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EFFECTS OF ALLOYING UPON CERTAIN PROPERTIES OF 55.1 NITINOL

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UNITED STATES NAVAL ORDNANCE LABORATORY, WHITE OAK, MARYLAND

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EFFECTS OF ALLOYING UPON CERTAIN PROPERTIES OF 55.1 NITINOL

Prepared by:
D. M. Goldstein, W. J. Buehler and R. C. Wiley

ABSTRACT: Ternary alloys of the intermetallic compound TiNi were hot hardness tested. Although hardness can be increased by such alloying, neither the base material nor the alloys offer promise for long time service use above 800°F. Silicon, aluminum, iron, and cobalt are effective room temperature hardeners. A unique interfacial compatibility between TiNi and tungsten bulk metal was discovered. It is believed that this will enable introduction of a new metal-metal composite system of fibrous tungsten in a Nitinol matrix. A rod of such material is shown to be capable of room temperature swaging, suggesting improved methods of working highly refractory metals. Silver-free TiNi brazing alloys for joining tungsten metals are a natural result of such compatibility.

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This report describes research directed principally toward an improvement in the elevated temperature strength of the TiNi intermetallic compound through alloy additions. Effects upon the properties and phase equilibria of TiNi with controlled additions of ternary and quaternary alloying elements are given in detail. The investigative work described in this report was performed under BuWeps Task Intermetallic Compounds, RRMA-02009/R007 06 01.

R. E. ODENING
Captain, USN
Commander

Louis R. Maxwell
L. R. MAXWELL
By direction

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INTRODUCTION

In the original U. S. Naval Ordnance Laboratory report[1] dealing with the TiNi intermetallic compound and non-stoichiometric TiNi-base alloys, certain interesting findings were disclosed. Prime among these was the discovery that a ductile equiatomic compound TiNi* was attainable at room temperature and below. In addition, this initial investigation showed that alloys varying by as much as 10 wt % nickel on either side of TiNi (55.1 wt % nickel, remainder essentially titanium) were non-magnetic, corrosion and abrasion resistant, and possessed moderate densities. Furthermore, it was discovered[1] that the alloys containing between 56 and 62 wt % nickel were hardenable by thermal treatment to very high hardness levels. Subsequent studies[2,3,4] on the near-stoichiometric TiNi composition alloys revealed martensitic (diffusionless) transitions in these alloys near room temperature which are responsible for unusual mechanical vibration damping and configuration changes.

During the analysis of both the basic and the engineering findings it became apparent that some effort should be directed toward the determination of the effects of introducing substitutional-type elements into the binary Nitinol alloys.

The initial investigation[1] revealed the apparent TiNi stoichiometry to occur at 54.5 wt % (49.43 at.%) Ni. This shift from the theoretical stoichiometric TiNi composition of 55.06 wt % Ni (50 at. %) was the probable result of impurities, principally iron. This same early study had shown an increase in the room temperature hardness of nominal 55.1-Nitinol from 31 R_c to 43 R_c when 4 wt % silicon was added. To the same Nitinol base alloy the addition of 4 wt % aluminum increased the hardness to 55 R_c. Based upon these results ternary alloying appeared to have promise as a means of producing significant and desirable property changes in the base 55.1-Nitinol alloy.

Ternary alloying of the 55.1-Nitinol alloys was undertaken with three major objectives in mind.

1. To improve the strength (particularly yield strength) of the overall alloy at room temperature without making serious concessions in ductility and toughness.

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* The name Nitinol was assigned to this class of alloys. Name derived from Ni-Ti-NOL. Prefix numerical value (e.g., 55.1-Nitinol) indicates the nominal nickel content in weight percent, balance titanium.

2. To improve the elevated temperature strength to the point of competing with the austenitic stainless steels.

3. To gain additional knowledge, from microstructure examination, on the effect of various elements, in moving the "apparent" stoichiometric TiNi composition and the critical "transition" temperature for damping and configuration change.

To accomplish the above ends, eleven elements were selected based upon scientific criteria such as atomic size, periodicity, electronegativity, etc., and the practical criteria of cost and availability.

Utilizing non-consumable arc melting the selected elements in varying quantities were made to blend with nominal 55.1-Nitinol. The resulting alloy systems were studied and evaluated.

TERNARY ALLOY SYSTEMS INVESTIGATED

Table I lists the "nominal" (intended) and "calculated" compositions of the homogeneous alloy melts prepared, based upon charge weights. The addition elements listed in Table I were added in every case to the 55.1-Nitinol alloy, thus maintaining a 1:1 atomic ratio of nickel and titanium.

Employing the non-consumable arc melting techniques previously described[1] and using high purity carbonyl nickel shot (99.9 + % pure) and titanium sponge (Brinell hardness $<$ 95), alloys of predictable good quality were made in every case. Composition determinations based upon charge weight were accepted as being accurate when it was found that the weight losses during melting were minimal, i.e., less than 0.1 wt %.

