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NSWC TR 86-196

EFFECTS OF STRESSES ON THE PHASE TRANSFORMATION OF NITINOL

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RESEARCH AND TECHNOLOGY DEPARTMENT

2 APRIL 1986

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87 2 26 039

UNCLASSIFIED
SECURITY CLASSIFICATION OF THIS PAGE

AD-19177-55

| REPORT DOCUMENTATION PAGE | | | | |
|--|--|--|--|--------------------|
| 1a REPORT SECURITY CLASSIFICATION UNCLASSIFIED | | 1b RESTRICTIVE MARKINGS | | |
| 2a SECURITY CLASSIFICATION AUTHORITY | | 3 DISTRIBUTION/AVAILABILITY OF REPORT Approved for public release; distribution is unlimited. | | |
| 2b DECLASSIFICATION/DOWNGRADING SCHEDULE | | | | |
| 4 PERFORMING ORGANIZATION REPORT NUMBER(S) NSWC TR 86-196 | | 5 MONITORING ORGANIZATION REPORT NUMBER(S) | | |
| 6a NAME OF PERFORMING ORGANIZATION Naval Surface Weapons Center | 6b OFFICE SYMBOL (if applicable) R32 | 7a NAME OF MONITORING ORGANIZATION | | |
| 6c ADDRESS (City, State, and ZIP Code) 10901 New Hampshire Avenue Silver Spring, MD 20903-5000 | | 7b ADDRESS (City, State, and ZIP Code) | | |
| 8a NAME OF FUNDING SPONSORING ORGANIZATION | 8b OFFICE SYMBOL (if applicable) | 9 PROCUREMENT INSTRUMENT IDENTIFICATION NUMBER | | |
| 8c ADDRESS (City, State, and ZIP Code) | | 10 SOURCE OF FUNDING NUMBERS | | |
| | | PROGRAM ELEMENT NO 6152N | PROJECT NO ZR00001 | TASK NO ZR02206 |
| | | WORK UNIT ACCESSION NO R01AA110 | | |
| 11 TITLE (Include Security Classification) Effects of Stresses on the Phase Transformation of NITINOL | | | | |
| 12 PERSONAL AUTHOR(S) Goldstein, David M.; Kabacoff, Lawrence T.; Tydings, John | | | | |
| 13a TYPE OF REPORT Final | 13b TIME COVERED FROM TO | 14 DATE OF REPORT (Year, Month, Day) 86/4/2 | 15 PAGE COUNT 56 | |
| 16 SUPPLEMENTARY NOTATION | | | | |
| 17 COSATI CODES | | | 18 SUBJECT TERMS (Continue on reverse if necessary and identify by block number) | |
| FIELD | GROUP | SUB-GROUP | NITINOL Phase Transformations | |
| 11 | 0b | | Shape Memory Alloy | |
| 13 | 08 | | NiTi | |
| 19 ABSTRACT (Continue on reverse if necessary and identify by block number) Sequential annealing treatments up to 400 °C were performed on a severely cold wrought alloy rich NiTi (NITINOL) alloy to demonstrate the shape memory performance of the alloy as a function of annealing. The strain recovery was 2.75%. The electrical resistance responses associated with the phase transformations of the specimen, subsequent to the various annealing treatments, are shown and interpreted. Supporting data were obtained on the same alloy for varied annealing cycles by use of a differential scanning calorimeter. Both residual and precipitation-associated stresses have a marked effect on electrical resistance and calorimetric responses during the phase transformation. The changed responses provide the basis for considering the transformation to occur via a metastable rhombohedral (R) structure. The extent to which the R may exist is shown to be related to the residual | | | | |
| 20 DISTRIBUTION/AVAILABILITY OF ABSTRACT <input type="checkbox"/> UNCLASSIFIED/UNLIMITED <input checked="" type="checkbox"/> SAME AS RPT <input type="checkbox"/> DTIC USERS | | 21 ABSTRACT SECURITY CLASSIFICATION UNCLASSIFIED | | |
| 22a NAME OF RESPONSIBLE INDIVIDUAL David M. Goldstein | | 22b TELEPHONE (Include Area Code) (202) 394-2468 | 22c OFFICE SYMBOL Code R32 | |

DO FORM 1473, 84 MAR

83 APR edition may be used until exhausted
All other editions are obsolete

SECURITY CLASSIFICATION OF THIS PAGE

U.S. Government Printing Office: 1985-528-612

0102-LF-014-6602

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SECURITY CLASSIFICATION OF THIS PAGE

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stresses. The stresses also have a significant effect on the shape memory response.

The substantial changes in the range of transition temperatures which can be obtained by various annealing treatments of this slightly nickel rich NITINOL are tabulated.

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PREFACE

A cold wrought nickel-rich NiTi (NITINOL) alloy recovers its capability to transform from austenite to martensite after certain annealing treatments. In this work, a series of discrete annealing treatments were used to reduce the stresses residual from prior cold work. The alloy then displayed the effect of these diminishing stresses on the linear contraction, electrical resistance, and calorimetry phenomena associated with the phase transformation. The significant influence of residual stresses on the transformation appears to have been overlooked by previous investigators. This may have caused much of the variance that appears in the literature on the transformation in NITINOL alloys.

A cohesive theory is presented in which residual stresses enable the formation and retention of an intermediate rhombohedral structure, "R," during the transition of austenite into martensite. The generation of R structure produces the "anomalous" resistance peak during the cooling of NITINOL alloys.

The residual stresses are a major factor in the shape memory response that this alloy is noted for, providing the forces that determine the direction of shape recovery, affect its completeness, and affect its temperature range.

Precipitation of the non-stoichiometric nickel in solution may occur during annealing. The early stages of precipitation generate stresses and have significant effects on the start and completion temperatures of the transformation. The change in matrix composition resulting from the precipitation has an effect independent of any associated stresses, and results in transformations at higher temperature.

Strain recovery of 2.75% in the cold worked alloy at 400°C was obtained. This is in contrast to the 6% recovery at 100°C obtained in an annealed alloy.

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FOREWORD

The first engineering quality alloy with shape memory characteristics was discovered by W. J. Buehler and R. C. Wiley at this laboratory (then named the Naval Ordnance Laboratory) in the early 1960's. Commercialization of the alloy proceeded in the 1970's, with specific compositions used very successfully for certain Naval applications.

The shape memory alloy family, based on the nickel-titanium system, was named NITINOL. The temperature ranges of its shape memory response often varied from nominal values in the prototype production of these alloys at this facility. This was ascribed to minuscule unintended variations in composition. Test data and conclusions reported in the literature by various investigators on materials prepared at their own facilities also varied significantly. The lack of full control implied by these discrepancies hindered development of the alloys for additional applications. Increased commercial use was inhibited by the lack of assured reproducibility of alloys with specific properties.

The current work approaches the shape memory feature of a single alloy by examining its development following a severe cold working operation, such as would be encountered in the routine production of wire. The ability of the alloy to exhibit shape recovery was tracked by changes in its linear dimensions, electrical resistance, and calorimetry, each as a function of thermal processing. From these data, conclusions were drawn as to the effect of stresses in the alloy, both residual and self-generated as a result of precipitation effects. Use of the theory of stress effects presented in this work appears to explain the earlier lack of full control and the variances in results reported in the literature.

The variations in the temperature range for shape recovery achievable by thermal processing are presented. These data are of significance to those interested in producing the alloy or in the design and fabrication of devices using the shape memory phenomenon.

The authors appreciate the discussions, review, and many helpful changes suggested by Drs. D. W. Ernst and A. G. Rozner on the text of this report. D. M. Goldstein wishes to acknowledge with gratitude his deep debt to his early mentor in metallurgy, Dr. R. M. Brick, whose teachings and philosophies have remained with him through the years.

NSWC TR 86-196

Funds for this work were provided by the NSWC Independent Research Program.

Approved by:

A handwritten signature in cursive script that reads "Jack R. Dixon".

JACK R. DIXON, Head
Materials Division

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INTRODUCTION

NITINOL alloys¹ are based on compositions close to equiatomic NiTi. They are noted principally for their unusual shape memory capability.²⁻⁶ Their commercial applications are based on the combination of shape memory capability and good engineering properties. A few applications are based on their low modulus of elasticity.⁷

The shape memory response is the subsequent return to (or toward) a prior shape or dimension, following any deformation from that shape or dimension. The response is accomplished by heating the deformed piece, usually to a temperature between -30°C and +100°C. The prior or "permanent" shape is the one that had been "set in" by an earlier annealing treatment. The shape memory phenomenon is repeatable if deformation is always performed at a temperature lower than the recovery temperature.

The temperature for the shape memory response can be lowered, within limits, by increasing the nickel content of the binary alloy. The shape memory response occurs at the same temperature range as does a phase change from martensite to austenite. It is now widely accepted that this phase transformation is the basis for the shape memory response of NiTi based alloys. Buehler et al² presented the first paper in the open literature which described shape recovery response in a near-stoichiometric [55.4 weight percent (w/o) Ni] alloy.

Equiatomic NiTi composition is 55.06 weight percent nickel. The phase diagram for the NiTi region of the nickel-titanium alloy system⁸⁻¹¹ is given in Figure 1.

A review of the crystal structures involved in the phase transformation follows.

The high temperature phase is an ordered body centered cubic structure, B 2,^{10,12-14} usually referred to as the austenitic phase.

The low temperature phase is a complex close packed crystal structure, usually referred to as martensite. It has been reported to be a monoclinic distortion of a B 19 cell by Sandrock,¹⁵ Hehemann & Sandrock,¹⁶ Otsuka et al,¹⁷ Khachin et al,¹⁸ Michal and Sinclair,¹⁹ and Kudoh et al.²⁰ Although agreement is now arising on the structure of martensite, the underlying reason as to why other structures were reported by earlier investigators is in itself of interest.

Initially, Duwez and Taylor¹³ and Poole and Hume-Rothery⁸ reported that TiNi decomposed into Ti₂Ni and TiNi₃. At variance with this report, Margolin et al²¹ and Pietrokowsky and Youngkin¹⁴ concluded that TiNi existed at room temperature. Buehler and Wiley,¹ on the basis of X-ray diffraction data,

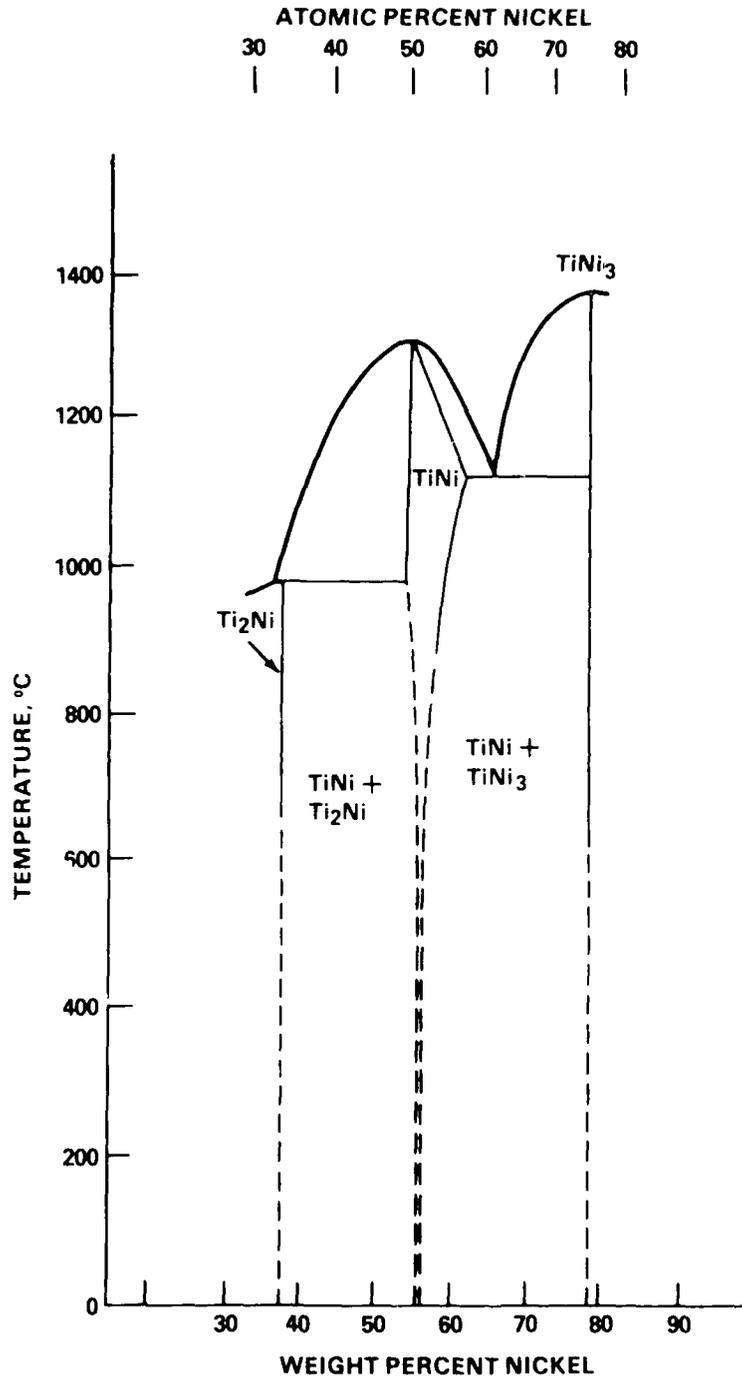


FIGURE 1. EQUILIBRIUM PHASE DIAGRAM OF THE NICKEL-TITANIUM SYSTEM NEAR THE NiTi PHASE

concluded that TiNi could exist in a stable or metastable form at room temperature, and first showed a martensite structure. In the same time frame, Purdy and Parr¹⁰ independently reported that TiNi decomposed rapidly and reversibly at 36°C into a pi phase, which they indexed tentatively as hexagonal. Subsequently, Dautovich and Purdy²² concluded the structure was triclinic. The possibility of simultaneously existing structures was raised by Marcinkowski et al,²³ who reported two co-existing monoclinic martensitic structures.

Jackson et al⁴ and Wasilewski et al²⁴ suggested that the different low temperature structures reported were due to inadequate characterization of the specimens used, i.e. of uncertain composition, with the further comment that they may have been in non-equilibrium.

The possible existence of non-equilibrium, metastable structures was thus recognized. The first reports of a structure intermediate to austenite and martensite were by Wang et al²⁵ and by Dautovich et al.^{22,26} The former indexed the structure as a complex cubic, and highly strained. The latter indexed it as a rhombohedral distortion of B 2, and stated that it was a transitional phase. Dautovich et al were also the first to report that its existence was limited and dependent upon anneals in the range of 400°-500°C. Other subsequent investigators,^{27,28} however, treated the intermediate structure as a stable phase. It is concluded that they were in fact examining structures representing different stages of transition, thus producing the conflicting conclusions on the structures extant near room temperature.

