the uncycled sample fractured at about 130 ksi (897 MPa). Rozner et al. reported values around 120 ksi (828 MPa) at about 80°C for their equiatomic Ni-Ti rod samples. Rozner and Buehler also reported an ultimate tensile strength of about 150 ksi (1035 MPa) for cold-worked samples with a 10% reduction in cross sectional area. In this study, the TFC'd samples had different amounts
of cross sectional area reduction depending on the number of cycles received (Fig. 34). The 5.3 million cycled sample had a reduction of about 9% in cross sectional area as a result of prior TFC.

Fig. 45 also shows that the fracture strains (about 40%) for the TFC'd samples are much smaller than the fracture strain (71%) for the uncycled sample. Rozner and Wasilewski\textsuperscript{74} reported a value of about 64% at about 80°C for their annealed sample, while Rozner and Buehler\textsuperscript{112} reported a decrease of elongation from about 57% to about 20% for cold-worked samples with a 10% reduction in cross sectional area. In general, the effect of prior TFC is to raise the yield stress, to raise the fracture stress, and to reduce the fracture strain. This is consistent with the results reported by Rozner and Buehler\textsuperscript{112} in which they measured the 0.2% yield stress, ultimate tensile stress, and elongation as a function of cross sectional area reduction by cold working. This consistency might indicate that the effect of prior TFC is similar to that of cold working in the sense of dislocation introduction. Perkins\textsuperscript{113} made a conclusion from his observation of martensitic transformation using electron microscopy that thermal cycling through transformation temperature range or the stress-induced martensite formation is a form of "cold work".

It is also noted that the difference between the 0.2% yield stresses of the TFC'd samples and the uncycled sample is the same as the difference between their fracture stresses (15 ksi or 10 MPa). This also suggests that the effectiveness of the dislocation density in retarding the formation of the stress-assisted martensite and in the work hardening of the product martensite is nearly the same. Another observation is
Fig. 45. The fracture strains for wire samples in as-received condition versus number of transformation fatigue cycles. The strains were measured at 78°C as shown in Fig. 43.
that the effects of TFC on the yield stress and the fracture strain show a leveling off with increasing number of TFC (Figs. 44 and 45). As far as the role of the dislocations is concerned, the result is consistent with the report by Wasilewski that the total number of dislocations increases rapidly at first, but at a progressively lower rate with increasing number of cyclings.

The result of the tensile tests performed on samples given one hour anneals at 400°C and 600°C is summarized in Fig. 46. The multiple stages observed for wires in the as-received condition are less distinguishable after the anneal. The first yielding of all the wires occurred at a stress level of about 70 ksi (483 MPa), which is about 10 ksi (69 MPa) or about 12% lower than that of the TFC'd samples in as-received condition. The 0.2% yield stress is calculated to be about 51 ksi (352 MPa) for all the annealed samples regardless of the amounts of prior TFC. This is about a 30% decrease for the TFC'd samples to the value of the uncycled sample, which remained nearly unchanged (Fig. 44).

All the wires after the anneal fractured at a lower stress level than in the as-received condition, although their fracture stresses differed slightly. However, the fracture strains were considerably higher in annealed condition than in as-received condition except for the 3.7 million cycled wire. Generally, the tensile properties were largely recovered as the result of the anneals at 400°C and 600°C, which is shown by the decrease of the yield stress and fracture stress and the increase of the fracture strain.

Two tensile tests were conducted at 21°C using the as-received
Fig. 46. Engineering stress-strain curves for wires of different prior cycling history in annealed (one hour anneals at 400°C and 600°C) condition.
uncycled and 2.7 million cycled samples. Both samples are believed to be in the low temperature phase at 21°C after being warmed from the liquid nitrogen temperature to ambient temperature. The stress versus strain curves are presented together with those obtained at 78°C in Fig. 47. Although the general shape of the curves obtained at 21°C is similar to that obtained at 78°C, different mechanisms are believed to be operating. Upon stressing, the existing martensite deformed elastically until the first yielding occurred by various mechanisms working in such a way as to relieve the applied stress. The mechanisms possibly involved include the stress-induced intramartensite twin boundary movement,\(^7\) the growth and shrinkage of the favorably and unfavorably oriented martensite variants,\(^4,111,114,115\) and the stress-induced reorientation of favorably oriented martensite by the utilization of the most favorably oriented twin systems, as suggested by Mohamed and Washburn.\(^13\) The next stage is the strain hardening of the newly formed martensite followed by its fracture.