Multiple melting of a given alloy was practiced to insure chemical homogeneity. In every case the alloys were first given a double-melt as a button, then in certain instances the buttons were further remelted into appropriate size bars. Furthermore, to assure complete chemical homogeneity a size of button was made (35-40 grams) which could be maintained almost completely molten with the arc plasma.

During the alloy preparation phase certain observations and alloying tests were made. These are described as follows:

1. Manganese and chromium, in spite of their higher vapor pressures, tended to go into solution readily and the loss of these elements from the melts was negligible.

2. Both tungsten and cerium additions were attempted. Massive chunks of tungsten did not readily go into solution in 55.1-Nitinol. However, when the tungsten was added in less massive form (powder) it dissolved in the master alloy. Additional discussion on this phenomenon will be described in a later section of this report.

TABLE I

NOMINAL AND CALCULATED CHARGE ADDITIONS TO 55.1 NITINOL-BASE ARC MELTED ALLOYS

TERNARY ALLOYING ELEMENT	NOMINAL TERNARY ADDITION (WEIGHT PERCENT)									
	.08	0.1	0.2	0.5	1.0	2.0	3.0	4.0	8.0	16.0
	CALCULATED CHARGE COMPOSITION (WEIGHT PERCENT)									
Cu				0.49	1.01	2.01		4.00	8.43	15.99
Ta		0.109		0.51	1.01	1.99		3.96	8.00	
Mo				0.53	1.05	2.04		3.98		
Cr				0.50	0.98	1.96		4.02	8.02	
Al				0.52	1.00	2.01		4.02	8.02	
Si				0.50	1.01	2.00		4.09		
Nb		0.093		0.53	1.03	2.02		4.03	8.00	
Fe	0.081		0.22	0.50	.98	1.96				
V		0.121		0.53	1.01	1.97		3.98	8.03	
Co				0.50	1.05	2.05	2.95	4.05		
Mn				0.53	1.00	2.01		4.04	8.01	

Cerium also resisted going into solution with the 55.1-Nitinol master and study on this system was discontinued.

3. The rate and extent of carbon (graphite) solution was determined by induction melting. The master alloy was held molten in a graphite boat for periods up to one hour at 1670°C. By using an atmosphere of argon good quality 55.1-Nitinol ingots resulted and there was virtually no erosion of the graphite boat wall. A diamond pyramid hardness traverse from ingot center to edge showed no change in hardness, indicating that the alloy had picked up very little, if any carbon. The strong carbide forming tendencies of titanium are apparently offset by the moderating effect of the nickel present. Based upon this observation, it appears that this titanium base alloy, unlike most other titanium base alloys, can be melted in a graphite crucible by adding titanium to molten nickel.

4. Additions of titanium boride (0.6 wt %) and tantalum carbide (6.2 wt %) had no effect on the as-cast hardness. Probably neither compound dissolved in the 55.1-Nitinol.

