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ON THE STRESSING OF ANNEALED NITINOL: THE ELECTRICAL RESISTANCE AND CALORIMETRIC EFFECTS

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The effects of stress on the electrical resistance and scanning calorimetry curves of NITINOL during its phase transformation are substantial. The generation of a peak occurs in the resistance curve, and an additional peak is generated in the calorimetry curve for the transformation during cooling, as compared to annealed metal. Explanation of the relation between stress and the formation of these peaks is presented for both cooling and heating cycles.

Straining the wire in the martensitic versus the austenitic condition also can result in differences in the subsequent phase transformation. These differences can be exploited for one-time higher temperature applications of this shape memory alloy.

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FOREWORD

Internal stresses significantly affect the near room temperature phase transformation occurring in NITINOL (TiNi) alloys. A knowledge and understanding of these effects is useful for the successful design and operation of devices using the shape memory effect of this alloy.

A prior report of this Center presented data on a programmed reduction of stresses in strained wire. The work reported now confirms those results and shows that the reversal of those effects can be generated in non-strained wire by the introduction of cold work. Furthermore, cold working the annealed alloy in its austenitic versus martensitic condition can change its phase transformation response during subsequent heating and cooling cycles.

The author expresses his appreciation to W. J. Buehler for early guidance in working with these unusual alloys. He would also like to express appreciation to his wife, Estelle, for her gracious support during the years of researching them.

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CONTENTS

	Page
INTRODUCTION	1
EXPERIMENTAL PROCEDURES	1
RESULTS AND DISCUSSION	2
RESISTANCE	2
CALORIMETRY	10
CONCLUSIONS	12
RECOMMENDATIONS	14
REFERENCES	15
DISTRIBUTION	(1)

FIGURES

Figure		Page
1	ELECTRICAL RESISTANCE OF NITINOL WIRE, HEAT D 4046. THERMAL TREATMENT: ANNEALED AT 750°C, 1/2 HR., AND AIR COOLED	3
2	ELECTRICAL RESISTANCE OF NITINOL WIRE, HEAT D 4046. THERMOMECHANICAL TREATMENT: ANNEALED AT 750°C, 1/2 HR., AIR COOLED, AND STRETCHED 1% AT 22°C	6
3	ELECTRICAL RESISTANCE OF NITINOL WIRE, HEAT D 4046. THERMOMECHANICAL TREATMENT: 2% WARM STRETCH OF SAME SPECIMEN TESTED FOR FIGURE 2	7
4	ELECTRICAL RESISTANCE OF NITINOL WIRE, HEAT D 4046. THERMOMECHANICAL TREATMENT: ANNEALED AT 750°C, 1/2 HR., AIR COOLED, AND WARM STRETCHED (AUSTENITIC CONDITION) 7%	8
5	ELECTRICAL RESISTANCE OF NITINOL WIRE, HEAT D 4046. THERMOMECHANICAL TREATMENT: ANNEALED AT 750°C, 1/2 HR., AIR COOLED, AND COLD STRETCHED (MARTENSITIC CONDITION) 7%	9
6	DIFFERENTIAL SCANNING CALORIMETRY TRACE OF NITINOL WIRE, HEAT D 4046. ANNEALED AT 750°C, 1/2 HR., AND AIR COOLED	13
7	DIFFERENTIAL SCANNING CALORIMETRY TRACE OF NITINOL WIRE, HEAT D 4046. ANNEALED AT 750°C, 1/2 HR., AIR COOLED, AND WARM STRETCHED 7%	13
8	DIFFERENTIAL SCANNING CALORIMETRY TRACE OF NITINOL WIRE, HEAT D 4046. ANNEALED AT 750°C, 1/2 HR., AIR COOLED, AND COLD STRETCHED 7%	13

TABLES

Table		Page
1	TRANSFORMATION TEMPERATURES OF NITINOL HEAT D 4046	11

INTRODUCTION

NITINOL is a nickel-titanium alloy with varied industrial and commercial applications.[1-3] Most of them are based on its "shape memory" effect. This effect is that warming the 6% cold strained alloy returns it to a previously "annealed-in" shape. The phenomenon is due to a crystallographic phase transformation, from martensite to austenite, usually over a 20°C temperature range selected between -30°C and +100°C.

The influence of residual stresses (from prior severe cold work) on this transformation was reported by Goldstein, Kabacoff, and Tydings.[4] They showed that the electrical resistance and calorimetry data associated with the shape memory effect were substantially affected by the stepwise reduction of these residual stresses. Strain, the easily measurable resultant of stress, was used as an approximation of the stresses present.

The results reported in Reference 4 imply that the reverse procedure, i.e. the introduction of stresses into a fully annealed NITINOL should generate the same phenomena sequence, in reverse. This prediction is examined now with respect to electrical resistance and calorimetry.

Resistance and calorimetry data are useful in the prediction of shape memory effect performance. They indirectly enable examination of details in the transformation process, including effects of stresses and annealing treatments on the shape recovery of the alloys.

EXPERIMENTAL PROCEDURES

The equiatomic NiTi composition is Ti-55.06 weight-percent nickel. A slightly titanium-rich composition of Ti-54.9 weight-percent nickel was selected for this experiment. The recovery transformation temperature of this binary alloy is above ambient, making it convenient to introduce strain in either its martensitic (cold) or austenitic (warm) condition. The "cold" structure is a slightly (monoclinic) distorted B 19 cell[5,6] and the "warm" structure is an ordered, body centered cubic B 2 cell.[7,8]

The alloy was induction melted, hot worked, and cold drawn to 0.031-inch diameter wire. It was annealed at 750°C for 1/2 hour, and air cooled. It was identified as Heat D 4046.