For both the uncycled and the 2.7 million cycled samples at 21°C, the first apparent yielding occurred at a much lower stress level (17 ksi or 117 MPa) than was observed at 78°C, while the fracture occurred at higher stress levels compared to the stress levels at 78°C (Fig. 47). This would suggest that the mechanisms responsible for the first yielding at 21°C require less energy than the formation of the stress-induced martensite. In the early stage of the test (at 21°C), the material (predominantly martensite) might be a stress-free transformation product in which the crystallographically equivalent martensite variants were
Fig. 47. Engineering stress-strain curves at 21°C and 78°C for wires (uncycled wire and 2.7 million cycled wire) in as-received condition. The strain rate is $0.9 \times 10^{-4}$ sec$^{-1}$ at 21°C and $1.1 \times 10^{-4}$ sec$^{-1}$ at 78°C.
present equally. Upon stressing, there must be at least some variants more favorably oriented relative to the stress axis, and the above-mentioned mechanisms are not as difficult to become operative. However, depending on the size of the martensite variants, the scale of the local deformation resulting from the continuous operations of the above-mentioned mechanisms may be larger and they may introduce a higher defect density. This might later contribute to the further higher strain hardening rate, as the continuous curves indicate in Fig. 47. The 2.7 million cycled sample has a higher dislocation density to begin with. Accordingly, it yielded and fractured at higher stress levels than the uncycled sample.
IV. CONCLUSIONS

The shape memory transformation behavior of nearly equiatomic Ni-Ti alloys was studied from the measurements of strain and electrical resistivity during transformation under externally applied tensile stress using hot-swaged and annealed Ni-Ti tubes and transformation fatigue cycled (TFC'd) wire. The measurement of transformation volume change by hydrostatic weighing and tensile tests were also conducted. From the above experiments, the following conclusions are drawn:

(1) The transformation strain in the stress direction increases with increasing stress. This is interpreted in terms of the preferred formation of martensite variants for which the transformation distortions give rise to extensions along the stress direction.

(2) The relative volume change for equiatomic Ni-Ti upon transformation on cooling was determined by hydrostatic weighing and by strain gage measurements. The results indicate that the volume change is an increase of about 0.2%, which is different from the value of 0.5% volume decrease as deduced from the lattice parameter measurements specifically for the B2 to distorted B19 transition. The discrepancy might be due to the participation of other transformations than the B2 to distorted B19 transformation, such as the transformation from B2 to an intermediate rhombohedral or R phase. Another possibility is that the discrepancy vanishes when the lattice parameters are corrected to a common transformation temperature.

(3) As for the Ni-Ti tubes, the wires also show an increase in total transformation strain with increasing tensile stress. The
interpretation is similar to that given in (1) above.

(4) With increasing tensile stress, the $M_S$ and $A_S$ temperatures increase. Upon cooling, the applied stress will assist the formation of certain martensite variants, which allows them to form with smaller amounts of undercooling, thus increasing $M_S$. Upon the reverse transformation on heating, the same applied stresses inhibit the transformation shear and $A_S$ increases.

(5) With increasing tensile stress, the low temperature phase resistivity is increased. This may be due to the increased retention of R phase. The resistivity-temperature curves also indicate an increase in $M_S$ and $A_S$ with increasing stress, consistent with the strain-temperature curves as indicated in (4) above.

(6) High-level transformation fatigue cycling (TFC) causes a decrease in the stress dependence of $M_S$ and $A_S$, of the total transformation strain, and of the low temperature phase resistivity. The TFC is known to introduce dislocations. These dislocations have stress fields that tend to mask the effect of the applied stress.

(7) High-level TFC causes the equiatomic Ni-Ti wire to undergo multi-stage phase transformation, as observed by electrical resistivity and strain measurements. The multi-stage character becomes more distinct with increasing number of TFC. The appearance of several stages of transformation for the TFC'd wires is believed to be due to the decrease in transformation start temperatures $M_S$ and $A_S$, which causes a separation in the B2\(\leftrightarrow\)M and B2\(\leftrightarrow\)R transformations.

(8) The tensile properties of Ni-Ti wires are affected by prior
high-level TFC. The yield stress is increased and the fracture strain is decreased. This is believed to be due to the production of dislocations during the TFC.

(9) Post-TFC annealing at 400°C partially restores the transformation properties to those characteristic of uncycled wires. Annealing at 600°C fully restores the transformation and tensile properties.
V. REFERENCES


83. Technical Information, Fluorochemical Liquid M-6015 (FC-80), Medical Products Division, Minnesota Mining and Milling Company, St. Paul, Minnesota 55101.