Still other investigators considered the transformation into martensite during cooling to be via another intermediate structure. Matsumoto²⁹ defined the transformation to have an intermediate tetragonal structure in an alloy of Ti 50 Ni 47 Fe 3. Khachin¹⁸ proposed that B 2 could transform to B 19 directly, or to B 19 via an intermediate rhombohedral structure. Ling³⁰ concluded that B 2 could transform to either martensite or to a rhombohedral phase, depending on which had the higher transformation temperature.

The intermediate R structure was considered to be a distortion of the B 2 phase by some investigators,²⁷ i.e. a "following" phenomenon. Sandrock, Perkins, and Hehemann³¹ considered it to be a premonitory, pre-martensitic structure, and thus a "leading" phenomenon. These distinctions are primarily semantic; the same set of atomic movements are being described, i.e. the formation of the rhombohedral, intermediate structure. Its generation and retention as a function of strain, and its significance in the transformation are the thrust of the present paper.

Dautovich,²² Chandra,³² Khachin et al^{18,33} (as reported by Ling^{27,30}), and Ling himself identified the intermediate structure as rhombohedral, or as "R". The use of that terminology will be continued in the present paper.

The phenomena associated with R structure are x-ray streaks condensing into spots, anomalous increased electrical resistance, reversibility without hysteresis, and second-order, non-displacive atomic movements.

Buehler et al² had also reported that large dimensional changes occurred during heating of a cold wrought 55.1 w/o Ni alloy. Details of that report stated that a cold drawn rod, heated for the first time, showed "very large irreversible contraction" (stage 1). During a subsequent heating to 320°C, the

rod contracted initially and then expanded, as shown in Figure 2, curve (a). The contraction was 0.8% during heating from 25°C to 125°C, the expansion was 0.2% during the continued heating from 125°C to 320°C. These subsequent dimensional changes were shown to be reversible on cooling. Similar dimensional changes in the opposite direction were shown by a swaged specimen, curve (b), of the same alloy rod stock during its heating from 25°C to 100°C. Also, they reported that the swaged stock no longer contracted sharply from 100°C to 25°C upon cooling from 547°C, i.e. its contraction from 100°C to 25°C simply continued along a straight line extension to the cooling curve from the higher temperature, and there was no "knee" in the curve.

They concluded that metastable phases were present in the alloy and contributed to the dimensional changes. The opposite directions of the initial dimensional changes in the 25°C to 125°C range [curve (a) vs curve (b)] were attributed to the different modes of deformation, swaging producing compressive stresses, and drawing producing tensile stresses. Transformation of the metastable phases was considered to be the basis of the very large irreversible contraction (stage 1) and also the reversible length changes during the subsequent heatings (stage 2) as shown in Figure 2.

This aspect of Buehler's work remained dormant however, and its significance was largely overlooked. Wasilewski³⁴ noted it and confirmed the phenomena.

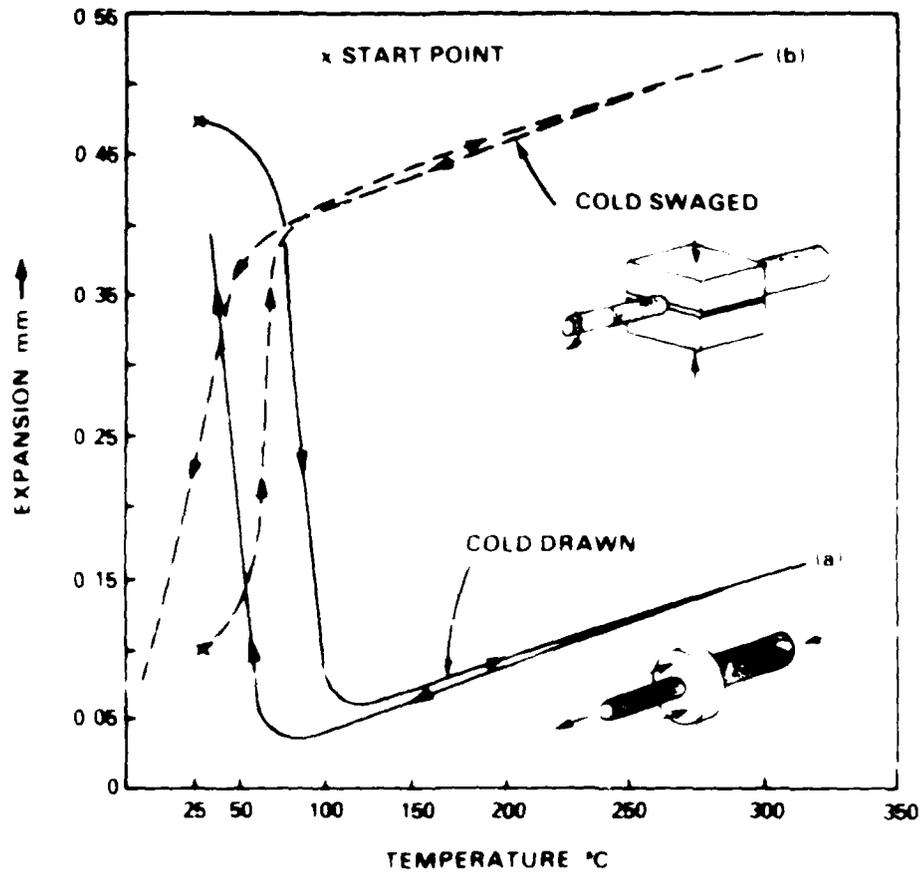
The purpose of the present investigation was to: (1) verify and explain the large irreversible stage 1 contraction reported by Buehler et al; (2) explain the directional dependence of the reversible stage 2 dimensional changes; (3) explore how a cold drawn alloy recovers the ability to undergo the phase transformation as a function of its annealing; (4) delineate the effect of stresses on the transition; and (5) provide understanding and guidance on techniques for the thermal processing of nickel-rich alloys intended for use in temperature-actuated devices.

The approach used in the present investigation was to track in detail the contraction (Buehler's stage 1) phenomenon. A series of annealing treatments were used to produce increasing amounts of stress relief and recrystallization in a cold-drawn rod. Thus, the data obtained were from a single rod of NiTiCo alloy, of nominal composition 55.1 weight percent nickel, balance titanium. This was nominally the same composition as that used by Buehler. The cumulative effect of the annealing treatments was tracked by the linear contraction and the changes of electrical resistance of the specimen.

Separately, wafers sliced from one end of the cold-drawn rod were individually annealed (noncumulative) at selected temperatures for various times. These were used in calorimetry tests to verify and extend the conclusions drawn from the contraction and resistance data obtained on the rod.

This approach of restoring the transformation capability differs significantly from that of other investigators, who generally used singly annealed and quenched (usually at about 650°C-1000°C) NiTiCo specimens to investigate the austenite/martensite transformation.

Also in this paper, as distinct from those of prior investigators, formation of the R structure is considered to be the starting step of the



(FROM REFERENCE 2)

FIGURE 2 EXPANSION OF 50 mm LONG NITINOL RODS COLD DRAWN VS COLD SWAGED

transformation of a stressed austenite into martensite. Its identification as a structure throughout the present paper, rather than as a phase, is intended to emphasize that it is a temporary structure, arising during the transition of B 2 into martensite, and is not an equilibrium phase that could be included in the equilibrium phase diagram of the Ni-Ti system. Furthermore, it cannot be considered a phase, since it is not a homogeneous entity, physically visible and discrete from B 2. It has not been observed metallographically, although it may be connected with the "wavy" martensite that Zjilstra³⁵ observed, the "mottled" structure that Wasilewski^{11,36} reported, and the "uneven surface" on metallographic specimens reported by Purdy and Parr.¹⁰ Ling and Kaplow²⁷ calculated the "d" spacings and interaxial angle of the rhombohedral cell from X-ray data obtained from specimens now known to contain residual stresses. The seeming stability of the K structure at ambient temperatures, a result of the presence of residual stresses, has misled some investigators to consider it to be a phase.

To summarize, it is proposed that in nickel-rich, near-equiatomic NiTi, the K structure is metastable and forms only as a part of the transition process. It is retained during transformation only in the presence of residual stresses. It will be shown that the removal of residual stresses by annealing enables an immediate, uninterrupted conversion of B 2 into martensite. Such immediate transformation is assumed to occur via a transient K structure.

EXPERIMENTAL PROCEDURES

The alloy used in this investigation was identified as Heat 83755. Its charge composition was 55.1 w/o nickel, balance titanium. In other work we have demonstrated to our satisfaction that the precision of chemical analysis for near NiTi alloys is inadequate for reliably reporting a quantitative change from the charge composition because of melting.

The charge was vacuum induction melted in graphite and poured as a 14.2 pound ingot. The cast ingot was hot forged, rolled into rod, cold wire-rolled to 0.115-inch diameter, and annealed in air at 600°C for two hours. It was then cold drawn to 0.0965 inch diameter, a 29.6% reduction in area. The heat treatments were done in an air convection furnace with digital controls and an internal tan. The temperature variation in the vicinity of the specimen during annealing was measured by a separate Omega digital pyrometer as $\pm 1^\circ\text{C}$.

Length Measurements

The dimensions of the test rod were 0.0965-inch diameter by 10 inches in length. This rod was contained in an open-ended nickel tube with an adequate clearance so that it did not interfere with lengthwise movement of the rod. The tube precluded any significant distortion of the rod during the series of annealing treatments and the subsequent length measurements. The latter were made at 22°C using a micrometer caliper with a dial indicator having 0.001-inch graduations. Dimensional changes in length were determined following air anneals at 100°C, 200°C, 300°C, and 400°C. Oxidation of the rod at temperatures up to 400°C produced only an iridescent thin film, insufficient to significantly affect the length measurements.

Resistance Measurements

Electrical resistance changes were measured with conventional four-point probes within an environmental chamber. The chamber was heated electrically by resistance elements to obtain test temperatures up to 125°C, and cooled by vaporizing liquid carbon dioxide to achieve -70°C. An internal fan helped reduce temperature gradients within the chamber. The resistance change measurements were made using 40 Hertz current with a Keithly Model 503 milliohmmeter, which was connected to the y axis of an x-y recorder. Temperature was sensed by a fine copper constantan thermocouple placed about 1/2 inch from the test piece. Its output was to the recorder's x axis. The abscissa, therefore, is proportional to the thermocouple output, which is close to, but not precisely, a linear temperature scale. Variations in room temperature were compensated for by an electronic feedback in the thermocouple circuit. Because of the mass differences of specimen and thermocouple, and other variables, the temperature of the specimen is estimated to be within $\pm 5^\circ\text{C}$ of the recorded value. This equipment was adequate for measuring the substantial changes in resistance within the specimen that occurred during transformation. Resistance profiles during the phase transformations were recorded for both the cooling and heating portions of the transition after each annealing treatment. These will be referred to subsequently as the "legs" of the cycle.

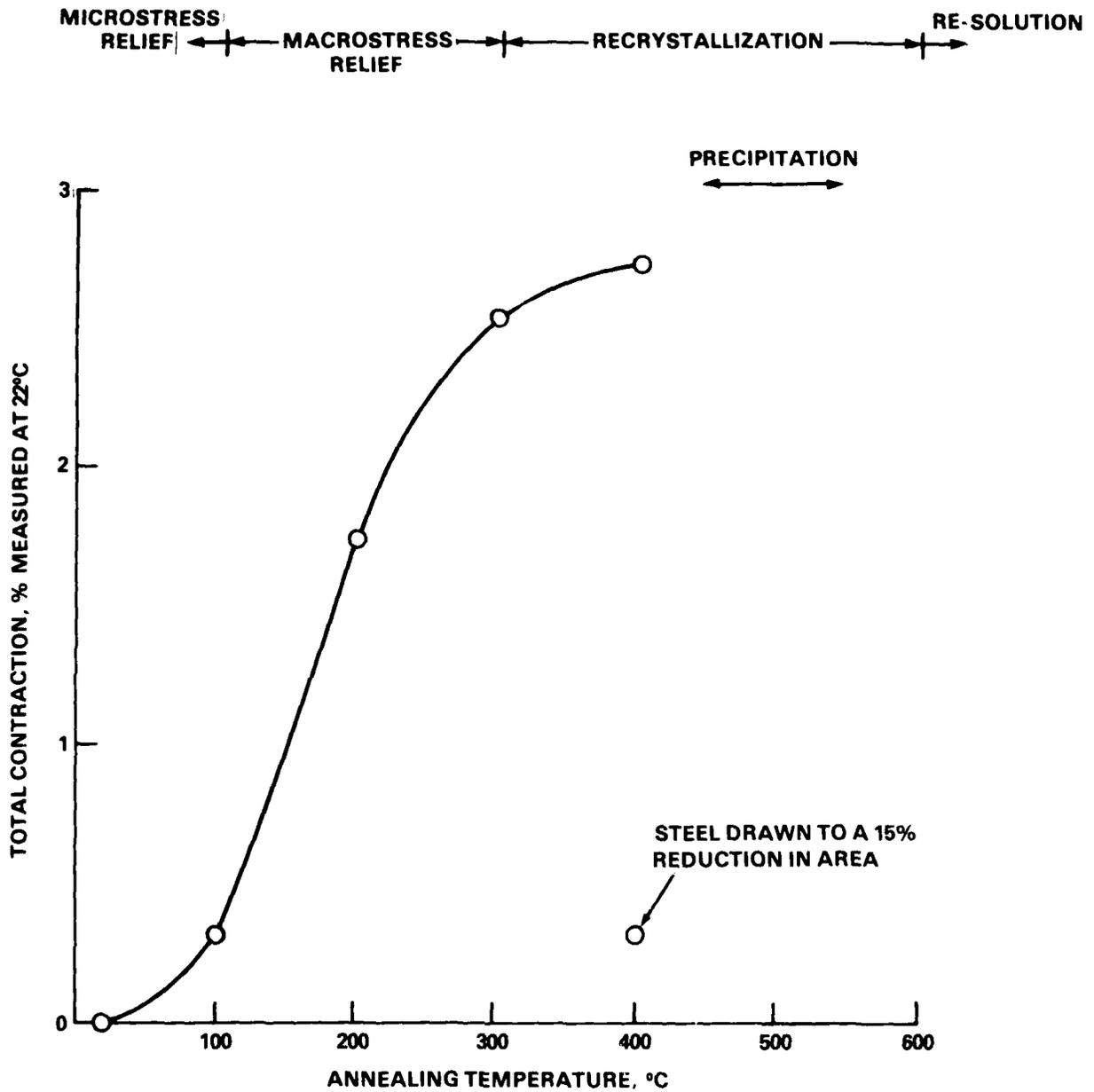
Calorimetry

The calorimetry specimens were cut from the cold drawn rod and given individual annealing treatments at specific temperatures between 400°C and 600°C. The annealed specimen wafers (10-40 mg) were weighed and placed in aluminum trays at ambient temperature. The trays were then placed in a Perkin Elmer Model DSC-2C differential scanning calorimeter and heated to 130°C. After holding at that temperature for a few minutes, the cooling cycle was initiated and data were automatically recorded. Liquid nitrogen surrounding the specimen pedestal permitted cooling to -120°C. Heating of the specimen followed immediately, and was also recorded. The energy evolved during cooling and absorbed during heating was recorded as a function of temperature. A standardized rate of temperature change of 20°C/minute was used. Precision of the differential scanning calorimetry (DSC) technique is estimated to be $\pm 2^\circ\text{C}$ for temperature and within 1% for energy changes.