The specimen wires were strained by tensile elongation in a hydraulic draw bench. Strain rate was 1/2 inch/inch/second. Total strain was calculated on the basis of the before and after distance between two crimped-on short copper sleeves. The specimen wires were 6-inch lengths, contiguous pieces from a single drawn length. Cold stretching was done while injecting a -45°C Freon spray into a 1/4-inch diameter plastic sleeve surrounding the wire. Warm stretching was done with 400°C heated air from a forced-air heat gun. These procedures assured that the wire specimen was martensitic or austenitic, as desired, during straining.

Non-linear changes in electrical resistance are often used to detect the temperatures of the phase transformation in NITINOL wires.[9,10] During cooling, the changes are good indicators for both 10% strained and fully-annealed wire. During heating, the changes in resistance are usually suitable indicators for strained wire but inadequate for fully annealed NITINOL wire.

Resistance measurements were performed within an environmental chamber fitted with conventional four point electrical contacts. Their output was to a Kiethley 503 Milliohmmeter, filtered, and recorded as the ordinate on an X-Y recorder. A 40 Hz current was used. Temperatures in the chamber were sensed by a copper constantan thermocouple placed within 3/4 inch of the midpoint of the specimen wire. The thermocouple output was corrected for room temperature with an electrical feedback circuit and fed to the x axis of the X-Y recorder. Thus, the abscissa of the graphed data is very slightly non-linear, reflecting the deviations of copper constantan thermocouples in this temperature regime. Heating of the chamber was done by electrical resistance elements; cooling was by the evaporation of carbon dioxide introduced as a liquid jet. Temperature gradients within the chamber were minimized during both heating and cooling by a high velocity internal blower. True temperature of the wire specimen is estimated to be within ±5°C of the recorded value.

Differential scanning calorimetry detects the heat of transformation[11-14] during heating and cooling. Our tests were performed in a Perkin Elmer Model DSC-2C. The calorimetry specimens were cut from the wires following resistance tests. They were heated in the DSC to 130°C and stabilized for a few minutes. Cooling to -120°C then commenced, with automatic recording of the energy evolved by the specimen. A standard rate of temperature change of 20°C/minute was maintained at the specimen during cooling and heating.

The precision of the calorimeter is estimated to be ±1/2% for temperature.

RESULTS AND DISCUSSION

RESISTANCE

The fully annealed D 4046 specimen has the resistance versus temperature curve (Figure 1) which is typical of fully annealed NITINOL alloys. The transformation during cooling initiated at 55°C and completed at 35°C. During heating, it started at 80°C and completed at 94°C. The change during cooling is the more pronounced of the two.

A strain free specimen transforms from austenite to martensite during cooling. The atomic movement path is via a rhombohedral (R) structure,[9,15,16] which is a slight repositioning of respective nickel and titanium atoms. In a strain free specimen, this repositioning is a transient that occurs during the transition from the ordered B 2 (austenite) phase into the complex martensite structure, or during its reversal. The R structure can