MICROSTRUCTURE EXAMINATION

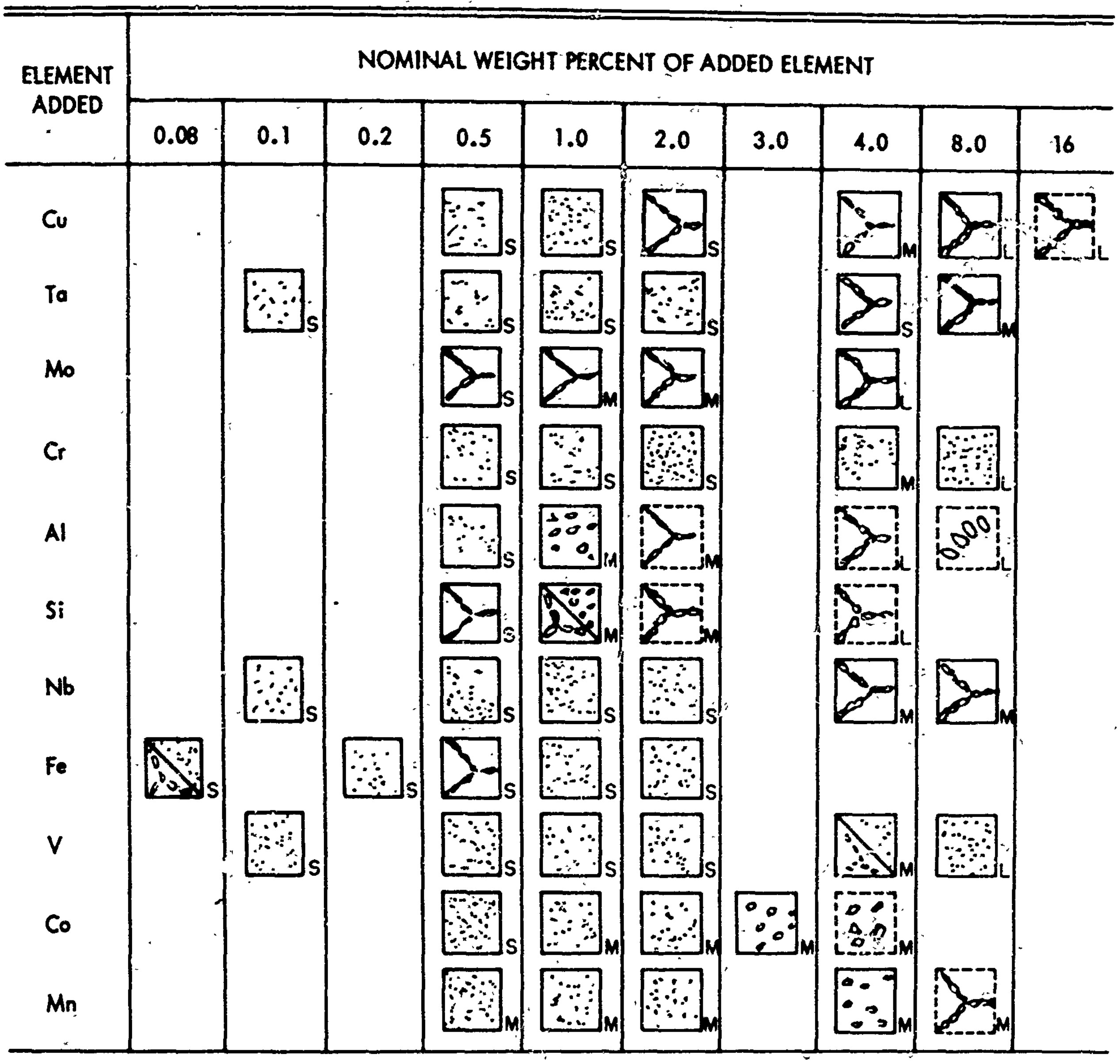
The microstructural effects of the addition elements are given schematically in Table II. In this table structures of both the wrought and cast alloys are summarized. The drawings presented with solid outline boxes are of specimens hot worked at 900°C, followed by a 24-hour soak at 900°C. Drawings with broken outline boxes are of specimens cast and soaked at 900°C for 24 hours. Figures 1, 2 and 3 are photographed microstructures of representative alloys with varying amounts of copper, aluminum, and iron added to a TiNi or 55.1-Nitinol base. All were etched with a 4 parts HF (conc.) - 14 parts HNO_3(conc.) - 82 parts H_2O by volume etchant. These actual photomicrographs provide a frame of reference for the symbolic representations given in Table II. Referring to Table II certain observations are possible:

1. Even the lowest quantities of addition elements (e.g., 0.08 wt % Fe and 0.1 wt % of Ta, Nb, or V) permit the existence of second phase particles similar to those appearing in the base TiNi. This observation raises the question of whether these small second phase particles are a result of ternary metal additions or interstitial impurities like O_2, N_2, and H_2.

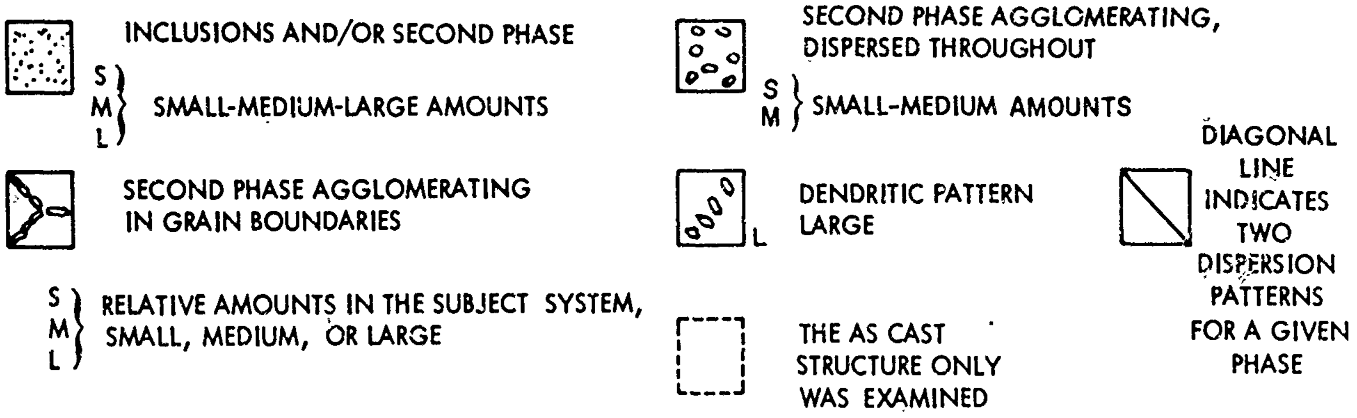
2. Using massive second phase agglomeration in the grain boundaries as a criterion, it appears that 55.1-Nitinol can tolerate more than 8% of Cr, or V, and less than 8% of Ta or Mn; 4% Cu or Nb; 2% Al or Si, and less than 1% Mo.