RESULTS AND DISCUSSION

Length Changes

The cold-drawn rod contracted in length during its first heating to 100°C and continued to contract during its subsequent annealing at successively higher temperatures. These annealing treatments were for two hours each at the temperatures of 200°C, 300°C, and 400°C, followed by air cooling. The extent of contraction, as measured after each of the (cumulative) annealing treatments, is shown in Figure 3. Heating the cold-drawn NITINOL rod to 100°C caused it to contract about the same amount as did a cold-drawn steel wire that was annealed at 400°C, also shown in Figure 3 as a single test point. This small contraction for both the NITINOL and the steel resulted from the relief of microstresses. The microstress relief is thus shown to be due to stress relaxation, i.e., small adjustments of atom positions within grains, and not considered to be peculiar to NITINOL.



NOTE: ANNEALING TREATMENTS WERE FOR TWO HOURS AT EACH TEMPERATURE. THE TEMPERATURE ZONES FOR THE METALLURGICAL PHENOMENA OCCURRING WITHIN THE NITINOL ARE SHOWN AT THE TOP OF THE FIGURE.

FIGURE 3. CUMULATIVE CONTRACTION OF ANNEALED DRAWN ROD, HEAT 83755

Stress is defined as a force acting on a unit area. As a general rule, the force is externally applied to the body under consideration. In this paper, however, stresses are internal (unless otherwise specified). They are retained from the prior cold working of the specimen, i.e., they are residual stresses. Their magnitudes are approximated by localized strain, the displacement distance of atoms from their equilibrium positions. Residual stresses are balanced out over the bulk of the metal, and are a measure of the driving forces exerted by the displaced atoms to return to their equilibrium positions.

The sequential annealing treatments of the NITINOL at successively higher temperatures, up to 400°C, produced further substantial contraction. The summing-up of the contraction was its total shape memory response, i.e., a return toward the length it had before the extension at 25°C. It is deduced that the following phenomena had occurred.

A significant portion of the strained structure that had been formed during the prior cold drawing of the rod was primarily R structure and secondarily martensite. These structures transformed to B 2 in increased total amounts during the subsequent two-hour annealing treatments of the rod at the increasingly higher temperatures. The transformation was enabled by the relief of macrostresses, i.e. the reduction of strains across the multi-grain areas of martensite/R structure. These areas of reduced strain were then able to transform into B 2 during the two-hour anneals. The B 2 formed was under lengthwise compressive stresses from the adjacent still-strained areas, thus producing a linear contraction at the elevated temperature.

The residual stresses in the drawn rod had their major effect during annealing treatments in the 100°C to 300°C range. When present, these stresses provided the directional guidance for the atomic movements of the martensite/R structures as they converted into B 2 producing, in this case, contractions of length.

Certain deductions are now drawn from Buehler's work² as reported in Figure 2.

1. The drawn rod was initially heated to a temperature lower than 547°C, since the subsequent 0.8% contraction was observed.
2. The "large contraction (stage 1)" resulting from the initial heating fits the definition of shape memory response, as does the lesser, but still substantial, reversible (stage 2) contraction.
3. The opposed branches of the graph at the lower temperature, i.e. below 125°C, for the swaged and drawn rods, indicates the alloy was sensitive to the residual stresses present. The stresses controlled the sense, i.e. contraction or expansion, of the dimensional change between 25°C and 125°C.*

* Wasilewski, in his own work,³⁷ concluded that the directional sense and the magnitude of the dimensional change during transformation was a function of the residual stresses from externally applied stresses. He attributed these residual stresses to a high density of dislocations at the transformation interfaces.

4. The slopes of the curves for both the swaged and drawn rods above 125°C were the same. Therefore, the rods are following a normal coefficient of thermal expansion (CTE) value for this alloy above 125°C. The value of the CTE as taken from Figure 2 is 10.7×10^{-6} mm/mm/°C.

5. The residual stresses were partly relieved during the first heating to 325°C, which contained the "very large" contraction. They were totally relieved at 547°C.

6. If a metastable phase(s) was involved in the gross dimensional changes between 25°C and 125°C, then that phase was sensitive to the absence or presence as well as the nature and amount of residual stresses.

7. For the drawn wire heated to 320°C, longitudinal compressive stresses existed during each subsequent reheating from 25°C to 125°C.

The 2.75% contraction shown in Figure 3 is irreversible and presumably corresponds to the "very large" contraction reported by Buehler. The principles drawn from the results shown in Figure 2 are probably applicable to this cold-drawn rod following its 400°C anneal. It is now deduced from Figure 3 that:

1. NITINOL can display shape memory effects in the presence of the substantial residual stresses.

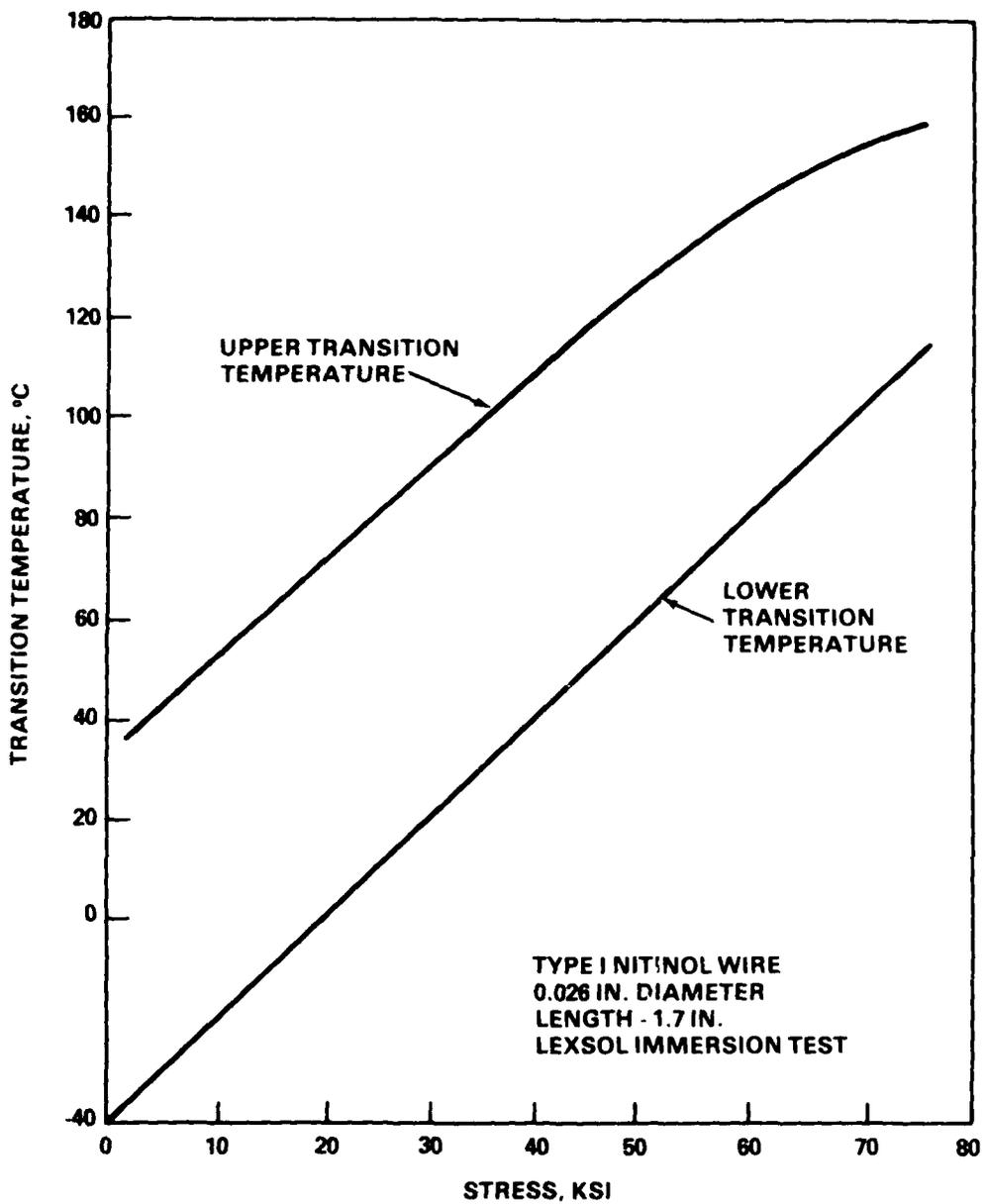
2. Temperatures well above 100°C are required for the shape memory effects to occur within time frames of two hours or less.

This shape recovery at elevated temperature in an internally stressed specimen is analogous to the work of Schuerch,³⁸ Figure 4. His work demonstrated that temperatures for shape recovery were a direct function of the magnitude of externally applied (opposing) stresses.

After annealing at 400°C, the residual stresses in the rod were less than after the prior annealing treatments. Any subsequent higher temperature annealing would reduce the residual stresses still further. Thus, in this experiment, further contraction of rod 83755 because of further annealing would be negligible.

Annealing at 400°C may recrystallize the specimen, depending on the length of time the specimen is held at temperature. The rod's subsequent shape memory response, if it were again deformed, would be influenced by the reduced stresses present as a function of its time at temperature.

Results analogous to ours were reported for very short (5 minute) anneals at 400°C to 700°C by Cross, Kariotis, and Stimler³⁹ for a cold-drawn, 0.1-inch diameter rod. Upon subsequent heating and cooling between 0°C and 150°C, the dimensional changes they observed diminished with the increasing annealing temperature used. No explanation for this behavior was presented, but their results are qualitatively consistent with those obtained in the present investigation, after allowing for the correlation of time at temperature.



(FROM REFERENCE 38, WITH PRELOAD WEIGHT CONVERTED TO PRELOAD STRESS)

FIGURE 4. TRANSITION TEMPERATURES VERSUS PRELOAD STRESS

Resistance Changes

The unusual changes in the electrical resistance of NITINOL alloys during transition were reported by Dautovich and Purdy,²² Hanlon et al,⁴⁰ and Wang et al.⁴¹ The resistance data for this NITINOL rod, Heat 83755, as it transformed during cooling and heating cycles, are illustrated beginning with Figure 5, and further discussed and illustrated later in this section.

The resistance test equipment was found to be stable in its ability to reproduce resistance traces with high precision during prior monitoring of the transformation of a separate control specimen. Only very small differences in resistance arise in these tests because of the slight variation in the placement of the voltage drop leads.

Inasmuch as the same specimen was used in all the resistance (and linear contraction) tests, the principal source of differences in its electrical resistance response during test are the changes that resulted from its annealing. The area under the curve is thus an approximate measure of the amount of B 2 that was formed during the annealing treatment and that was involved in the subsequent transformation.

The resistance versus temperature profiles are reliable indicators of shape recovery performance, as reported by Cross, Kariotis, and Stimler.³⁹ Based on the area under the curves shown in Figure 5, a small amount of martensite can be formed, starting at -35°C , upon cooling, after a two-hour annealing treatment at 200°C . Martensite becomes visible in an electron microscope at the peak temperature of the resistance curve during cooling, as shown by Sandrock et al.³¹

The R structure started to form at about $+38^{\circ}\text{C}$ during cooling. It is this structure that began conversion to martensite at -35°C . Since a transformation to martensite did occur, some non-deformed B 2 structure had to be formed during the prior 200°C annealing treatment.

During cooling, the residual stresses caused the R structure to form at a higher temperature than it would in a lesser stressed specimen. A simplified physical interpretation of this phenomenon can be visualized by considering how an isolated cube, Figure 6, (a) can be modified into a partially 'rhombohedral' structure (b) by stress. Consider that an external force, applied along one edge of a cube in the diagonal (110) plane, distorts an opposite, parallel, pair of cube faces into rhombs, i.e. it diagonally "squashes" the cube, changing some of the interaxial angles, but not changing any of its edge lengths. Internal (residual) stresses are theorized to act on the cubic B 2 in a similar way, assisting in the "squashing" action. Ling and Kaplow⁴² presented a schematic for true rhombohedral distortion of a B 2 structure under an externally applied tensile force. Their model is considered to be applicable also to (internal) residual stresses. A partial figure from their work is reproduced here as Figure 7, showing that a tensile force acting in the $\langle 111 \rangle$ direction within the (110) plane of a produces a rhombohedron. Again, a comparable "squashing" action occurs, this time in the (111) plane perpendicular to the $\langle 111 \rangle$ direction of extension. Since they aid R structure formation, these stresses enable its start to occur earlier, i.e., at a higher temperature than when stresses are negligible.