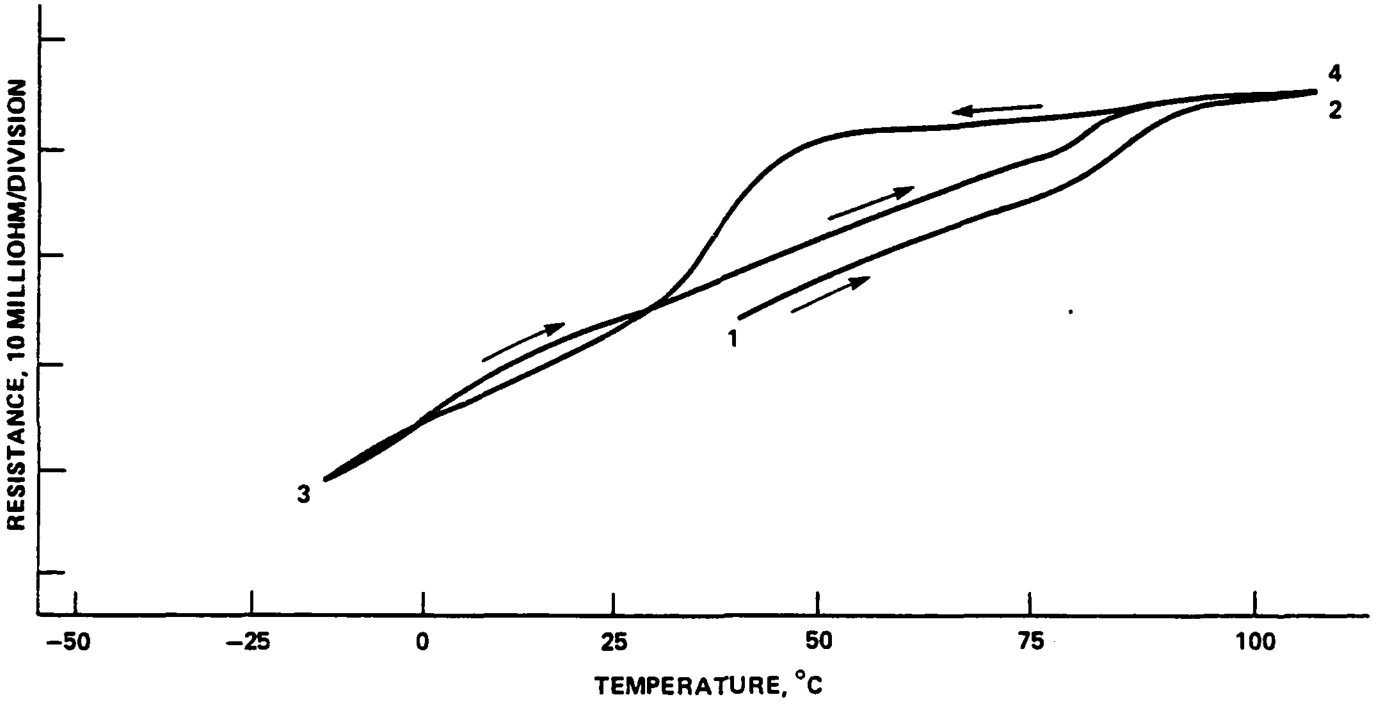

FIGURE 1. ELECTRICAL RESISTANCE OF NITINOL WIRE, HEAT D 4046. THERMAL TREATMENT: ANNEALED AT 750°C, ½ HR., AND AIR COOLED

be retained over an extended temperature band during cooling simply as a function of residual and/or self-generated age hardening stresses present in the alloy.[4]

In strained NITINOL the formation of an R structure which does not immediately transform to martensite during the continued cooling produces additional stress in the parent phase (from which R is being formed). This, in turn, materially affects electrical resistance, increasing it sharply. Thus the increasing stress, which is concomitant with the increasing amount of R formed, causes the observed increase in electrical resistance which develops during the cooling leg of the transformation cycle. On further cooling, the R structure/austenite becomes increasingly unstable. When shear strength is exceeded locally, R starts transforming into martensite. This is signalled by a reduction in electrical resistance. As cooling continues the electrical resistance falls with the increased amount of martensite formed and the consequently reduced stress.

There is a substantial difference in the magnitude of the resistance peaks obtained during the cooling and subsequent heating of a strained specimen. For example, the peak may constitute a 15% increase in resistance[9,17,18] during cooling, but be barely detectible during heating. This peculiarity results from the alloy having a high electrical resistivity,[*] having moduli, i.e. two levels of stress-sensitivity, and a reversing (not reversible) martensite/austenite transformation in the near room temperature regime. (In comparison, a steel which forms martensite at 200°C does not reverse itself and form austenite until above 723°C.)

A further explanation of this difference in the cooling and heating resistance curves arises by considering the two starting structures. The parent austenitic phase has no stress relief mechanisms available to it other than those occurring during heating well above 100°C. Thus, it does not self relieve any strains generated during cooling below 100°C, and reflects this in its electrical resistance. On the other hand, a daughter martensitic structure can internally self relieve strain by lath growth, reorientation, and internal twin reorientation[19] despite its temperature being under 100°C. Thus, during cooling, R structure forming from parent austenite creates high stresses, and a substantial resistance peak. During heating, R forming from the daughter martensite creates much less stress in the matrix due to the self relief mechanisms, and therefore has a smaller resistance peak. The result is that electrical resistance is a less sensitive indicator of transformation during the heating of NITINOL than during its cooling.

The respective sensitivities of martensite and austenite to stress are illustrated by their different onsets of strain hardening. As determined from tensile tests,[18] these values are 4% for martensite and 0.2% for austenite.

A specimen of annealed D 4046 wire was strained 1% at 22°C (martensitic condition), and measured for resistance changes as compared to an

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[*] The electrical resistivity of NITINOL is high, ranging from 80 micro ohm cm for annealed austenite to 132 micro ohm cm for the severely strained metal. Copper has a resistivity of about 2 micro ohm cm.

annealed wire. Based on the 4% strain hardening limit, no significant change in resistance was to be expected and none, as shown by comparing Figure 2 with Figure 1, was found. This same specimen was then heated into the austenitic condition and strained 2%. This permanent strain caused the transformation into martensite to occur via the intermediate R structure, which was retained, as previously discussed. Formation of R caused the increase of resistance, as shown in Figure 3, commencing at 62°C and peaking at 45°C.

At 45°C, the R started to transform into martensite, reducing strain and lowering the resistance. The 2% straining of the austenite caused the formation of this electrical resistance peak. Therefore, the inference arises that data based on binary alloy specimens with significant increases in resistance during cooling are based on testing of non-equilibrium specimens.

Verification and extension of the results shown in Figure 3 were obtained by warm straining another specimen 7%. This resulted in the data shown in Figure 4, with a more pronounced peak during cooling and slight strengthening of the peak during heating.

The curves (a), (b), and (c) of Figure 5 illustrate the effect of 7% martensitic (cold) strain on resistance during successive transformations. These data are from a single specimen, obtained by three cool-heat cycles performed without disturbing the specimen. They illustrate the relationship between strain in the alloy and the resistance curves during transformation. They also show that the temperature at which straining is done on a NITINOL alloy affects its subsequent transformation characteristics.

This specimen was martensitic and remained so during its straining and its subsequent transfer (at room temperature) to the resistance testing chamber. This deduction is based on the observation that it did not transform during the cooling leg 1-2 of curve (a) of Figure 5, nor during its heating leg, 2-3, up to the temperature of 96°C. Therefore, the trace of this martensitic wire was essentially reversible to -31°C, leg 3-4.

Upon subsequent heating, leg 4-5 of curve (b), the transformation from the 7% strained martensite into austenite began at 105°C and completed at 120°C. The newly formed austenite was strained to the extent that there was retained within it plastically deformed untransformed martensite. This martensite was of greater volume than its corresponding austenite, thus straining the newly formed B 2 structure. Cooling this specimen thus generated R structure from the strained B 2, starting at 64°C of leg 5-6. Martensite formation commenced at 42°C, and terminated at 12°C. Curve (b) thus demonstrates again the previously postulated influence of stress on the transformation of NITINOL in producing the pronounced peak in resistance.