3. An overall microstructure comparison of ternaries in the wrought condition was not possible in Table II because the higher weight percentages of the Cu, Al, Si, Co, and Mn alloys (shown by square dashed outline) were hot short and could therefore be observed in the "as arc-cast and soaked" condition only.

TABLE II
SCHEMATIC REPRESENTATION OF MICROSTRUCTURAL DETAILS OF 55.1 NITINOL BASE TERNARY ALLOYS



ELEMENT ADDED	NOMINAL WEIGHT PERCENT OF ADDED ELEMENT									
	0.08	0.1	0.2	0.5	1.0	2.0	3.0	4.0	8.0	16
Cu				S	S	S		M	L	L
Ta		S		S	S	S		S	M	
Mo				S	M	M		L		
Cr				S	S	S		M	L	
Al				S	M	M		L	L	
Si				S	M	M		L		
Nb		S		S	S	S		M	M	
Fe	S		S	S	S	S				
V		S		S	S	S		M	L	
Co				S	M	M	M	M		
Mn				M	M	M		M	M	



INCLUSIONS AND/OR SECOND PHASE

S } SMALL-MEDIUM-LARGE AMOUNTS
M
L

SECOND PHASE AGGLOMERATING IN GRAIN BOUNDARIES

S } RELATIVE AMOUNTS IN THE SUBJECT SYSTEM, SMALL, MEDIUM, OR LARGE
M
L

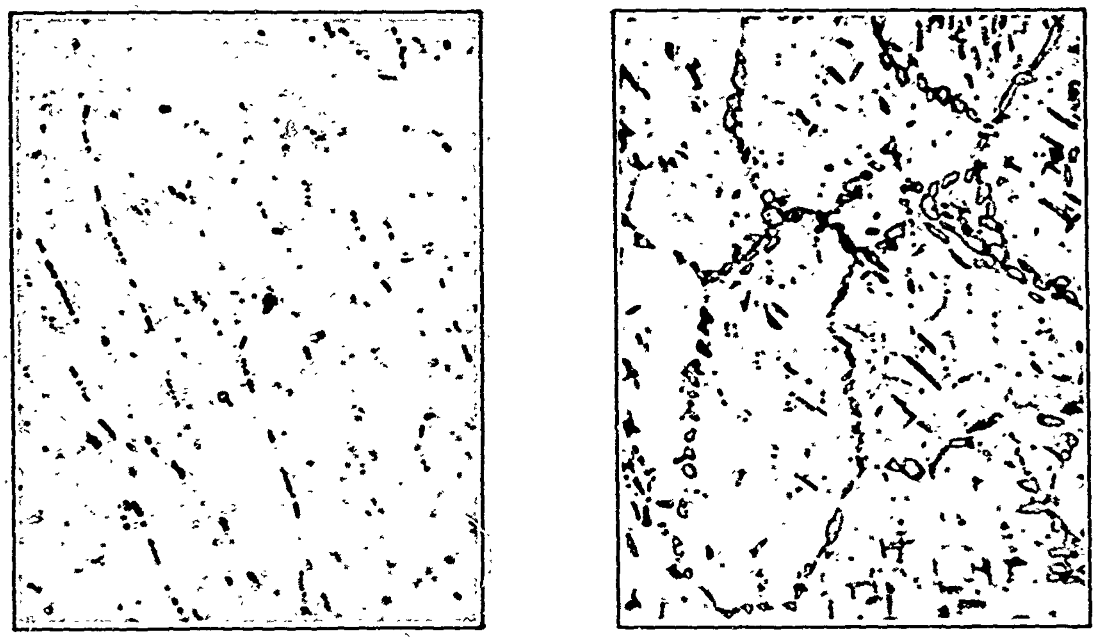
SECOND PHASE AGGLOMERATING, DISPERSED THROUGHOUT

S } SMALL-MEDIUM AMOUNTS
M

DENDRITIC PATTERN LARGE

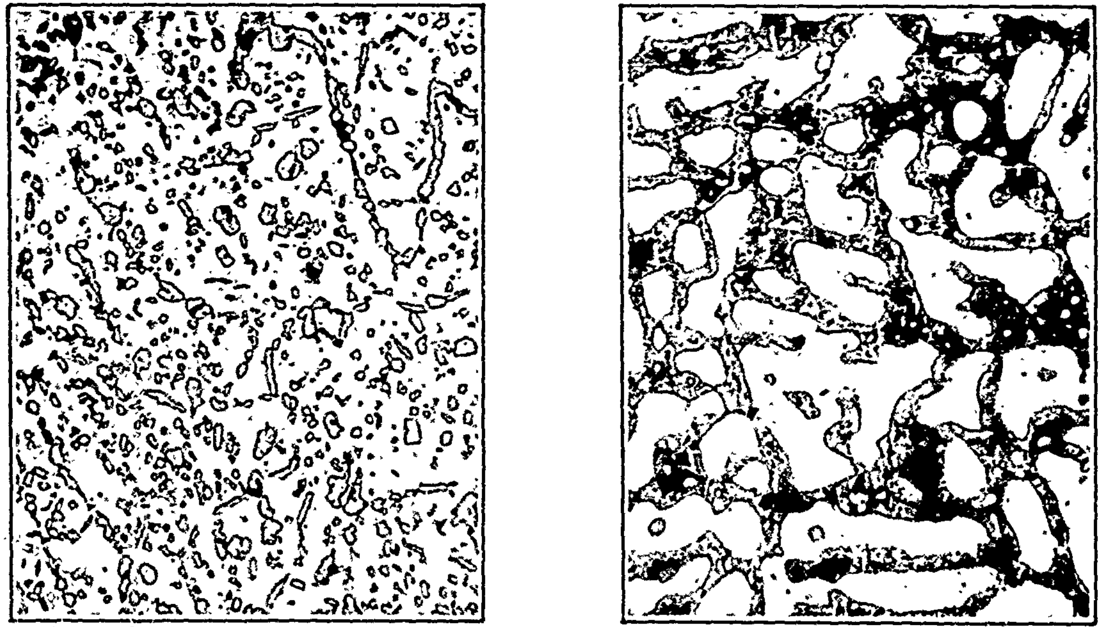
THE AS CAST STRUCTURE ONLY WAS EXAMINED

DIAGONAL LINE INDICATES TWO DISPERSION PATTERNS FOR A GIVEN PHASE



(a) 2.0 WEIGHT PERCENT.
HOT WROUGHT AT 900°C.

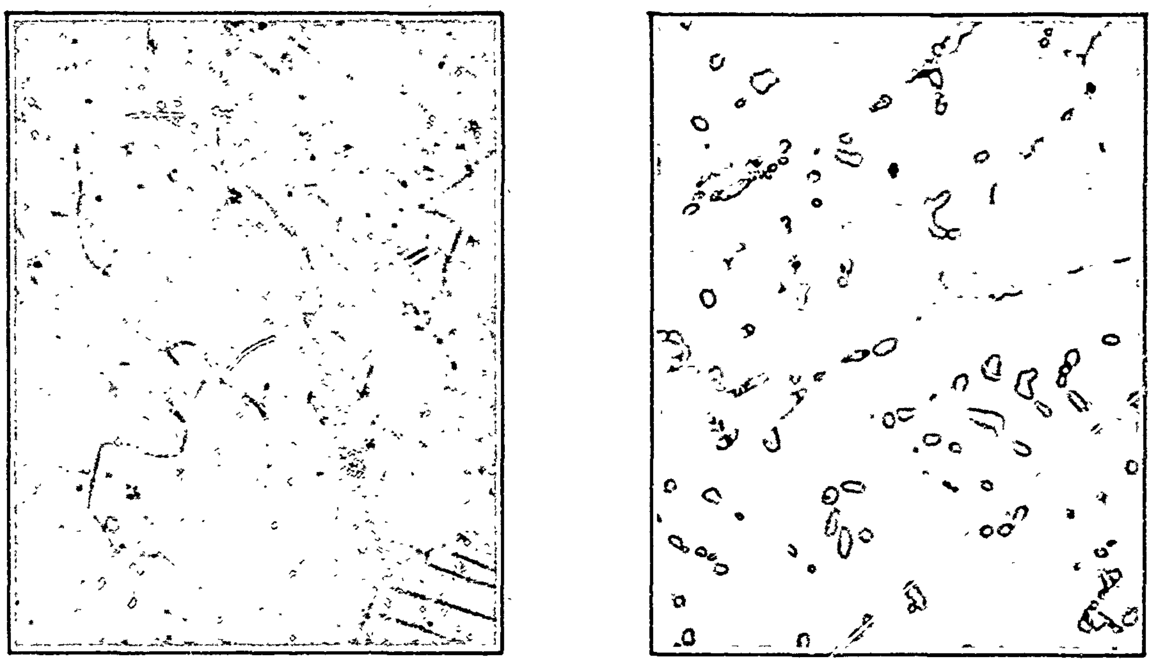
(b) 4.0 WEIGHT PERCENT.
HOT WROUGHT AT 900°C.



(c) 8.0 WEIGHT PERCENT.
HOT WROUGHT AT 900°C.