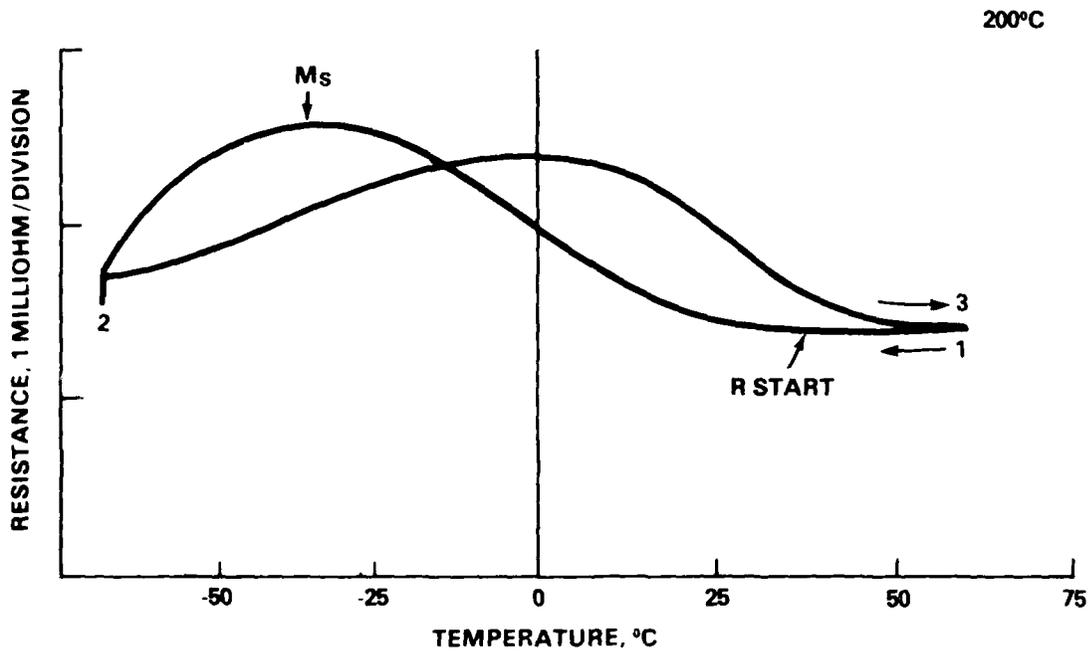


FIGURE 5. ELECTRICAL RESISTANCE OF NITINOL ROD, HEAT 83755, AFTER TWO HOUR ANNEALING TREATMENT AT 200°C, FOLLOWING THE PRIOR LOWER TEMPERATURE ANNEALING TREATMENT

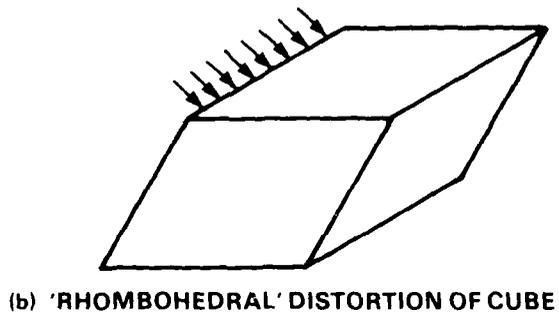
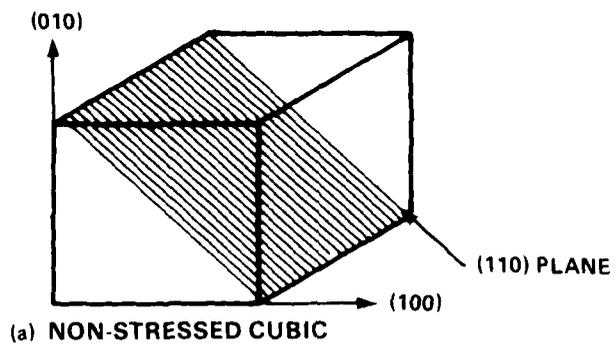


FIGURE 6. SCHEMATIC OF PSEUDO 'RHOMBOHEDRAL' STRUCTURE FORMED BY FORCE EXERTED IN (110) PLANE OF A CUBE

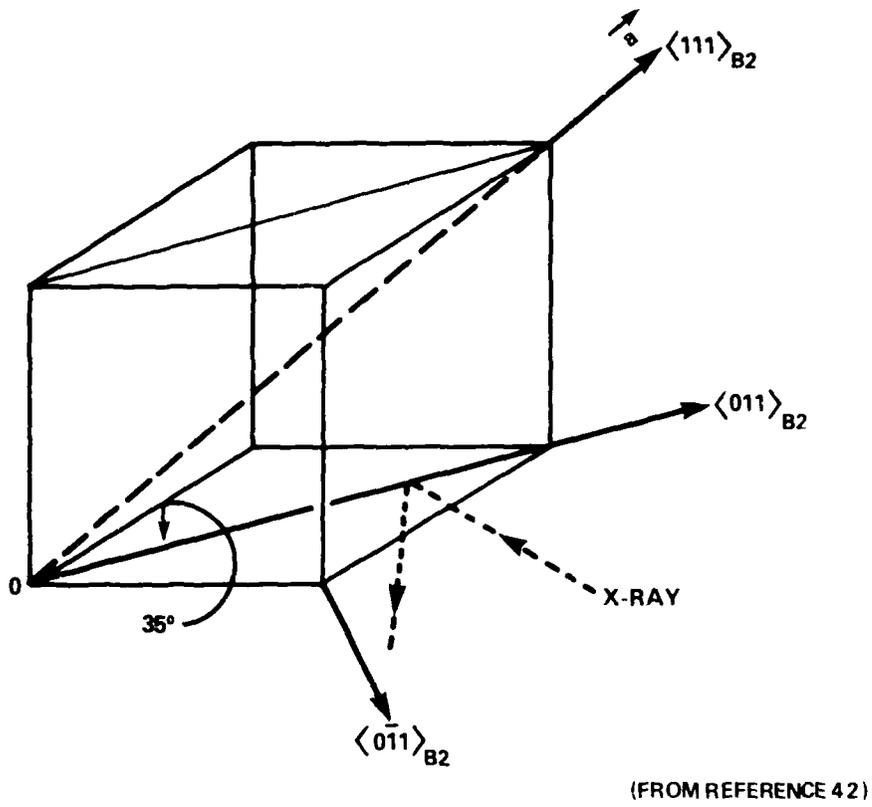


FIGURE 7. SCHEMATIC OF TENSILE STRESS IN $\langle 111 \rangle$ DIRECTION REQUIRED TO PRODUCE RHOMBOHEDRAL STRUCTURE

A small amount of martensite was formed in the specimen during cooling from -35°C to -65°C , the lower temperature limit of the cooling chamber. During its subsequent heating, the martensite started to revert into R structure at -35°C . Since this freshly formed R structure must maintain cohesion with both the pre-existing R structure (formed during cooling but not transformed into martensite), and also with the original stressed, non-transformed matrix, it too is a stressed structure. As R continued to form from martensite with increasing test temperatures, it increased the specimen's total resistance, peaking at about $+3^{\circ}\text{C}$, at which temperature it started to convert to a B 2 structure, completing at $+50^{\circ}\text{C}$, as shown in Figure 5 and listed in Table 1.

After annealing at 300°C , the volume of transformable B 2 structure has greatly increased, as represented by the increased area under the curves shown in Figure 8, for both heating and cooling. The temperature for formation of R structure during cooling was not significantly changed (Table 1) but the temperature for the conversion of R structure into martensite was increased to -13°C . (This change in the martensite start temperature will be discussed later. It is consistent with calorimeter data obtained for this rod when it was annealed at still higher temperatures.) The greater amount of martensite formed in this specimen, together with the retained R structure, began its reversion into B 2 at about $+20^{\circ}\text{C}$, an inflection point on the heating curve. On heating above this temperature, the resistance trace is no longer precisely reversible, further indicating that the temperature for B 2 structure formation has been exceeded.

The major change resulting from the 400°C annealing treatment, as shown in Figure 9, was in the quantity of material that transformed during cooling. The narrowing of the transformation temperature range during heating, shown in Table 1, has continued.

The greatly increased volume of transformable B 2 generated by the 400°C annealing treatment (versus that at 300°C) corresponds with the reduced rate of linear contraction in the annealing range between 300°C and 400°C (Figure 3). The diminished amount of contraction shown in Figure 3 was attributed to diminished residual stresses. These reduced residual stresses acted on the greatly increased amount of B 2 in the subsequent resistance test, thus causing the formation of the large amount of R represented by the area under the cooling curve in Figure 9.

Annealing at 450°C had a small additional effect on electrical resistance changes [Figure 10(A)] when added to the effect of the 400°C annealing treatment. The small reduction in residual stresses resulting from the 450°C annealing treatment lowered the temperature for the start of formation of R structure from 50°C to 40°C during the cooling leg. Ling and Kaplow⁴³ reported similar lowering of the temperature for the start of formation of R structure following 30-minute annealing treatments at 500°C to 540°C for one alloy, and at 400°C to 500°C for a second alloy, both nominally 50.12 atomic percent nickel.

The reduced stresses after the 450°C annealing treatment of the Heat 83755 rod also reduced the extent of strained B 2 formed during the heating leg, completing transformation at 55°C , versus the prior 65°C (Table 1).

The inflection points on the electrical resistance curves for cooling and heating can now be specified in terms of transition phenomena as shown in Figure 10(B). Cooling started at point A. The R structure started to form from

TABLE 1. TRANSITION TEMPERATURES BASED ON ELECTRICAL RESISTANCE CURVES
TEMPERATURES, °C

| FIGURE | ANNEALING TEMPERATURE °C | COOLING | | HEATING | |
|--------|--------------------------------|------------------------|---------------------|-----------------------|---------------------|
| | | "R" STRUCTURE START | MARTENSITE START | R, AUSTENITE START | AUSTENITE FINISH |
| 5 | 200 | +38 | -35 | -35 | +50 |
| 8 | 300 | +40 | -13 | +20 | +72 |
| 9 | 400 | +50 | -5 | +20 | +65 |
| 10 | 450 | +40 | -8 | +20 | +55 |
| 11 | 500 | +40 | +5 | +20 | +55 |
| 13 | 550 | +30 | +15 | - | - |
| 14 | 600 | +25 | +7 | - | - |

NOTES: THE INITIAL INFLECTION POINTS OF THE RESPECTIVE CURVES ARE TAKEN TO REPRESENT THE START OF FORMATION OF THE RESPECTIVE STRUCTURES. THESE DATA ARE FOR HEAT 83755 FOLLOWING CUMULATIVE TWO-HOUR ANNEALING TREATMENTS AT THE SEQUENTIAL TEMPERATURES SHOWN.

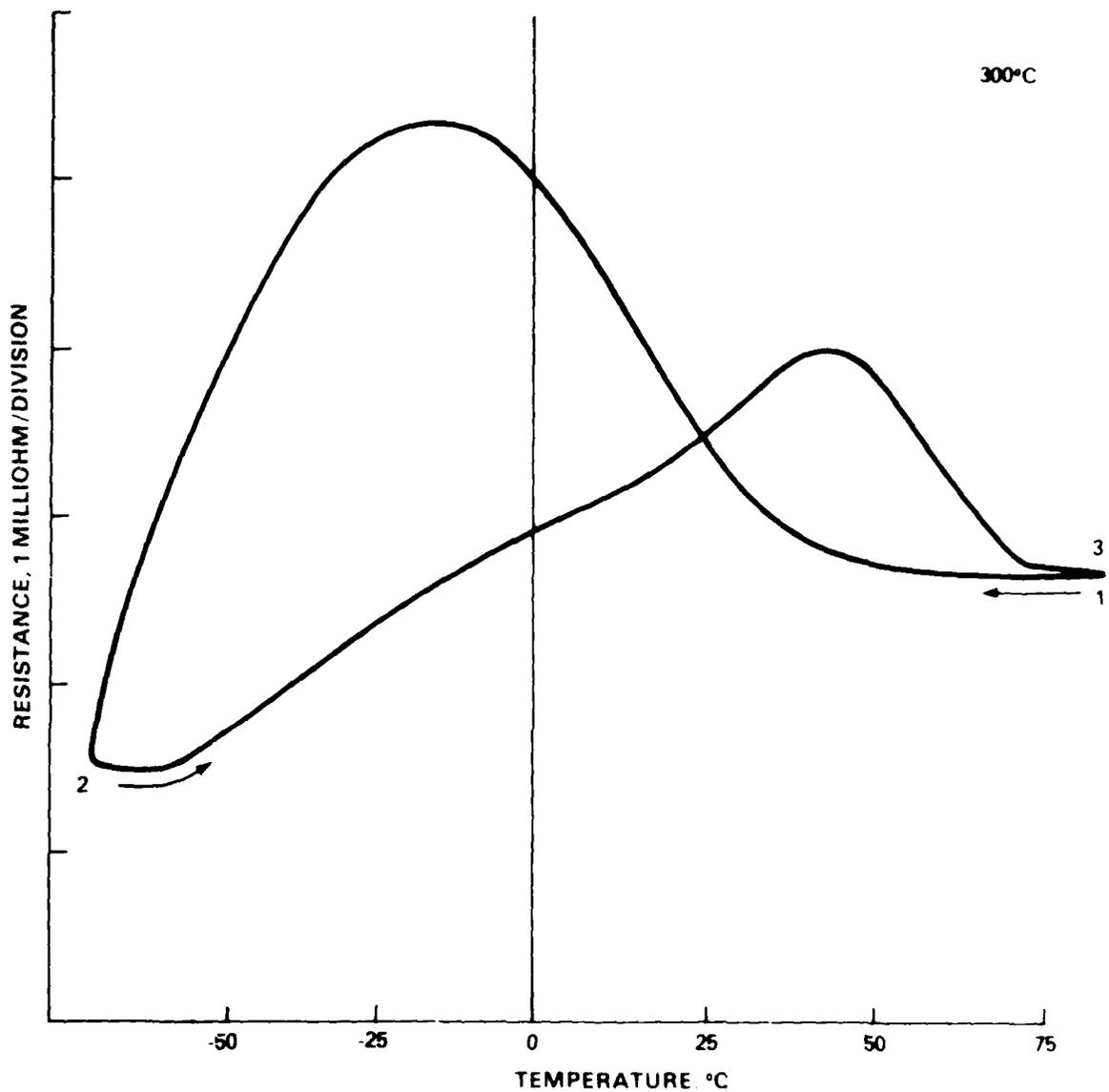


FIGURE 8. ELECTRICAL RESISTANCE OF NITINOL ROD, HEAT 83756, AFTER TWO HOUR ANNEALING TREATMENT AT 300°C, FOLLOWING PRIOR LOWER TEMPERATURE ANNEALING TREATMENTS