Curve (b), heating leg 4-5, resulted from the 7% martensitically strained specimen undergoing its first transformation, starting at 105°C. Its transformation upon heating a third time, leg 6-7 of curve (c), started at a much lower temperature, estimated as 50°C. The variance between the two curves (leg 4-5 versus 6-7) is caused by the difference in the respective daughter martensites from which each transformation started. Curve (b) started with a 7% strained martensite; curve (c) started with a martensite which had been altered by the immediately preceding heating and cooling. During that prior heating to 120°C, 4 of the 7% martensitic strain was eradicated during the conversion of the specimen into austenite. Therefore,

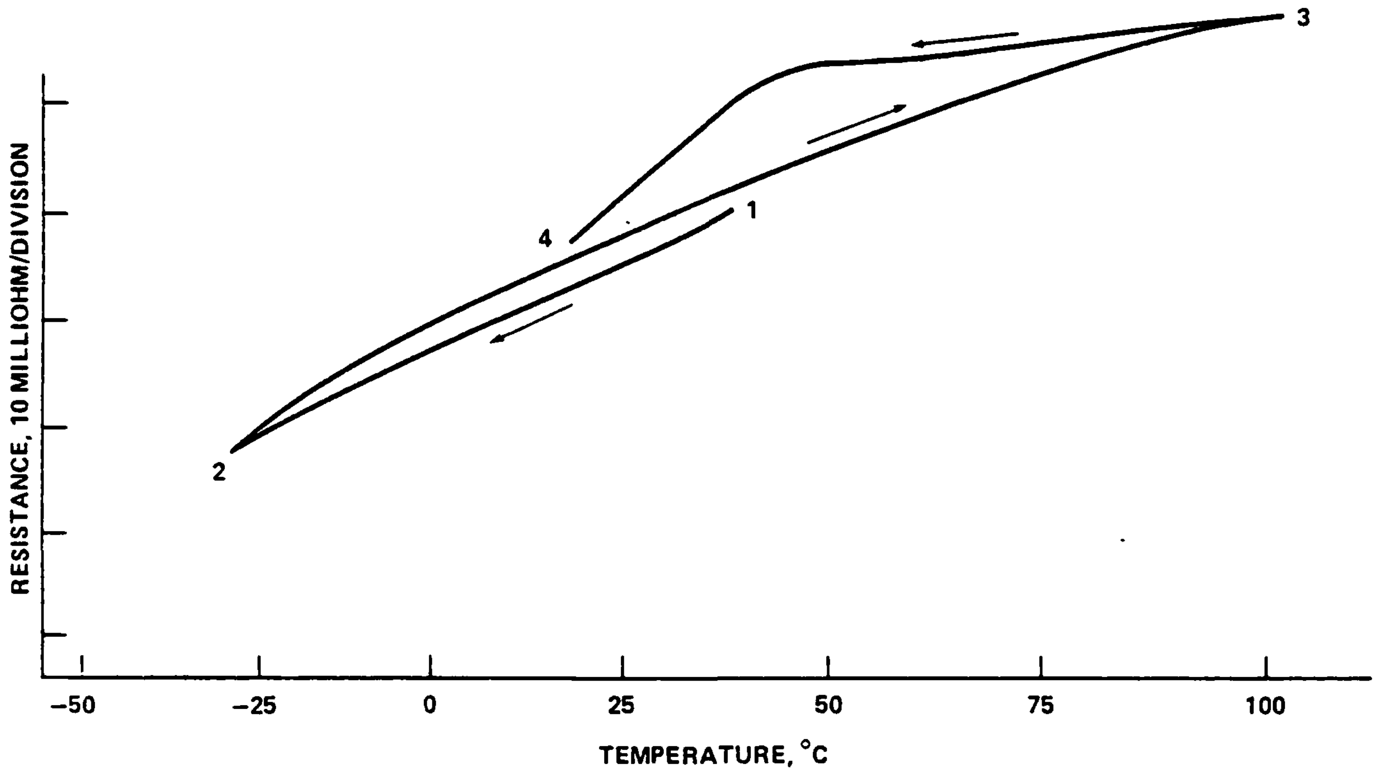

FIGURE 2. ELECTRICAL RESISTANCE OF NITINOL WIRE, HEAT D 4046. THERMOMECHANICAL TREATMENT: ANNEALED AT 750°C, ½ HR., AIR COOLED, AND STRETCHED 1% AT 22°C