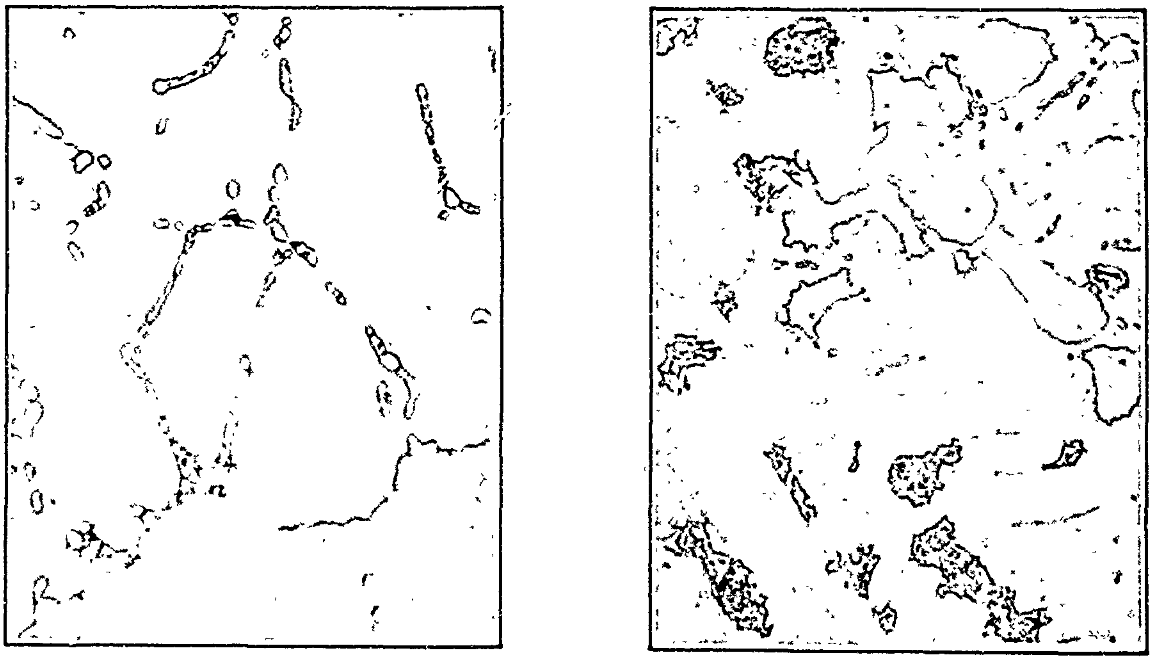
(d) 16.0 WEIGHT PERCENT.
AS CAST.

FIG. 1 PHOTOMICROGRAPHS OF TiNi (55.1 NITINOL) WITH ADDITIONS OF COPPER. 710 MAGNIFICATIONS.



(a) 0.5 WEIGHT PERCENT.
HOT WROUGHT AT 900°C.

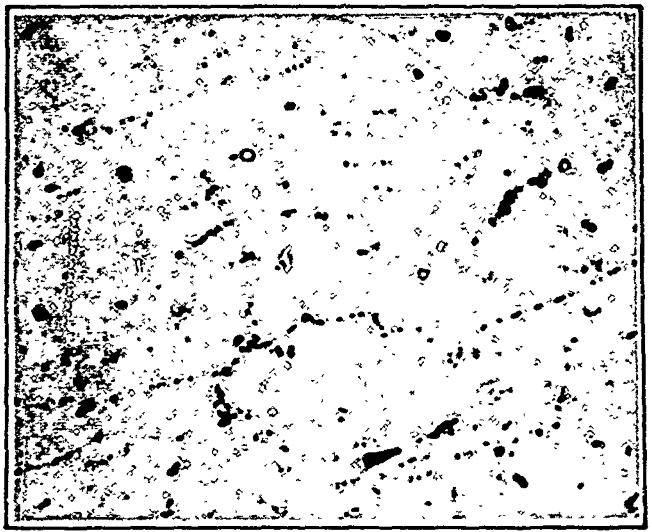
(b) 1.0 WEIGHT PERCENT.
HOT WROUGHT AT 900°C.



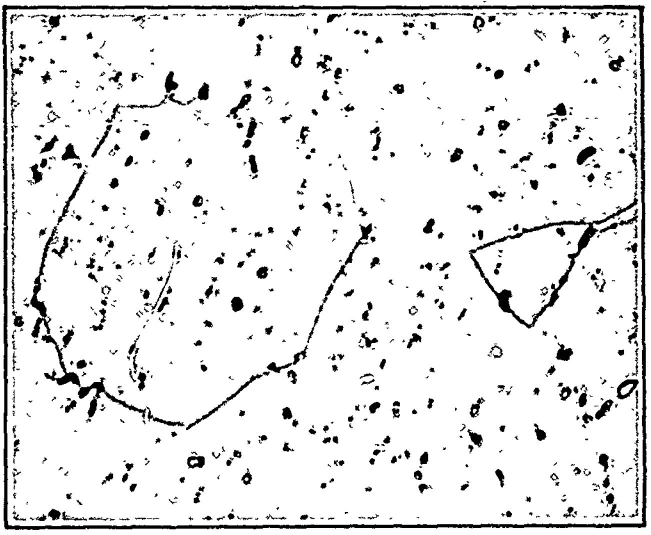
(c) 2.0 WEIGHT PERCENT.
AS CAST.