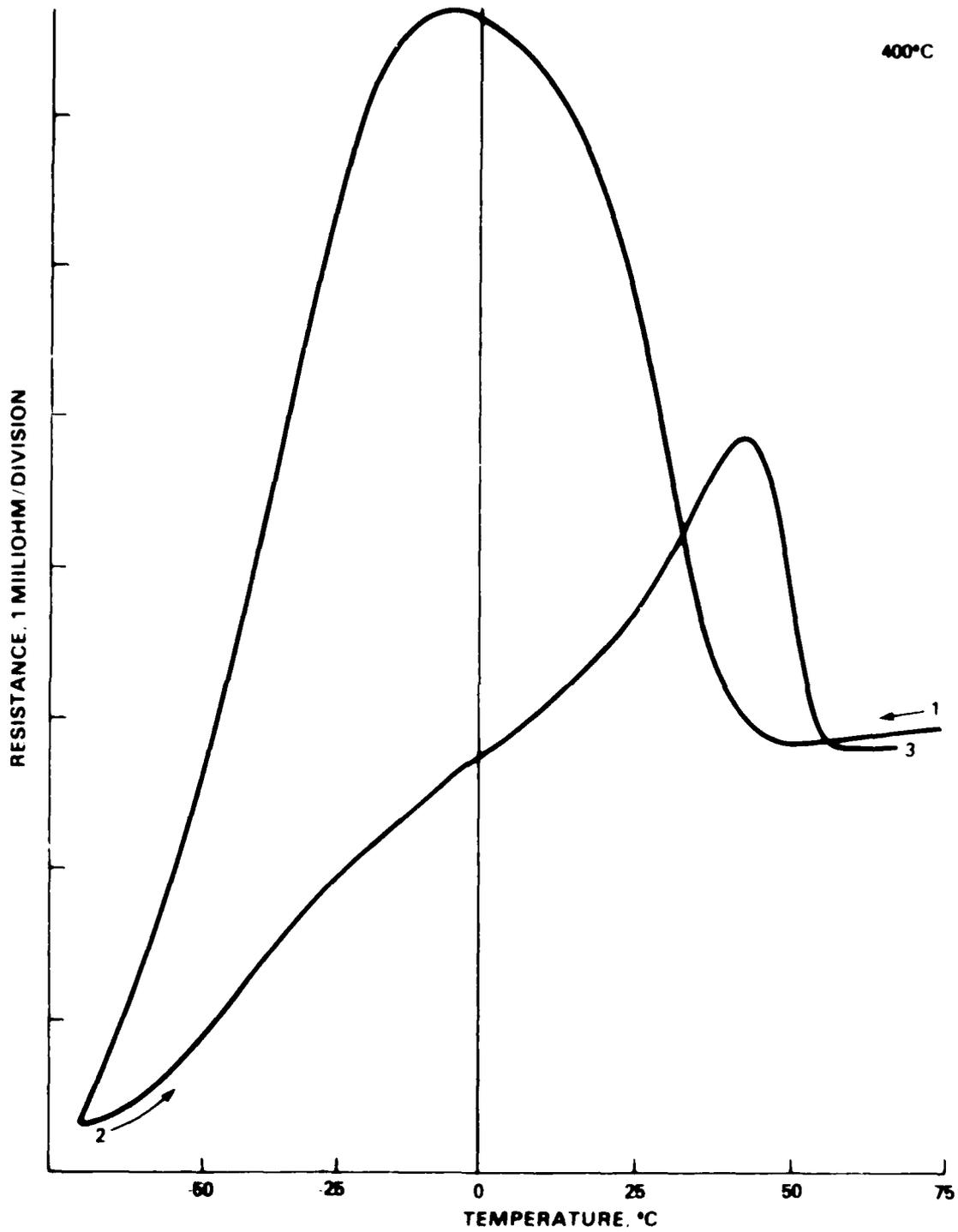
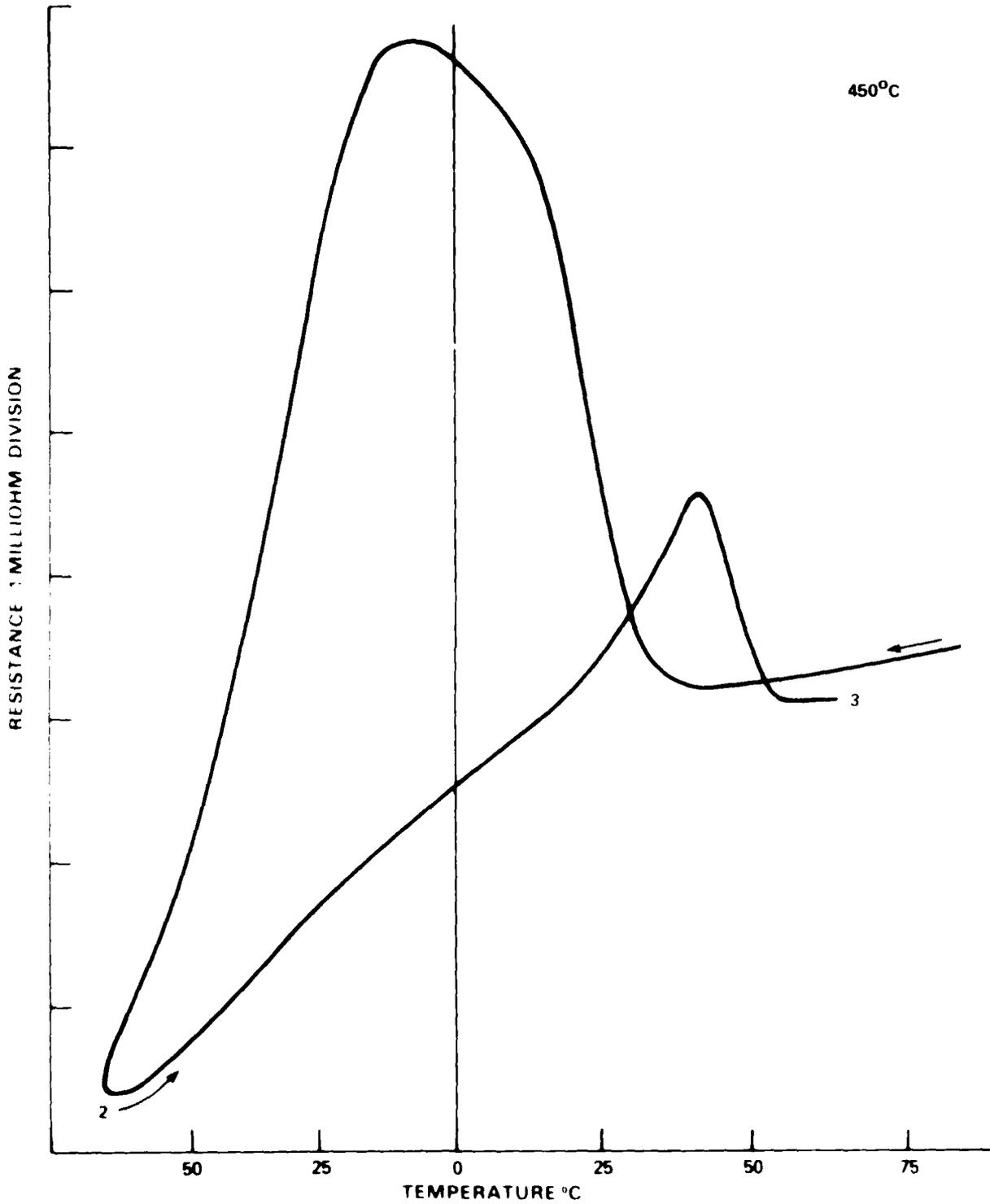
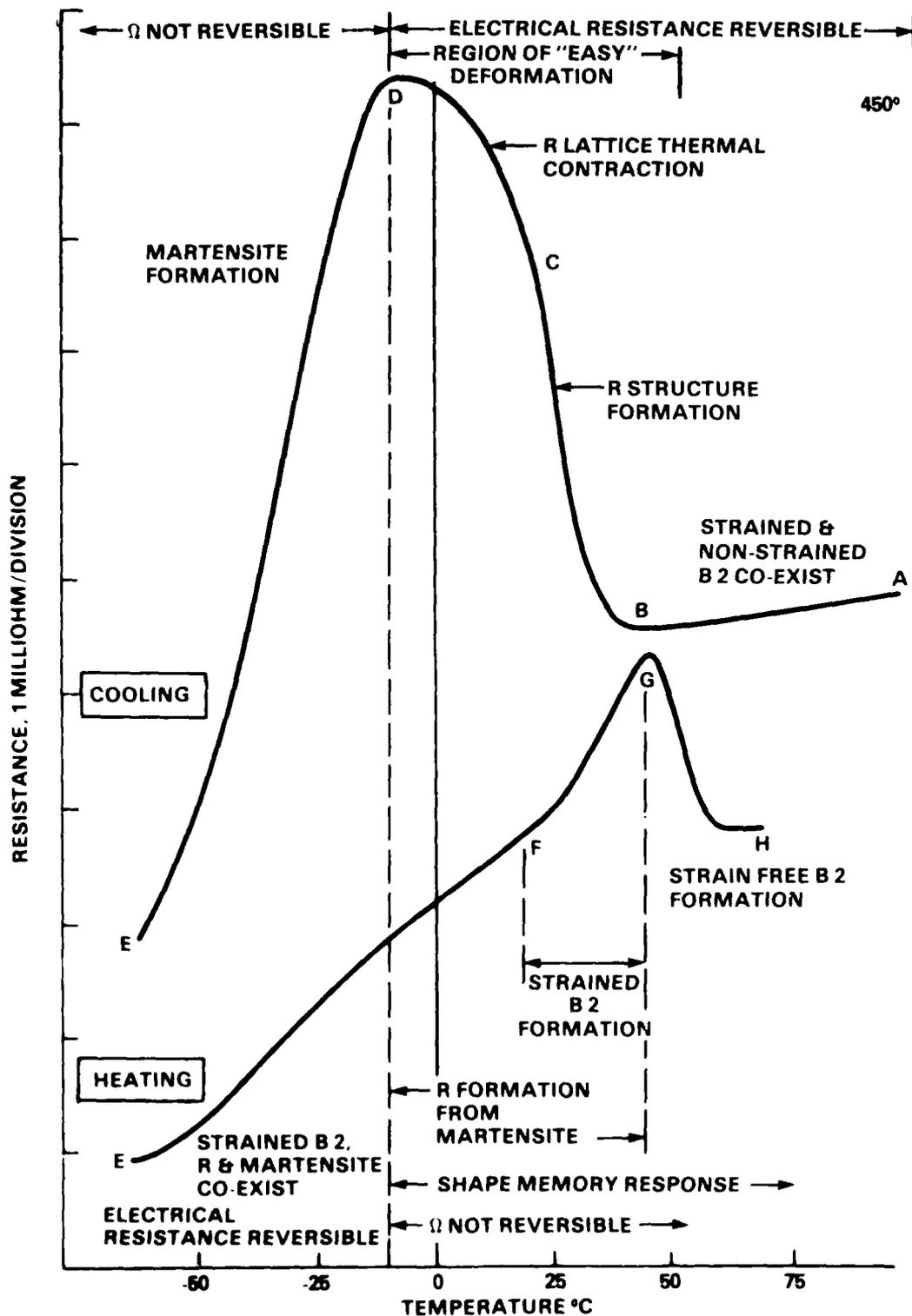


FIGURE 9 ELECTRICAL RESISTANCE OF NITINOL ROD, HEAT 83756, AFTER TWO HOUR ANNEALING TREATMENT AT 400°C, FOLLOWING PRIOR LOWER TEMPERATURE ANNEALING TREATMENTS



(A) DRAWING TO SAME SCALE AS FIGURES 5, 8, 9, 11, 13, AND 14

FIGURE 10 ELECTRICAL RESISTANCE OF NITINOL ROD HEAT 83755 AFTER TWO HOUR ANNEALING TREATMENT AT 450°C. FOLLOWING PRIOR LOWER TEMPERATURE ANNEALING TREATMENTS



(B). DRAWING NOT TO SAME SCALE AS FIGURES 5, 8, 9, 11, 13, AND 14

FIGURE 10. ELECTRICAL RESISTANCE OF NITINOL ROD, HEAT 83756, AFTER TWO HOUR ANNEALING TREATMENT AT 450°C, FOLLOWING PRIOR LOWER TEMPERATURE ANNEALING TREATMENTS (Cont)

non-deformed B 2 at point B, an inflection point of the curve. Additional stresses were generated in the specimen during the formation of R structure, increasing its electrical resistance. The formation of R structure was essentially complete at point C. From points C to D the R structure continued to contract, in accordance with its normal thermal coefficient of contraction. The resultant decreased volume increased the strain in the R structure and, therefore, its electrical resistance. (In this temperature range, if the structure were strain-free, the specimen would have transformed to martensite and have been of increased volume. Thus, the volume decrease due to thermal contraction is effectively producing increased strain.) In support of this premise, Ling and Kaplow³⁰ reported the contraction in length of wire in the R phase to be 0.05% during its cooling from the temperature of R formation to the temperature just above martensite formation. Furthermore, the contraction was reversible, as is customary for the coefficient of expansion. Additionally, they reported X-ray data that showed the unit cell parameters were decreasing with decreasing temperature.

This evidence supports the premise that the dimensional change in the R structure was due to thermal contraction and that it produced a consequent increase in internal stresses. At D, the limiting shear stress of the structure is locally exceeded and martensite forms locally by shearing, reducing stress and electrical resistance. Thus, at temperatures below point D, any existing stressed* structure (most likely of R, B 2, or near B 2 configuration) which is unable to transform, is retained and becomes surrounded by martensite. This interpretation fits the data of Ling and Kaplow, who reported²⁷ that Beta, a structure encompassing both B 2 and R, was retained to -150°C , even though martensite formation was completed at -70°C . The authors were unable to present a rationale for this. It is strongly surmised that the retained B 2 portion of the beta structure was residually stressed.

Sandrock³¹ viewed the zone of increasing electrical resistance, i.e. from points B to D of Figure 10(B), as a region of mechanical instability of the B 2 lattice, and of softening of its elastic moduli. Specimens in the R structure are palpably less stiff than they are at temperatures outside of its range of existence. Deformation of the alloy is accomplished most easily when it is in the R structure and at a temperature near that at which shear (Point D) occurs. Although they did not identify an intermediate structure, Wasilewski⁴⁴ and Rozner and Spinner^{45,46} reported very pronounced minima in the dynamic elastic moduli as a function of temperature. The minima were in the normal temperature ranges for transformations. Cross, Kariotis, and Stimler³⁹ reported the yield stress versus elongation curves over a wide temperature band, again with pronounced minima in the transformation region.

The structures existing or formed during the heating leg are identified on Figure 10(B). They are essentially a reversal of the events of the cooling leg. Matsumoto²⁹ had also postulated "event-reversal" previously.

* At the annealing temperature of 450°C , an additional source of strain affecting these structures may arise because of precipitation effects. If present, the effect of this strain on the resistance curve shown in Figure 10 cannot be assessed. Precipitation effects resulting from annealing treatments at 450°C will be discussed in detail in the subsequent section on calorimetry.

Honma et al⁴⁷ reported that alloying with transition elements in minor amounts, replacing nickel, will also produce and stabilize the intermediate structure.

Buehler and Wang⁴⁸ noted that thermal cycling within the transition range increased the area under the cooling leg of the electrical resistance curve and lowered the temperature value of its peak. Perkins subsequently showed that thermal cycling produced dislocations. In other alloys, it has been shown that cold work produces dislocations. Perkins⁴⁹ thus concluded that Wang's thermal cycling was therefore a form of cold work. If this is so, then it is to be expected from the theory presented in this paper that thermal cycling would indeed lower the temperature for the start of martensite formation. Mukherjee, Milillo, and Chandrasekaran⁵⁰ confirmed that the temperature for the start of martensite formation was lowered by thermal cycling, using changes in hardness measurements at temperature as the criterion of the lowering. They also showed that with increasing cycles (up to 30), the hardness level of the alloy increased and considered dislocations as its possible cause. Honma et al⁵¹ also concluded that the appearance of a transition structure, based on X-ray diffraction patterns, was possibly a result of dislocations induced by thermal cycling of slightly nickel-rich alloys. This evidence is in agreement with the results obtained in the present study, supporting the thesis that stress affects the phase transformation.

The amount of R structure that was formed during the cooling of the specimen after the 500°C annealing treatment (Figure 11) was less than that after the 450°C annealing [Figure 10(A)], based on the areas under their respective curves. The peak value indicating the start of martensite formation moved to a higher temperature. This is consistent with the diminished residual stresses that resulted from the successive annealing treatments at increasingly higher temperatures.

The reduced residual stresses existing after the 500°C annealing treatment resulted in a B 2 structure whose re-formation during the heating leg is barely detectable by the resistance method.

Reviewing Figures 5 and 8 through 11, which show the electrical resistance changes during transformation, and the listing in Table 1, it can be observed that there is a progression of the martensite formation temperature (Point D) to higher values with each succeeding annealing treatment. Also, after the 400°C annealing treatment, the specimen developed a greatly increased amount of R structure during cooling. This resulted from the increased amount of B 2 that was able to transform during cooling in the presence of the residual stresses still in the specimen. Further, the start of the transformation into R structure was at a high value, 50°C, as a result of the residual stresses aiding in the formation of R structure, as previously described. Stresses started the formation of R structure earlier, i.e. at 40°C and 50°C for annealing treatments up to 450°C, as compared to a 30°C start after annealing at 550°C, with the lesser stresses then present. Thus it appears that stresses first assist in the formation of R structure and then delay its conversion into martensite. The first part of the transformation, the formation of R structure, is reversible with temperature. The second part, the formation of martensite by shearing, is not reversible in its electrical resistance response as a function of temperature. Together, the two parts constitute the complete transformation from austenite to martensite.