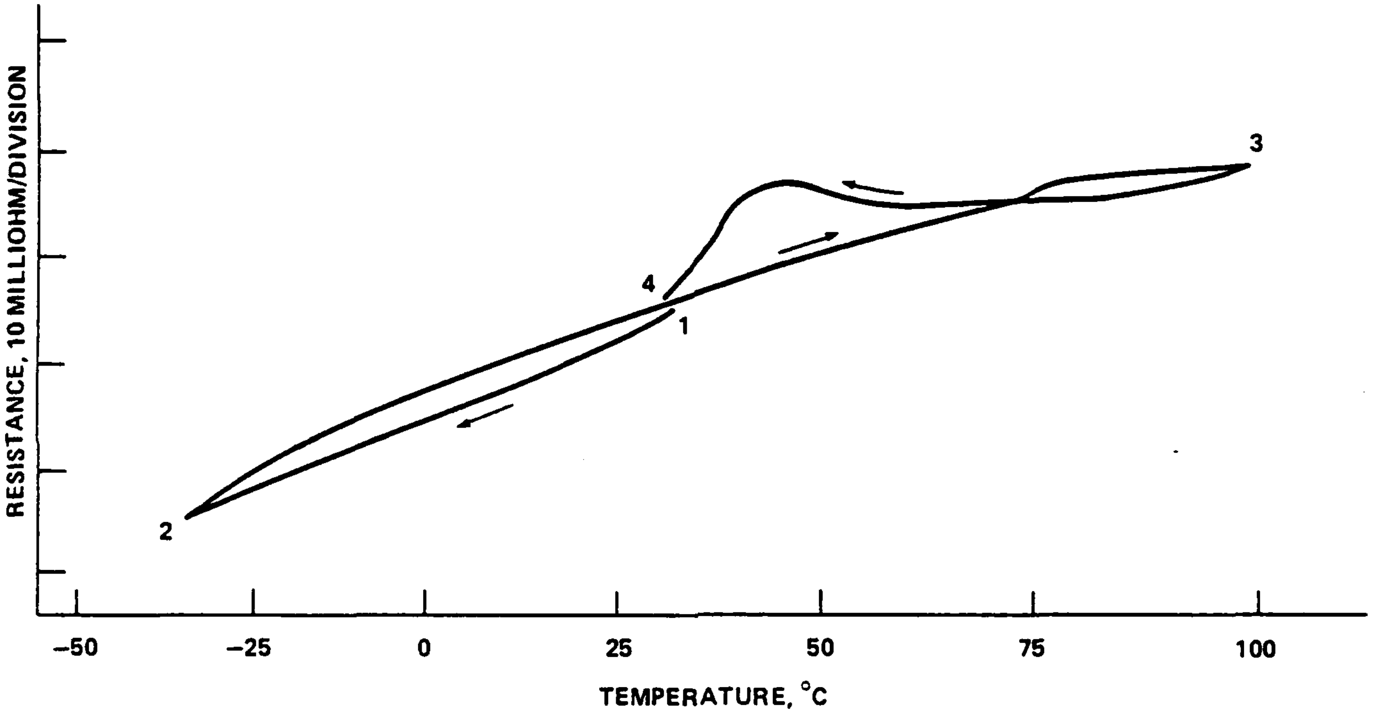

FIGURE 3. ELECTRICAL RESISTANCE OF NITINOL WIRE, HEAT D 4046. THERMOMECHANICAL TREATMENT: 2% WARM STRETCH OF SAME SPECIMEN TESTED FOR FIGURE 2

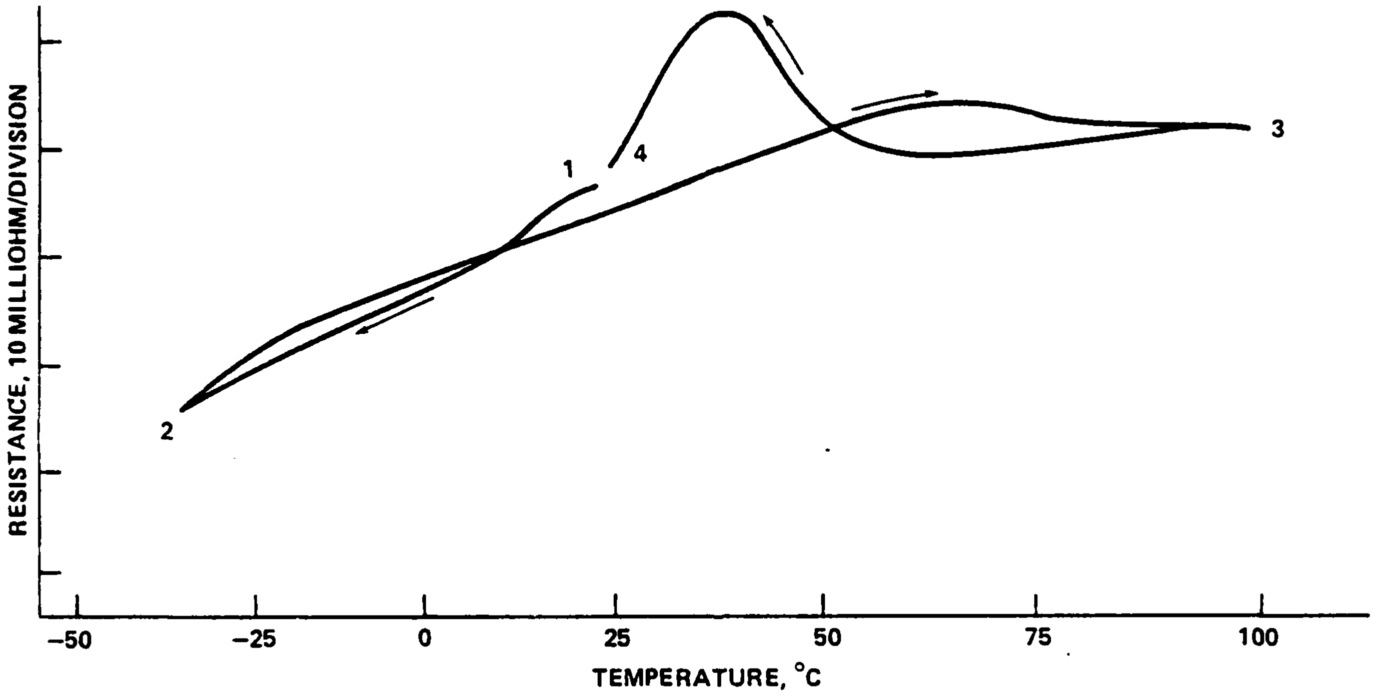

FIGURE 4. ELECTRICAL RESISTANCE OF NITINOL WIRE, HEAT D 4046. THERMOMECHANICAL TREATMENT: ANNEALED AT 750°C, ½ HR., AIR COOLED, AND WARM STRETCHED (AUSTENITIC CONDITION) 7%