(d) 8.0 WEIGHT PERCENT.
AS CAST.

FIG.2 PHOTOMICROGRAPHS OF TiNi (55.1 NITINOL) WITH ADDITIONS OF ALUMINUM, 710 MAGNIFICATIONS.



(a) 0.08 WEIGHT PERCENT. HOT WROUGHT AT 900°C.



(b) 2.0 WEIGHT PERCENT. HOT WROUGHT AT 900°C.

FIG.3 PHOTOMICROGRAPHS OF WROUGHT TiNi (55.1-NITINOL) WITH ADDITIONS OF IRON. 710X MAGNIFICATIONS.

4. In almost all instances the observed microstructure was reasonably homogeneous. Major variations were only in second (multiple) phase size and distribution. Structural non-uniformity was observed and taken into account as a symbolic diagonal line (Table II).

In these microscopic studies no attempt was made to identify the phase(s) present. X-ray diffraction patterns were made of the most highly alloyed specimen in each ternary system to assist in establishing the presence of new phases. Table III lists the alloy addition effects as determined by the X-ray diffraction. In all instances where a second phase appears the alloy was brittle. Additionally, 8 wt % Mn was brittle, although its metallographically visible second phase was not detected by the X-ray scan.

Two simplified tests, involving room temperature impacting of the arc-cast alloy buttons, and the hot rolling (near 900°C) of arc-cast alloy buttons were employed to gain additional insight into the effects of ternary alloying. These results are given in Table IV and will be discussed more completely in the following section dealing with the "Evaluation of Properties."

EVALUATION OF PROPERTIES

Utilizing the alloys listed in Table I a determination of brittleness at room temperature was established both as a criterion for the elimination of those compositions with minimum engineering usefulness and to gain some qualitative insight into the structure effects of the additions. This property measurement was performed by striking the arc-cast buttons with a free-falling pivoted hammer. Increasing impact loads were used until either the sample failed or the maximum impacting load of the machine was reached. In this test, only the alloys containing in excess of 4 wt % Al failed. This is a severe test for intermetallic compounds, and indicates the high impact resistance of these TiNi-base alloys.

A second screening test used in establishing the optimum alloying range in the alloys of Table I was their ability to be hot worked without cracking. Table IV lists, in addition to the impact-brittle alloys, those alloys which failed during hot deformation.

Comparing the results listed in Table IV with the microstructures given in Table II it can be seen that in each case of impact brittleness or hot shortness during rolling, the second phases were present in massive quantities and in all cases, except 4 wt % Co, agglomerated in the apparent grain boundaries. Based upon these criteria of microstructure, impact strength and ease of fabrication, the potentially useful engineering ternary combinations were separated from those of probable little value. This simple and early screening technique minimized the more tedious hot hardness test program.

TABLE III

PRESENCE OF SECOND PHASE IN TiNi MATRIX AS DETERMINED BY X-RAY DIFFRACTION

ELEMENT	MAXIMUM WEIGHT PERCENT ADDED	TiNi PEAKS ONLY	TiNi PLUS PEAKS FROM SECOND PHASE
Cu	16		X
Ta	8	X	
Mo	4	X	
Cr	8	X	
Al	8		X
Si	4		X
Nb	8	X	
Fe	2	X	
V	8	X	
Co	4		X
Mn	8	X	

TABLE IV

ARC-CAST 55.1 NITINOL-BASE TERNARY COMPOSITIONS EXHIBITING ROOM TEMPERATURE BRITTLE FAILURE OR 900.°C HOT SHORTNESS DURING ROLLING

ALLOY COMPOSITION (WEIGHT PERCENT)	FAILED DURING ROOM TEMPERATURE IMPACTING	FAILED DURING ROLLING AT 900°C
8 Al - TiNi	X	
4 Al - TiNi	X	
2 Al - TiNi		X
16 Cu - TiNi		X
8 Mn - TiNi		X
4 Co - TiNi		X
4 Si - TiNi		X
2 Si - TiNi		X

A determination of magnetic susceptibility was made on the prepared ternary alloys. Measurements were made at temperatures of about -70°C (dry ice and acetone) and room temperature. In every case the ternary alloys, like the basic alloy, proved to be non-magnetic.

Hardness Measurement (Room Temperature)

Following the impact, deformation, and magnetic evaluations, the selected ternary alloys were subjected to mechanical property investigation in the form of hardness testing. Both cast and wrought hardness data were obtained from the carefully prepared button specimens. The results of these hardness tests are shown graphically as a function of amount of addition element in Figures 4(a) to 6(d).

Graphical data are not given for varying tungsten additions since subsequent X-ray radiography indicated a failure of the tungsten to dissolve properly. This was one of the very early indications of the relatively low solubility of massive tungsten in molten TiNi. The tungsten-TiNi compatibility will be discussed later in this report.