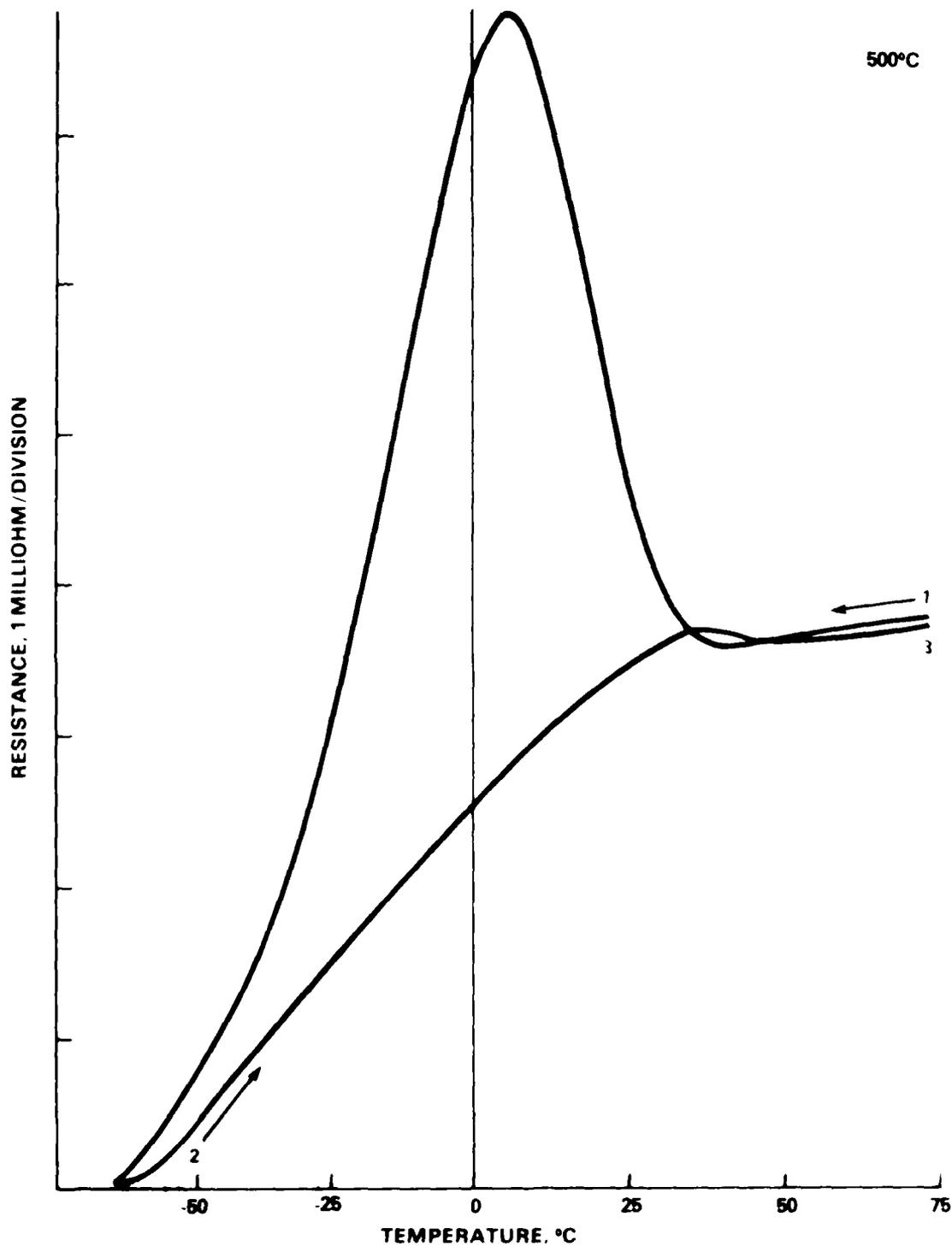


FIGURE 11. ELECTRICAL RESISTANCE OF NITINOL ROD, HEAT 83755, AFTER TWO HOUR ANNEALING TREATMENT AT 500°C, FOLLOWING PRIOR LOWER TEMPERATURE ANNEALING TREATMENTS

Annealing this alloy at 500°C and 550°C introduces another phenomenon that affects the phase transformation of this and other nickel-rich NITINOL alloys: the precipitation of excess nickel in solution. Submicroscopic precipitates were reported by Dautovich and Purdy,²² Hanlon et al,⁴⁰ and later by Otsuka and Shimizu.⁵²

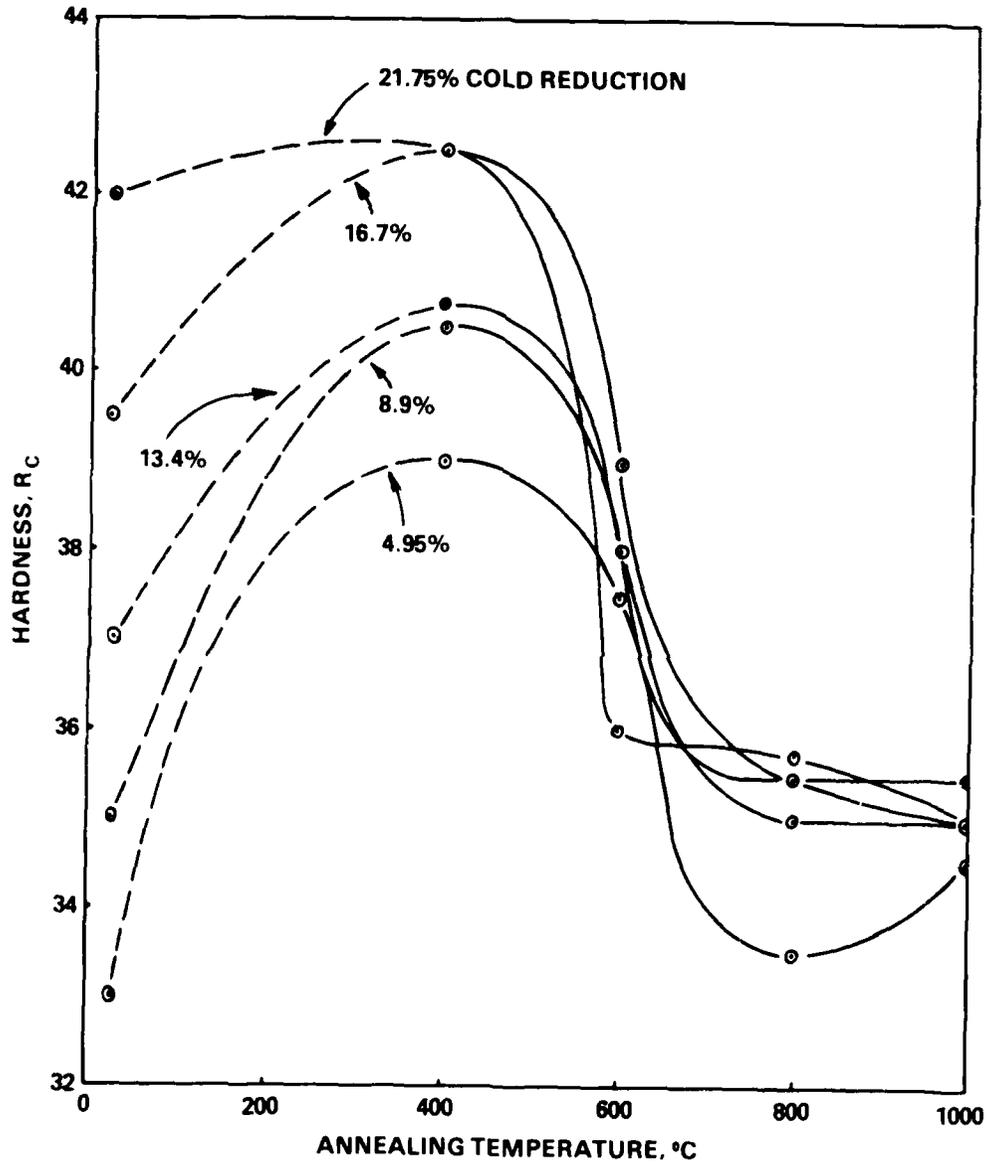
The Heat 83755 specimen reported on in the present work is supersaturated with nickel by virtue of its earlier solution treatment at 600°C, before its cold drawing. However, neither the composition of this specimen, nor the phase boundaries of the NiTi compound in the Ni-Ti system are known with sufficient accuracy to pinpoint their proximity, and thus predict when precipitation would be most pronounced. Thus, although precipitation has been occurring at ambient temperature and during all the previous annealing treatments, it was minimal because of negligible diffusion at the low temperatures. Its effect on the transformation was small and was masked by the residual stress effects. In the 500°C+ range, however, atomic diffusion was sufficiently rapid to effect structural and local compositional changes within two hours, via precipitation. Thus, after 500°C annealing treatments, the decreasing residual stresses from cold working may be partly offset by new stresses generated by the initiation of precipitation of excess nickel in the form of TiNi₃.*

To appreciate the potential magnitude of these precipitation-associated stresses, note that NITINOL alloys of 56+ weight percent nickel are considered precipitation-hardening alloys, with hardnesses of 56 and higher on the Rockwell C scale, when aged after solution treatment. It is assumed that hardness is a measure of internal stresses, and that in these alloys the hardening mechanism is analogous to the age hardening found in the aluminum-copper alloy system. Interestingly, Buehler et al, in their first report on this alloy,¹ presented data (reproduced here as Figure 12) that suggest precipitation hardening occurred as a result of heat treating, at 400°C for one hour, in a strip cold-rolled as much as 16.7%. The authors did not discuss the source of the hardening in this particular test.

At 550°C, the alloy is still in a two-phase field and the annealing treatment may have precipitated more nickel, thus leaving the matrix richer in titanium. The net effect of the precipitation stresses and the reduced residual stresses was the formation of R structure, during cooling, at a lowered temperature (Figure 13 and Table 1). A reduced amount of R structure was formed during the transformation. Recrystallized grains, which were strain-free, formed during the 550°C annealing treatment. Therefore, they could transform instantly during cooling to martensite, and make no positive contribution to the increased resistance. The great reduction in residual stresses that resulted from this annealing treatment is manifested both by the reduced amount of R structure formed on cooling and by the virtual absence of a stress-induced peak during the heating leg of the test cycle.

After annealing at 600°C (Figure 14) recrystallization of the specimen was complete. This alloy composition was in the single phase region at 600°C, which

* Wasilewski et al^{11,24} reported that Ni₃Ti₂, a phase with structure close to that of TiNi, formed at 625±20°C in nickel-rich compositions. Jackson et al⁴ pointed out that this may be a transitional structure in the formation of equilibrium TiNi₃.



(FROM REFERENCE 1)

FIGURE 12. HARDNESS CHANGES OCCURRING IN COLD REDUCED TiNi COMPOSITION SPECIMENS HEATED 1 HOUR AT INCREASING TEMPERATURES

550°C

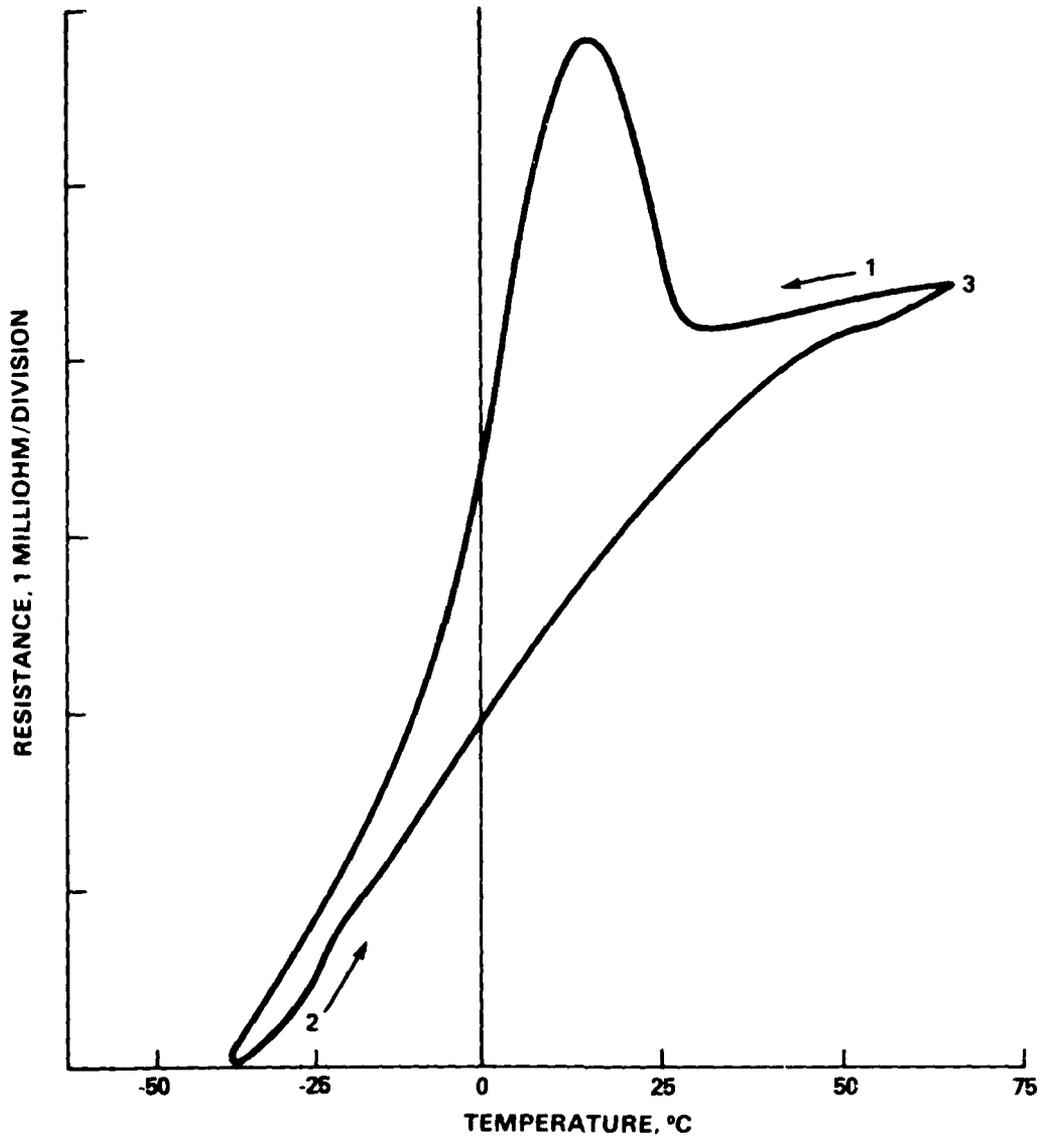


FIGURE 13. ELECTRICAL RESISTANCE OF NITINOL ROD, HEAT 83755, AFTER TWO HOUR ANNEALING TREATMENT AT 550°C, FOLLOWING PRIOR LOWER TEMPERATURE ANNEALING TREATMENTS