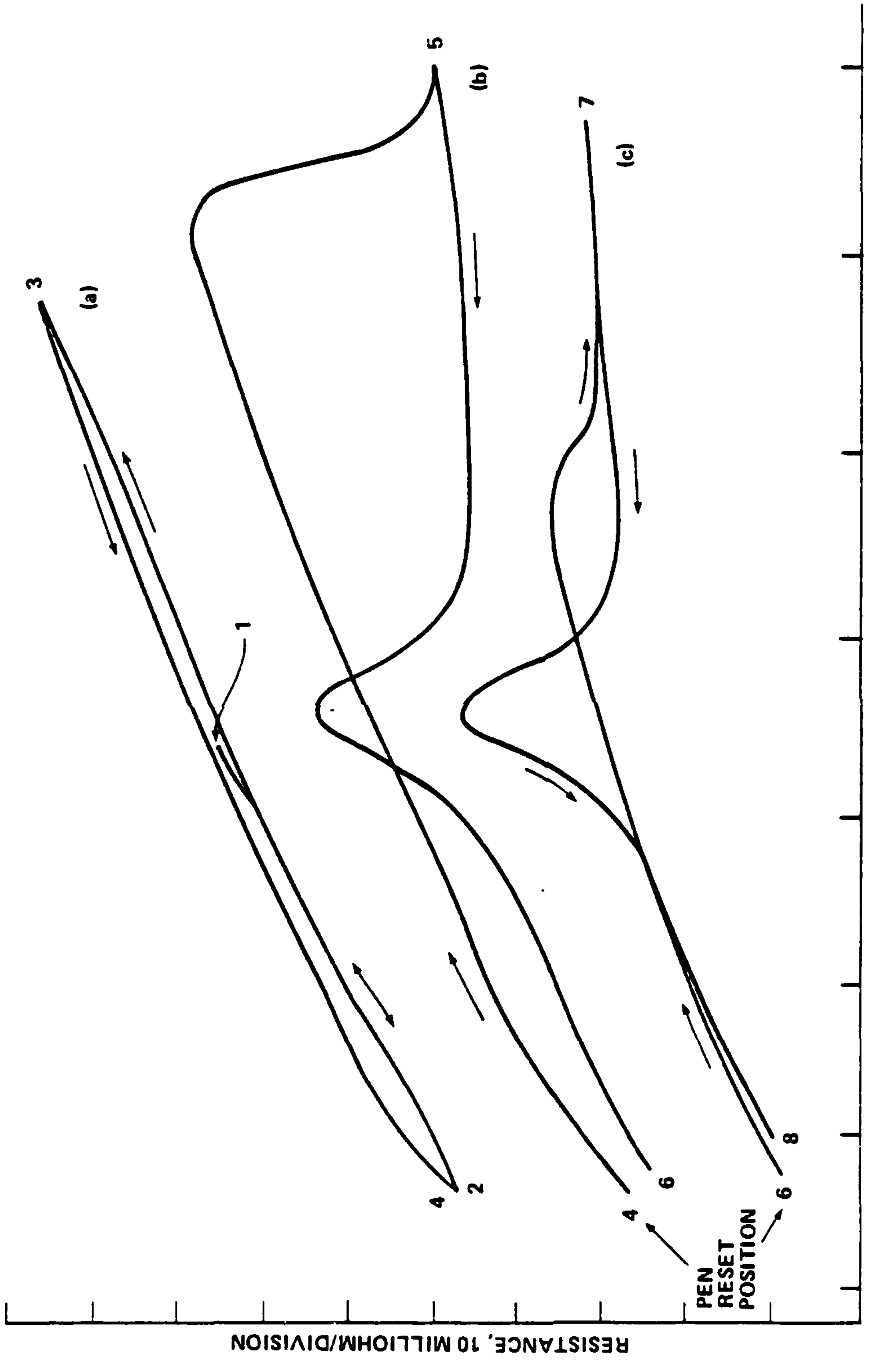

FIGURE 5. ELECTRICAL RESISTANCE OF NITINOL WIRE, HEAT D 4046. THERMOMECHANICAL TREATMENT: ANNEALED AT 750°C, ½ HR., AIR COOLED, AND COLD STRETCHED (MARTENSITIC CONDITION) 7%

the martensite being heated the third time was effectively a 3% plastically strained martensite. Furthermore, this conversion (leg 6-7) was via the intermediate R structure into austenite. Thus this second conversion into austenite was less pronounced, and at lower temperatures than in curve (b) because of the previously discussed strain relief mechanisms available to the freshly formed daughter martensite. Cooling again, leg 7-8, is the same as the previous cooling leg 5-6, indicating a relative stability of the formation process for R structure for low numbers of temperature cycles.

After the resistance tests were completed, the strain in the martensitic wire was measured and was in fact 3% at 22°C, following the last cooling cycle.

Reference 4 reported that reduction of width and amplitude of the resistance curve peaks of cold-worked NITINOL resulted from increased annealing times and temperatures. In the current work, it is shown that straining generated and increased the resistance peaks in fully annealed wires which previously had no transformation peaks.

Also, it was shown[4] that it was necessary to heat a severely cold worked alloy to temperatures over 100°C to allow first time shape recovery (contraction) effects to occur. In the current work, it required a temperature of 100°C for the annealed material to complete its transformation, and 120°C if it was martensitically strained 7%. Furthermore, the plastic portion (3%) of this strain survived the short time heating to 120°C, and then affected the subsequent heating transformation, changing its finish temperature from 120°C to 85°C. Based on the prior work, heating substantially above 120°C for prolonged time would be necessary to relieve the 3% strain.