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VII. APPENDIX A: MASS CORRECTIONS

For the weighing of the Si standard in air

\[ W_A^{(Si)} = W_A^{(W, Si)} \]  \hspace{1cm} (1)

where \( W_A^{(Si)} \) is the apparent weight in air of the Si and \( W_A^{(W, Si)} \) is the apparent weight in air of the balance weights. By applying Archimedes' Law, Eq. 1 becomes

\[ M^{(Si)} - d(A) V^{(Si)} = M^{(W, Si)} - d(A) V^{(W, Si)} \]  \hspace{1cm} (2)

where \( d(A) \) is the density of air, \( M^{(Si)} \) and \( M^{(W, Si)} \) are the masses of the Si and the balance weights, respectively, and \( V^{(Si)} \) and \( V^{(W, Si)} \) are the volumes of the Si and the balance weights, respectively. Furthermore,

\[ V^{(Si)} = \frac{M^{(Si)}}{d^{(Si)}} \quad \text{and} \quad V^{(W, Si)} = \frac{M^{(W, Si)}}{d^{(W)}} \]

where \( d^{(Si)} \) and \( d^{(W)} \) are the densities of the Si and balance weights, respectively. Substitution of \( V^{(Si)} \) and \( V^{(W, Si)} \) into Eq. 2 gives

\[ M^{(Si)} = \frac{1 - \frac{d(A)}{d(W)}}{1 - \frac{d(A)}{d^{(Si)}}} M^{(W, Si)} \]  \hspace{1cm} (3)

The density of air, \( d(A) \), is calculated by using an expression given by Bowman et al.\(^{116}\)

\[ d(A) = d \frac{T_0}{P_0} \left[ B - e(1 - \frac{M_w}{M_g}) \right] \]  \hspace{1cm} (4)

where \( d_0 \) is the density of dry air (0.00129304 gm/cm\(^3\)) at the reference
temperature $T_0 = 273.16 \, ^\circ K$, $P_0$ is the reference pressure (760 mm Hg), $B$ is the barometric pressure, $e$ is the vapor pressure of water at the experimental temperature, and $M_W$ and $M_G$ are the molecular weights of water and air, respectively.
VIII. APPENDIX B: RESISTIVITY AND STRAIN CURVES
Fig. B1. Nominal resistivity and strain versus temperature for unycled wire in as-received condition
Fig. B2. Nominal resistivity and strain versus temperature for 1 million cycled wire in as-received condition
Fig. B3. Nominal resistivity and strain versus temperature for 2.7 million cycled wire in as-received condition.
Fig. B4. Nominal resistivity and strain versus temperature for 3.7 million cycled wire in as-received condition.
Fig. B5. Nominal resistivity and strain versus temperature for 5.3 million cycled wire in as-received condition
Fig. B6. Nominal resistivity and strain versus temperature for uncycled wire. After 1 hr at 400°C
Fig. B7. Nominal resistivity and strain versus temperature for 1 million cycled wire. After 1 hr at 400°C
Fig. B8. Nominal resistivity and strain versus temperature for 2.7 million cycled wire. After 1 hr at 400°C.
Fig. 89. Nominal resistivity and strain versus temperature for 3.7 million cycled wire. After 1 hr at 400°C.
Fig. B10. Nominal resistivity and strain versus temperature for 5.3 million cycled wire. After 1 hr at 400°C
Fig. B11. Nominal resistivity and strain versus temperature for unculated wire. After an additional 1 hr at 600°C.
Fig. B12. Nominal resistivity and strain versus temperature for 1 million cycled wire. After an additional 1 hr at 600°C
Fig. B13. Nominal resistivity and strain versus temperature for 2.7 million cycled wire. After an additional 1 hr at 600°C
Fig. B14. Nominal resistivity and strain versus temperature for 3.7 million cycled wire. After an additional 1 hr at 600°C
Fig. B15. Nominal resistivity and strain versus temperature for 5.3 million cycled wire. After an additional 1 hr at 600°C.
IX. APPENDIX C: STRESS-STRAIN CURVES
Fig. C1. Engineering stress-strain curves for the uncycled wire at 78°C in as-received and annealed conditions. The anneal includes 1 hr at 400°C and an additional 1 hr at 600°C. Strain rate: $1.1 \times 10^{-4}$ sec$^{-1}$
Fig. C2. Engineering stress-strain curves for the 1 million cycled wire at 78°C in as-received and annealed conditions. The anneal includes 1 hr at 400°C and an additional 1 hr at 600°C. Strain rate: $1.1 \times 10^{-3}$ sec$^{-1}$
Fig. C3. Engineering stress-strain curves for the 2.7 million cycled wire at 78°C in as-received and annealed conditions. The anneal includes 1 hr at 400°C and an additional 1 hr at 600°C. Strain rate: $1.1 \times 10^{-4}$ sec$^{-1}$
Fig. C4. Engineering stress-strain curves for the 3.7 million cycled wire at 78°C in as-received and annealed conditions. The anneal includes 1 hr at 400°C and an additional 1 hr at 600°C. Strain rate: 1.1x10⁻⁴ sec⁻¹.
Fig. C5. Engineering stress-strain curves for the 5.3 million cycled wire at 78°C in as-received and annealed conditions. The anneal includes 1 hr at 400°C and an additional 1 hr at 600°C. Strain rate: 1.1x10^{-4} sec^{-1}