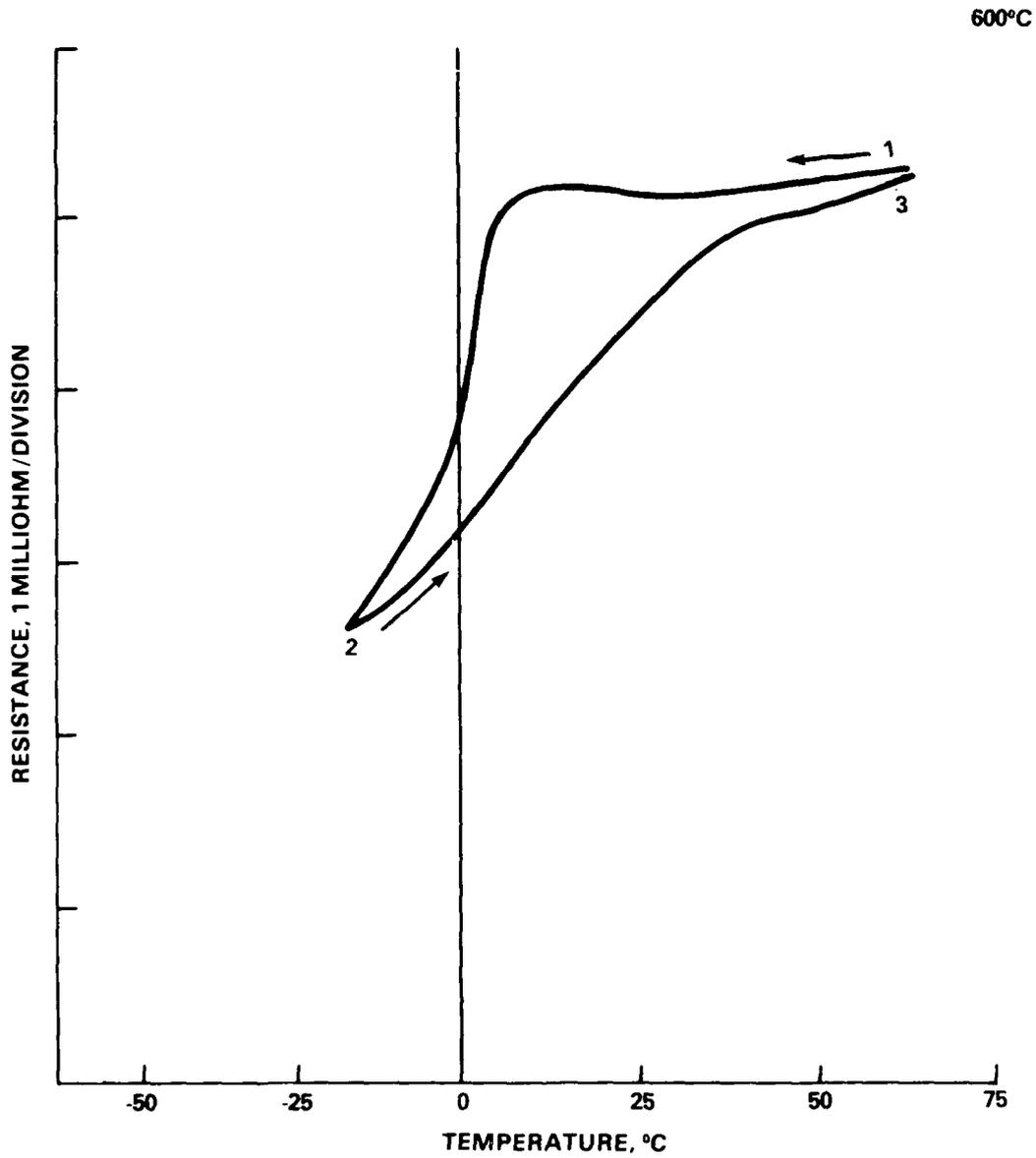


FIGURE 14. ELECTRICAL RESISTANCE OF NITINOL ROD, HEAT 83755, AFTER TWO HOUR ANNEALING TREATMENT AT 600°C. FOLLOWING PRIOR LOWER TEMPERATURE ANNEALING TREATMENTS

caused the previously precipitated nickel to re-dissolve in the matrix. The temperature for martensite formation was lowered to $+7^{\circ}\text{C}$, the consequence of the newly nickel-enriched matrix. During cooling, an almost negligible amount of R formed during the transformation of austenite into martensite. The transformation was almost strain-free during the resistance test cycle. The alloy was recrystallized and supersaturated, since negligible precipitation occurs during the air cooling from 600°C of a small cross-section rod. It was, therefore, metastable and essentially stress-free at ambient temperature, since no aging treatment had been performed on it. Wasilewski⁴⁴ reported that specimens quenched from 650°C had higher internal stresses than if slowly cooled. Gilfrich,⁵³ based on the metallography of a hot-rolled strip, concluded that TiNi structures with more than 54 w/o Ni could be metastable at 25°C , forming martensite under the small stresses generated during the preparation of samples for metallographic examination.

Calorimetry

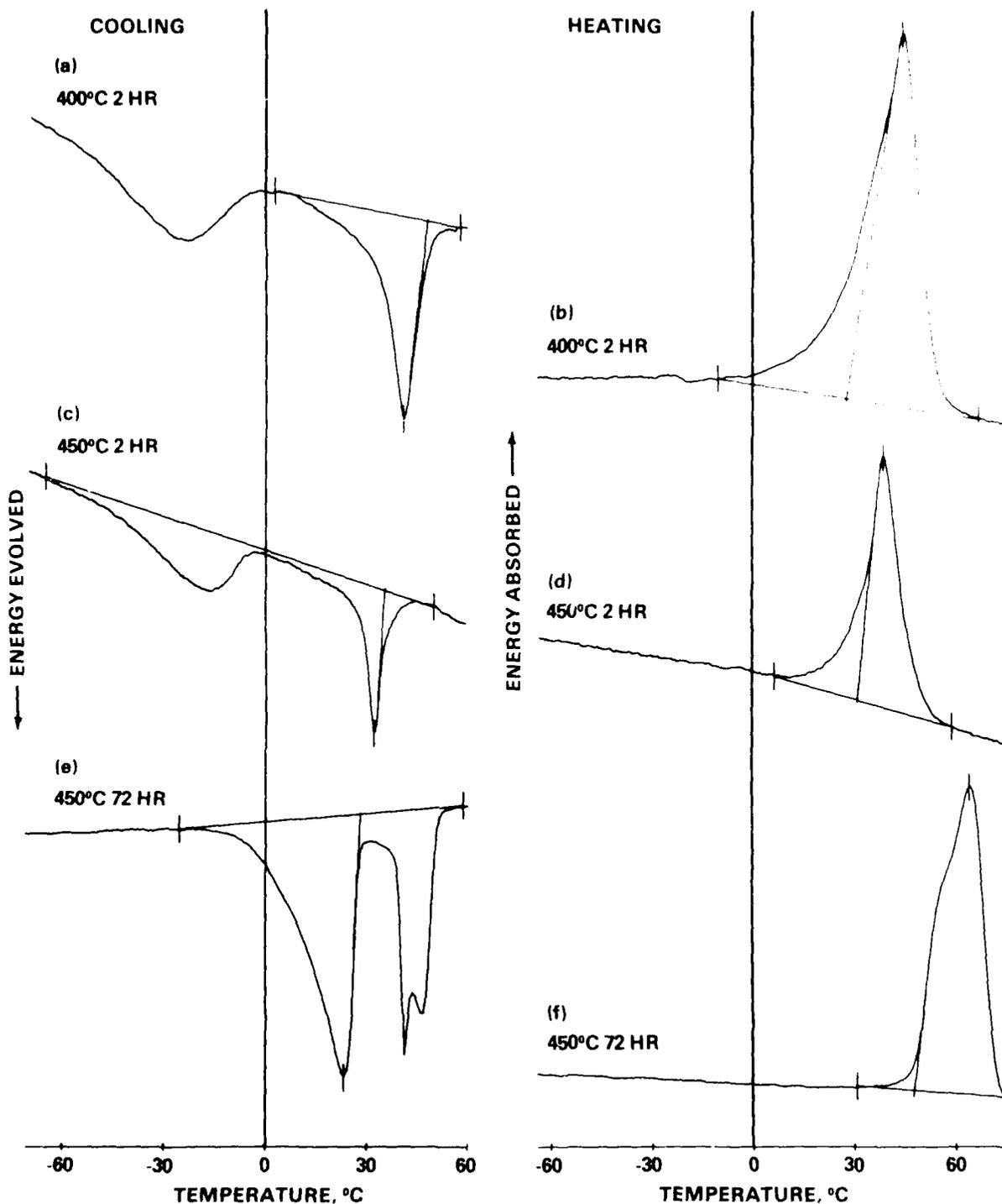
The cooling trace produced by DSC on a wafer sliced from the cold-drawn rod and annealed at 400°C for two hours is shown in Figure 15(a). The first peak, developed at 53°C while cooling, represents the heat evolution to the environment by the specimen during formation of R structure. As cooling continued, R structure converted to martensite, starting at -4°C , and produced the second peak. Other investigators have reported peaks for heating,^{26,54} or for both heating and cooling,^{37,55} but have not explained the dual peaks. The heating curve is shown in Figure 15(b).

The reduced residual stresses after annealing at 450°C for 2 hours resulted in formation of R structure at 43°C , Figure 15(c), vs 53°C for the 400°C annealing treatment, Figure 15(a) and Table 2. The R structure to martensite transformation is similar for these two annealing treatments. These results are in agreement with the electrical resistance data for the equivalent annealing treatments (Figures 9 and 10, and Table 1). The calorimetry heating curve is shown in Figure 15(d).

Longer time annealing at 450°C , for 72 hours, caused significant precipitation of excess nickel. Relative enrichment of the matrix titanium content (by the nickel precipitation) raised the transformation start temperature to 52°C , versus the 43°C obtained after the 450°C two-hour annealing treatment [Figure 15(e), cooling]. Also the formation and retention of R structure is due to the stresses associated with precipitation, since the diminishing residual stresses after the long time anneal would tend to lower, not raise, the transition start temperature. The heating curve is shown in Figure 15(f).

Hanlon et al⁴⁰ reported a similar result with a highly nickel-enriched alloy of 51.6 atomic percent nickel. After cooling it from 900°C to 600°C , they held it at that temperature for 108 hours. Some of the excess nickel that was in solution at 900°C precipitated at 600°C , raising the alloy's transformation temperature.

The jog in the cooling curve [Figure 15(e)] and the inflection in the heating curve [Figure 15(f)] are changes in the rate of evolution and absorption of heat, respectively, and will be considered subsequently.



NOTE: THE AREAS UNDER THE CURVES ARE FUNCTIONS OF SPECIMEN MASS.

FIGURE 15. DIFFERENTIAL SCANNING CALORIMETRY TRACE OF NITINOL, HEAT 83755, FOLLOWING ANNEALING TREATMENTS AT 400 AND 450° C

TABLE 2. TRANSITION TEMPERATURES BASED ON CALORIMETRY CURVES

| FIGURE | TIME (HOURS) | ANNEALING TEMPERATURE | TEMPERATURES, °C | | | | |
|-----------|-----------------|--------------------------|-------------------------|---------------------|----------------------|--------------------------|---------------------|
| | | | COOLING | | | HEATING | |
| | | | R STRUCTURE START | MARTENSITE START | MARTENSITE FINISH | R, AUSTENITE START | AUSTENITE FINISH |
| 15(a),(b) | 2 | 400 | 53 | -4 | -60 | 10 | 56 |
| 15(c),(d) | 2 | 450 | 43 | -5 | -60 | 20 | 50 |
| 16(a),(b) | 2 | 500 | 40 | 13 | -35 | 22 | 58 |
| 17(c),(d) | 2 | 550 | 30 | - | -10 | 32 | 55 |
| 17(e),(f) | 2 | 600 | 10 | - | -10 | 25 | 40 |
| 15(e),(f) | 72 | 450 | 52 | 30 | -10 | 45 | 72 |
| 16(c),(d) | 15 | 500 | 43 | 35 | 15 | 52 | 68 |
| 16(e),(f) | 65 | 500 | 45 | - | 35 | 64 | 80 |

NOTES: THE INITIAL INFLECTION POINTS OF THE RESPECTIVE CURVES ARE TAKEN TO REPRESENT THE START OF FORMATION OF THE RESPECTIVE STRUCTURES. THESE DATA ARE FOR HEAT 83755 WITH TWO-HOUR ANNEALING TREATMENTS IN THE TOP GROUPING AND EXTENDED ANNEALING TIMES IN THE BOTTOM GROUPING.

The calorimetry data indicate that the more rapid diffusion during the 500°C annealing treatment [Figure 16(a)] produced similar precipitation in 2 hours as was produced at 450°C in 72 hours [Figure 15(e)]. Such behavior is typical of diffusion-controlled phenomena.

The results of annealing at 500°C for 2, 15, and 65 hours, respectively, are shown in Figure 16(a) through (f) and also in Table 2. The 2-hour annealing treatment data, Figure 16(a), affirm the electrical resistance graphical data (Figure 11). The 15-hour annealing treatment, Figure 16(c), has almost converged the martensite peak onto the R structure peak. The 65-hour annealing treatment, Figure 16(e), accomplished the merging of the two peaks, indicating the direct transformation of B 2 into martensite during cooling. Thus, the R structure is a transient that can exist during transition. Its existence is predicated on the presence and magnitude of stresses; i.e. the temperature range over which it can exist is a direct function of the magnitude of the stresses.

The precipitation of excess nickel from the matrix during the 500°C annealing treatment produced a substantial change in the transition temperatures of this alloy. The range of the start and finish temperatures for austenite formation during heating, taken arbitrarily from the inflection points of the heating DSC graphs, are listed in Table 3 for the 500°C annealing treatment. The transformation start temperature on heating of this alloy was as low as 22°C and as high as 64°C, depending on the nickel content of the matrix. The transformation ranges for the other annealing treatments included in Table 3 illustrate the variances arising from their non-equilibrium conditions.

The jogs and inflections in the DSC curves, Figure 16(a) and (b), for the two-hour annealing treatment at 500°C, and the previously referred to 72-hour annealing treatment at 450°C, Figure 15(e) and (f), represent change in the rate of formation of a particular structure during the heating or cooling leg of the test. We have postulated that matrix composition and stresses are two interacting parameters that influence the transformation structures formed and the temperatures at which they form. Therefore, these jogs and inflections are considered to result from this same interaction, i.e. a combination of stresses with localized variations of the matrix composition. In this and in other unpublished work with slightly nickel-rich NITINOL alloys, similar jogs and inflections have appeared during the transitions of materials annealed specifically in the 450°C to 550°C range. Although both stress and matrix composition are affected by thermal processing over the range from 100°C to 600°C, the anneals in the 450°C to 550°C range produce the greatest change in them. Thus the jogs and inflections are considered to be transient effects resulting from compositional and stress changes generated by precipitation during the annealing treatments in the 450°C to 550°C temperature range.