The resistance data of the current work using a slightly titanium-rich alloy are compatible with the prior work[4] with a slightly nickel-rich alloy. They suggest that typical manual demonstrations of the shape memory effect in NITINOL, which is usually strained over 6% during such demonstrations, are being performed using material that <u>then</u> has enough residual stress in it to significantly influence its transformation phenomena.

CALORIMETRY

Sections of three specimen wires were evaluated for transformation characteristics in the differential scanning calorimeter following their resistance tests. Table 1 lists the data obtained in calorimetry and resistance.

As was the case in resistance, straining made more drastic changes in calorimetry during cooling than during heating. This reflects again the difference in strain relief in martensite versus austenite, as was earlier presented with respect to electrical resistance.

The transition of austenite into martensite for a fully annealed specimen is represented by the smooth, almost symmetrical calorimetry curve shown in Figure 6(c).* The presence of stress causes the drastic changes

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*The parenthetic (c) and (h) refer to the cooling and heating legs of the differential scanning calorimetry curves.

TABLE 1. TRANSFORMATION TEMPERATURES OF NITINOL HEAT D 4046

THERMOMECHANICAL PROCESSING	RESISTANCE DATA ARE TAKEN FROM FIGURE	CALORIMETRY DATA ARE TAKEN FROM FIGURE	TRANSFORMATION TEMPERATURES, °C							
			COOLING				HEATING			
			R STRUCTURE OR MARTENSITE				R STRUCTURE OR AUSTENITE			
			START		FINISH		START		FINISH	
			Ω	DSC	Ω	DSC	Ω	DSC	Ω	DSC
750°C, ½ HR., AIR COOLED	1	6	55	58	35	37	80	66	94	90
ANNEALED AS ABOVE AND WARM STRAINED 7%	4	7	62	66	10	4	50	53	83	78
ANNEALED AS ABOVE AND COLD STRAINED 7% NOTE: EFFECTIVE STRAIN FOR LINE 5c IS APPROXIMATELY 3%	5 a		NT		NT		NT		NT	
	5 b		64		12		105		120	
	5 c	8	64	57	15	17	50	60	84	85

NOTE: HEAT D 4046 IS A Ti-54.9 WEIGHT PERCENT Ni BINARY ALLOY

NT SIGNIFIES NO TRANSFORMATION OCCURRED

shown in Figure 7(c). The transformation started earlier during the cooling leg, was interrupted, and then finished later, i.e. at a lower temperature, all the result of the 7% austenitic straining.

The martensitically stressed specimen, Figure 8(c), was still strained (to about a 3% level) after its resistance testing. Thus, it produced an intermediate curve if compared to Figures 6(c) and 7(c). Also, the width of its transformation temperature range (40°C) is intermediate to those of the annealed (21°C) and the 7% austenitic strained specimens (62°C). The stress in the specimen was insufficient to produce dual peaks, such as are shown in Figure 7(c).

Comparison of the heating curves of Figures 6-8(h) shows that the width of the transformation temperature range is the same, 25°C, in each case. The temperatures for start and finish of transformation listed in Table 1 are based on visual examination of the figures. Transformation was arbitrarily considered to start at the sharp increase in transformation rate. Determination of the inflection points of the curves was aided by judicious placement of tangent 45° angular protractors. The values thus obtained are considered to represent the start and finish of almost all of the transformation product. This enables a more meaningful comparison of the data. They are also the values that are probably more useful to product designers than are the values which would be obtained from extrapolation of the branches of the curves. The correspondence of the resistance and calorimetry data presented in Table 1 is considered very reasonable in light of the difficulty in determining end points which sometimes appear asymptotic.

Both the start temperatures (e.g., 66°C, 60°C, and 53°C, Table 1) and finish temperatures (e.g., 90°C, 85°C, and 78°C) of transformation during heating were lowered as a function of increased residual stress. This is because the residual internal stress aids[4] and starts R structure formation earlier, i.e. at a lower temperature during heating. This is quite different than an <u>applied</u> opposing external stress, such as that described by Schuerch,[20] which requires higher temperatures to effect shape memory transformation during heating.

In the latter case, the external stress opposes the normal atomic movement of the alloy in returning to the parent austenite shape. This is usually the case in industrial applications intended to develop the force and movement associated with the NITINOL transformation. Thus, directionality as well as magnitude of the stress, with respect to the specimen's "annealed in" shape, affects the transformation temperatures of NITINOL.

CONCLUSIONS

This work has shown that the unusual electrical resistance and calorimetry peaks demonstrated by NITINOL during its transformation can be generated and influenced by the introduction of stress into the alloy.

Strain, the readily quantifiable measure of stress, can be introduced into either the equilibrium austenitic or the martensitic structure of NITINOL, and survive temperatures up to 120°C. The temperature for the first time transformation of strained martensite into austenite is a function of the amount of strain present. Subsequent transformations may be at a

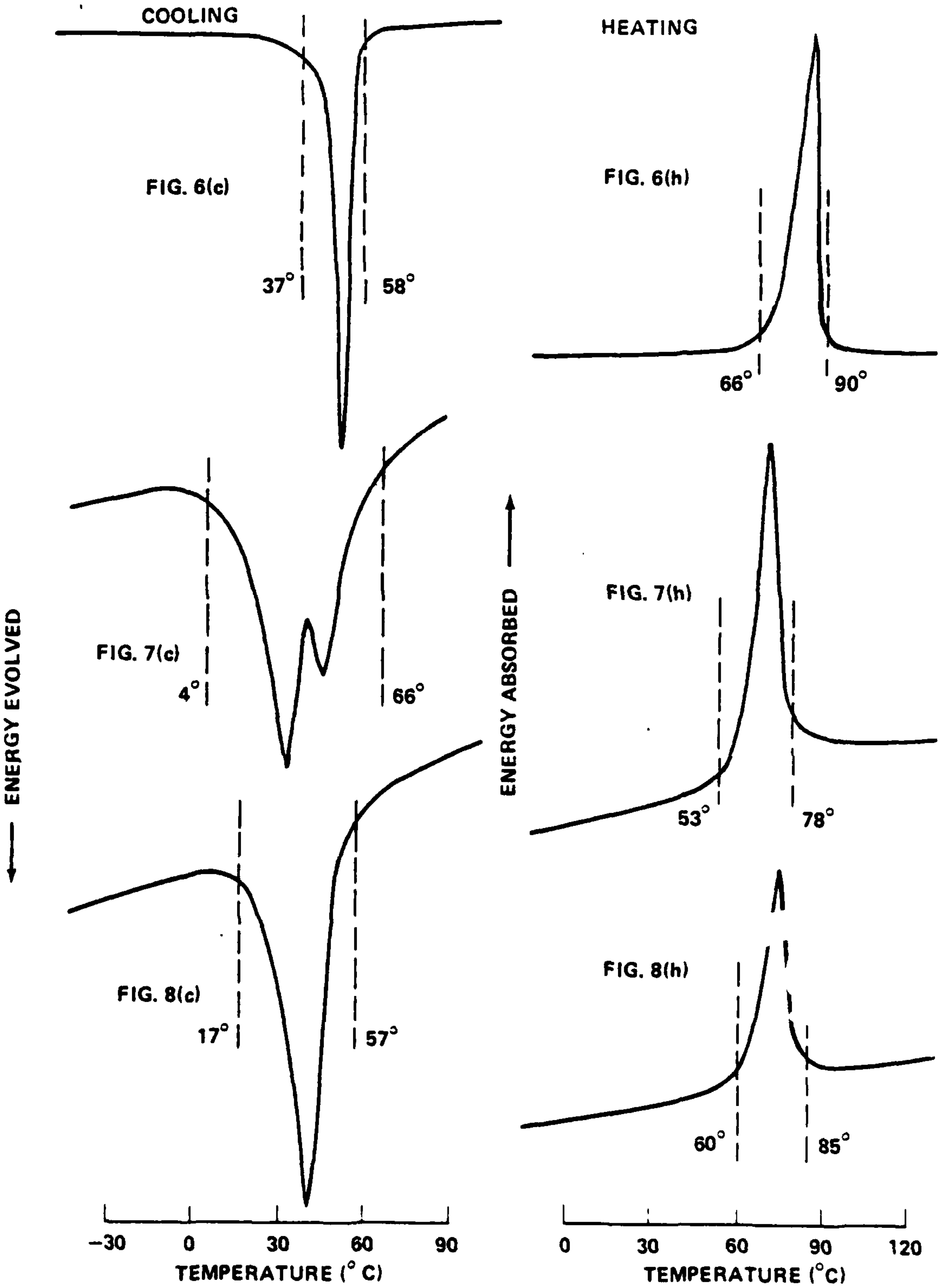

FIGURE 6. DIFFERENTIAL SCANNING CALORIMETRY TRACE OF NITINOL WIRE, HEAT D 4046. ANNEALED AT 750°C, ½ HR., AND AIR COOLED

FIGURE 7. DIFFERENTIAL SCANNING CALORIMETRY TRACE OF NITINOL WIRE, HEAT D 4046. ANNEALED AT 750°C, ½ HR., AIR COOLED, AND WARM STRETCHED 7%

FIGURE 8. DIFFERENTIAL SCANNING CALORIMETRY TRACE OF NITINOL WIRE, HEAT D 4046. ANNEALED AT 750°C, ½ HR., AIR COOLED, AND COLD STRETCHED 7%

different (but consistent) temperature from the first one due to the eradication of part of the strain during the first transformation. The results obtained in this work support a previously presented thesis, namely, stresses have a very considerable effect on the transformation of NITINOL. These conclusions are based on results obtained from a slightly titanium-rich NITINOL.

RECOMMENDATIONS

This is the second paper emanating from the Naval Surface Weapons Center aimed at illuminating the great effect that stress has on the transformation of NITINOL. The first[4] dealt with the effects of residual stresses and also with the stress effects arising from the precipitation of excess nickel in solution. The removal of those stresses in a cold worked, nickel-rich NITINOL was reviewed as a function of annealing treatments. The resultant data were couched in terms of length contraction (shape memory response), electrical resistance, and calorimetry.

In this second paper, the same phenomena, i.e. the effect of stress on the transformation, was again examined, this time by the introduction of stress into the fully annealed alloy. Using again the criteria of resistance and calorimetry changes, the results on a titanium-rich NITINOL confirmed and expanded the prior work. Among the results are that the stresses introduced into the alloy have some similar and some differing consequences, depending on the temperature or the atomic structure extant during the stressing.

Although it would be desirable to correlate x-ray data with the resistance and calorimetric effects, there is an even more informative and commercially useful third investigation considered to be of primacy. This would be quantitative correlation of the shape memory response with resistance and calorimetry in adequately characterized strained materials, both nickel and titanium-rich, respectively. Such information would enable designers to construct devices using NITINOL with performance nearer the intended with respect to temperatures, forces, extent of recovery, and durability of the recovery phenomenon. It would also contribute much to a suitable quality control program as is needed to assure the known and stable property performance of primary alloy production.

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