As discussed earlier, increased diffusion during higher temperature annealing can correspond with results obtained by longer time annealing at a lower temperature. A 550°C annealing treatment for 2 hours has a calorimetry heating trace [Figure 17(d)] similar to that of the 500°C annealing treatment for 15 hours [Figures 16(d) and 17(b)]. However, their traces on cooling are significantly different. The traces from both annealing treatments are shown in Figure 17(a) through (d). The single peak developed during cooling, Figure 17(c), indicates significantly reduced internal stresses compared with the double peaks for the 500°C annealing treatment, Figure 17(a). On the other

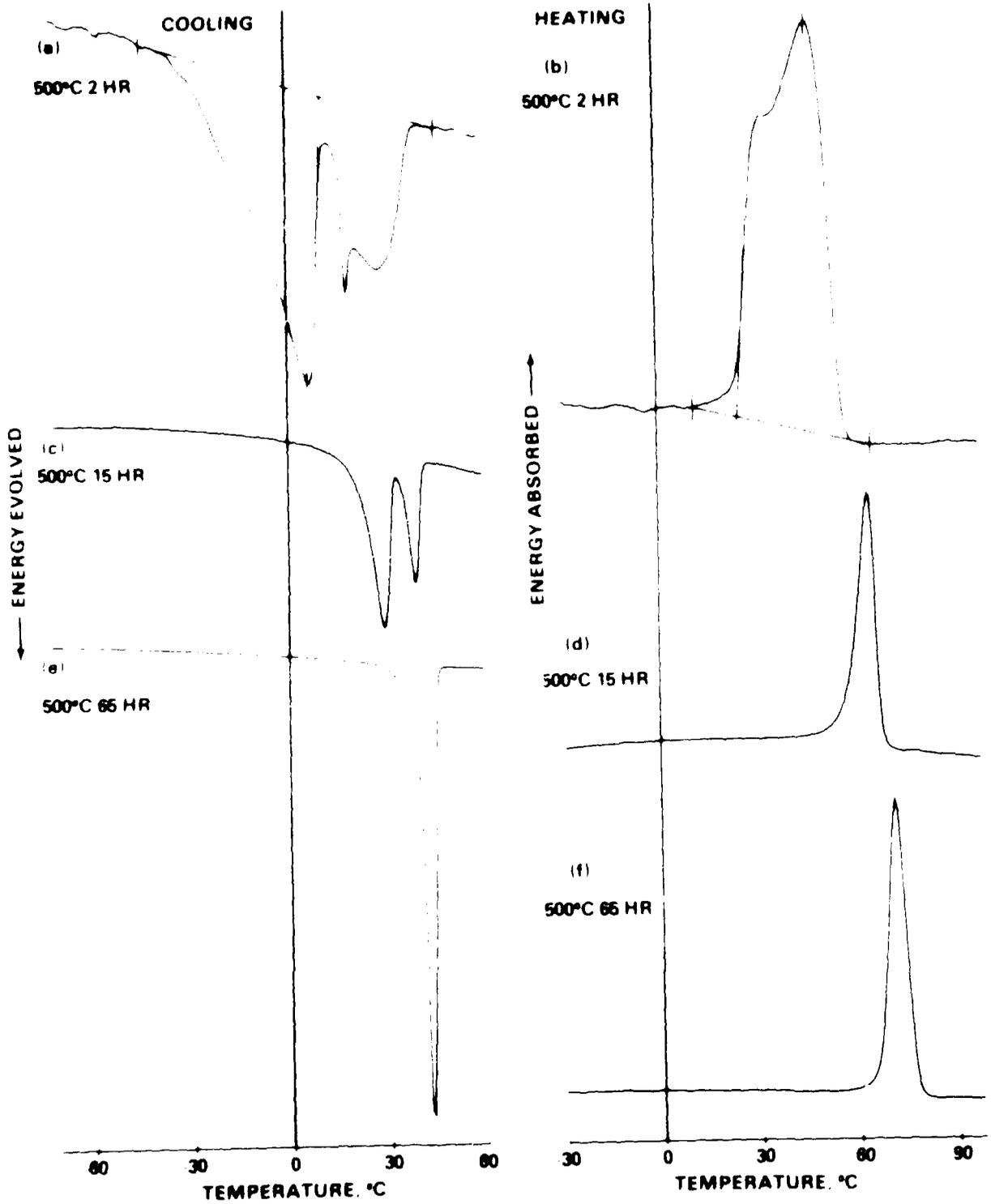


FIGURE 16 DIFFERENTIAL SCANNING CALORIMETRY TRACE OF NITINOL, HEAT 83755, FOLLOWING ANNEALING TREATMENTS AT 500°C

TABLE 3. TRANSFORMATION TEMPERATURE RANGES FOR COLD WROUGHT AND ANNEALED NITINOL HEAT 83755

| ANNEALING TEMPERATURE °C | ANNEALING TIME (HOURS) | | | |
|-----------------------------|---------------------------|-------|-------|-------|
| | 2 | 15 | 65 | 72 |
| 400 | 10-56 | | | |
| 450 | 20-90 | | | 45-72 |
| 500 | 22-98 | 52-98 | 64-80 | |
| 550 | 32-55 | | | |
| 600 | 25-40 | | | |

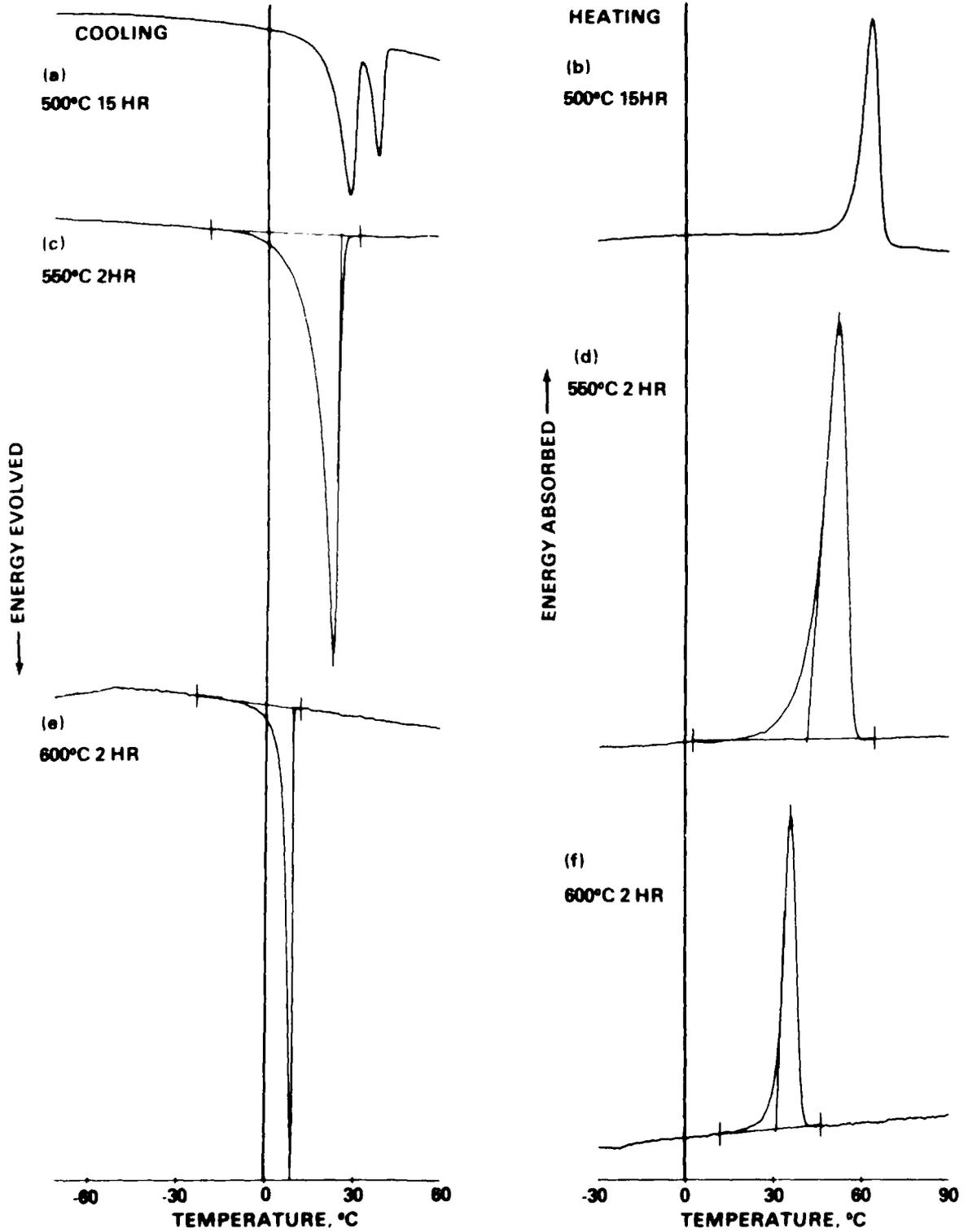


FIGURE 17. DIFFERENTIAL SCANNING CALORIMETRY TRACE OF NITINOL, HEAT 83755, FOLLOWING ANNEALING TREATMENTS AT 500°, 550° AND 600°C

hand, the longer time at 500°C was the more efficient in reducing the amount of nickel in solution, producing transformation during heating at the higher temperature, Figure 17(b) versus 17(d). The practical application of this is that long time anneals at lower temperatures can, within limits, produce shape recovery at higher temperatures than would shorter anneals at higher temperatures.

Annealing at 600°C returned the specimen to a single-phase field, as noted in the earlier resistance data. The calorimetry and resistance data correlate well and confirm that nickel had re-dissolved in the matrix during the two-hour annealing treatment. The sharply lowered transition temperatures, Figure 17(e) and (f), with no indications of R structure agree with the resistance data (Figure 14) showing negligible indications of strain.

CONCLUSIONS

The peculiar first-time expansion and contraction behavior reported by Buehler and his co-workers for a near equiatomic NiTi alloy, which they named "NITINOL," has been reproduced and examined in considerable detail. Data were obtained from linear contraction, electrical resistance, and differential scanning calorimetry measurements as a function of annealing cycles. These data support the theory that residual stresses have very great effects on the near room temperature phase transformation of nickel-rich NITINOL alloys. The principal postulations of this theory follow.

A strain-free NITINOL compound will transform from its austenitic (B 2) structure to a martensite structure with an immediate and continuing decrease in electrical resistance during cooling. If residual and/or precipitation stresses are present, they cause substantial "anomalous" increases in the electrical resistance of the alloy at the beginning of the transformation on cooling. Subsequently, the resistance decreases sharply as the formation of martensite initiates and continues. The extent of stresses present significantly affect the temperature of start and finish of the transformation, as well as the profile of electrical resistance peaks developed during transformation, both in cooling and heating. Annealing relieves these stresses, causing large changes in the electrical resistance curves observed during the phase transition.

Residual stresses also provide the force that controls the direction of shape recovery, i.e. contraction, expansion, or bend movement. They influence the extent of shape recovery generated in the reduced strain, or strain-free, adjacent volumes of the alloy. Microstress relief in the cold-worked alloy used in this work permitted 0.3% total length (dimensional) recovery during two hours of warming at 100°C. The subsequent macrostress relief during annealing at 400°C for two hours permitted a 2.75% total dimensional recovery. Although not discussed in this work, it is widely accepted that NITINOL alloys are capable of a 6% strain recovery at temperatures up to 100°C.

Stress induces the formation and retention of a rhombohedral distortion of cubic B 2, designated as "R structure," during cooling. This structure is intermediate to the B 2 and martensite phases and is of higher resistivity than either. During cooling, stresses induce earlier formation of R structure (i.e.

at a higher temperature), and delay its conversion to martensite to a lower temperature. The differing amounts of R structure formed and retained during transformation for specimens with different annealing treatments can be inferred from the area under their respective electrical resistance curves. In a fully annealed NITINOL, the B 2 structure transforms directly to martensite, with the atoms shifting instantaneously through the R structure positions during the transition.

Internal stresses can be generated in nickel-rich, supersaturated, near-TiNi alloys by the early stages of precipitation of $TiNi_3$ during annealing treatments in the 450°C-550°C range. Thus a partially annealed specimen deformed at ambient temperature to demonstrate the shape memory effect may have cumulative stresses within it from several sources: residual, from cold work prior to its (incomplete) anneal, from precipitation hardening, and from the cold deformation subsequent to the anneal.

A heavily cold-worked specimen with large amounts of residual stresses will show a first time significant shape memory response upon being heated well above 100°C, e.g., 300°C.

Recrystallization of the cold-worked alloy begins at a temperature higher than 300°C. If the alloy has excess nickel in solution, precipitation occurs at temperatures up to about 550°C with re-solutioning of nickel occurring near 600°C. The excess nickel may be readily retained in solution by quenching into water. Excess nickel in solution lowers the transformation temperature range, and precipitation of the excess nickel raises it. The phase boundary for the single phase field lies between 550°C and 600°C for this slightly nickel-rich alloy.

Differential scanning calorimetry tracks the near-room temperature transformation from the austenitic structure into the martensitic structure, and the reverse, very well. The effects of stress relief, resulting from annealing this alloy, upon the transformation are shown unambiguously. The two separate peaks representing the formation of R structure and its subsequent conversion into martensite, during continued cooling, are clearly delineated. The subsequent merger of the two peaks into a single peak as a result of long time annealing (65 hours at 500°C) demonstrates that the R structure is metastable. Specimens that are in equilibrium have only a single major peak during the heating or the cooling transformation.

The nickel in solution in the alloy matrix (as compared to the total nickel content of the alloy), and both the residual and precipitation stresses interactively affect the temperature range of the shape memory transformation. Therefore, transformation temperatures reported in the literature for a given nickel-rich NITINOL alloy must be considered in light of its prior thermomechanical treatment.

RECOMMENDATIONS

The work presented and discussed in this paper should be buttressed by X-ray studies showing the formation of rhombohedral (R) structure as a function

of temperature during both cooling and heating intervals of the transformation cycle.

The force requirements for shape distortion in the K structure during cooling versus those in the martensitic phase should be determined. These will be of considerable significance to designers interested in the power requirements of their devices, such as for robotic applications or for heat engine development.

The effects of stresses introduced to the martensitic structure are surmised to be of considerable influence in generating two-way memories in NITINOL alloys. These are worthy of further investigation.

Aside from stress effects on it, control of the temperature band during which transition occurs should be investigated. Such control is necessary for sharply triggering actions, i.e. at very specific temperatures, and for biomedical applications requiring precise temperature ranges for complete shape recovery.

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