Observing Figures 4 to 6, it can be seen that in most cases there is an expected increase in hardness with increased alloying element addition. Chromium, aluminum, iron and cobalt appear to be the most efficient hardeners, each producing a Diamond Pyramid Hardness number over 300 (R_c 30) with a 2 wt % addition. Somewhat anomalous behavior appears to be associated with the refractory metals of vanadium, niobium, tantalum, and chromium. Vanadium (see Figure 6(b)) shows very rapid hardening near 0.5 wt % addition followed by a significant decrease and leveling off for the higher vanadium additions. Chromium shows a similar behavior (see Figure 4(d)) but the drop-off is significantly less drastic than with vanadium. Niobium and tantalum (Figures 5(c) and 4(b)) show these elements to produce no apparent change in the base alloy hardness out to 8 wt % of each.

Hardness Measurement (Elevated Temperatures)

1. Ternary Alloys

One of the major considerations in this ternary alloying investigation was the improvement in high temperature strength. In this regard there have been a number of papers relating elevated temperature mechanical properties to hot hardness. A correlation of elevated temperature tensile strength and long time creep with hot hardness has been reported by S. V. Glorioso[5] for the materials PH15-7MO-RH950 and René 41. Hot hardness, hot tensile, and creep-rupture properties were plotted against the Larson-Miller parameter[6] of T (C + log t)*. Upon cross plotting he found that there was

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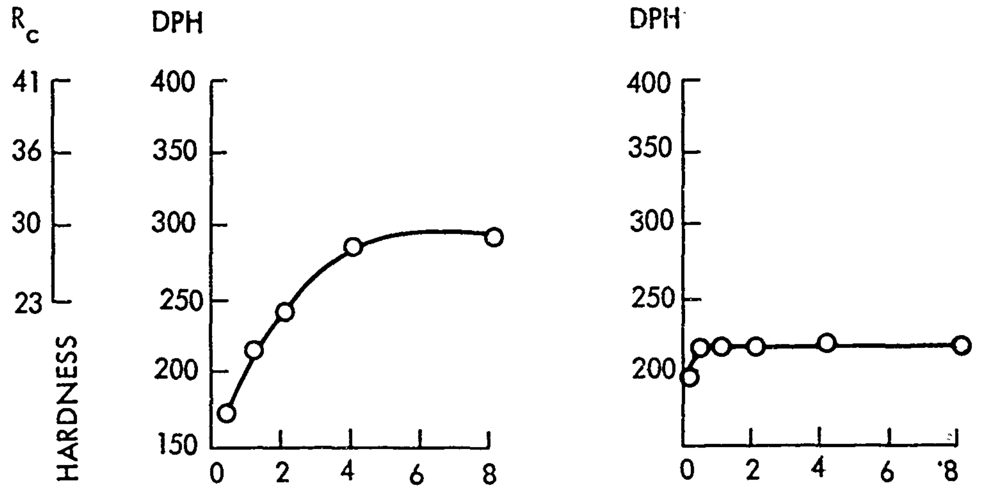
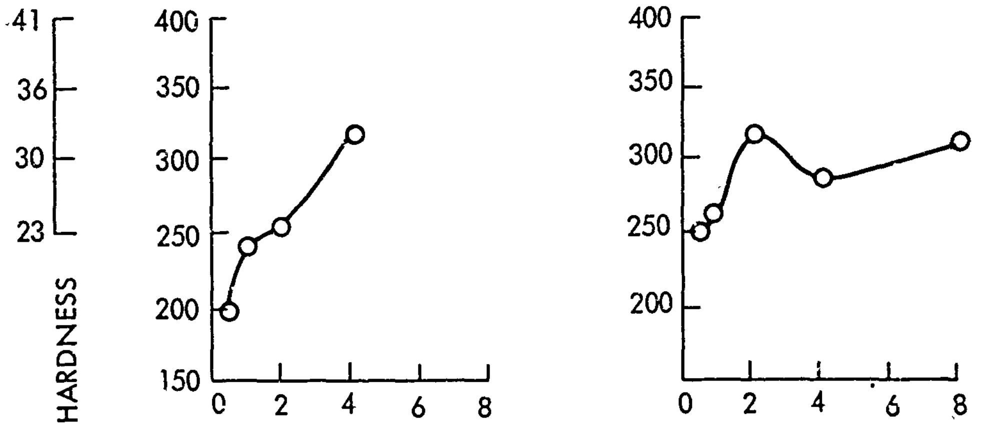
* where T, absolute temperature
C, a constant
t, time in hours



(a) WEIGHT PERCENT COPPER

(b) WEIGHT PERCENT TANTALUM



(c) WEIGHT PERCENT MOLYBDENUM

(d) WEIGHT PERCENT CHROMIUM

FIG. 4 HARDNESS AT ROOM TEMPERATURE AS A FUNCTION OF ALLOYING ADDITIONS. THESE NITINOL ALLOYS ARE IN THE HOT WROUGHT CONDITION.

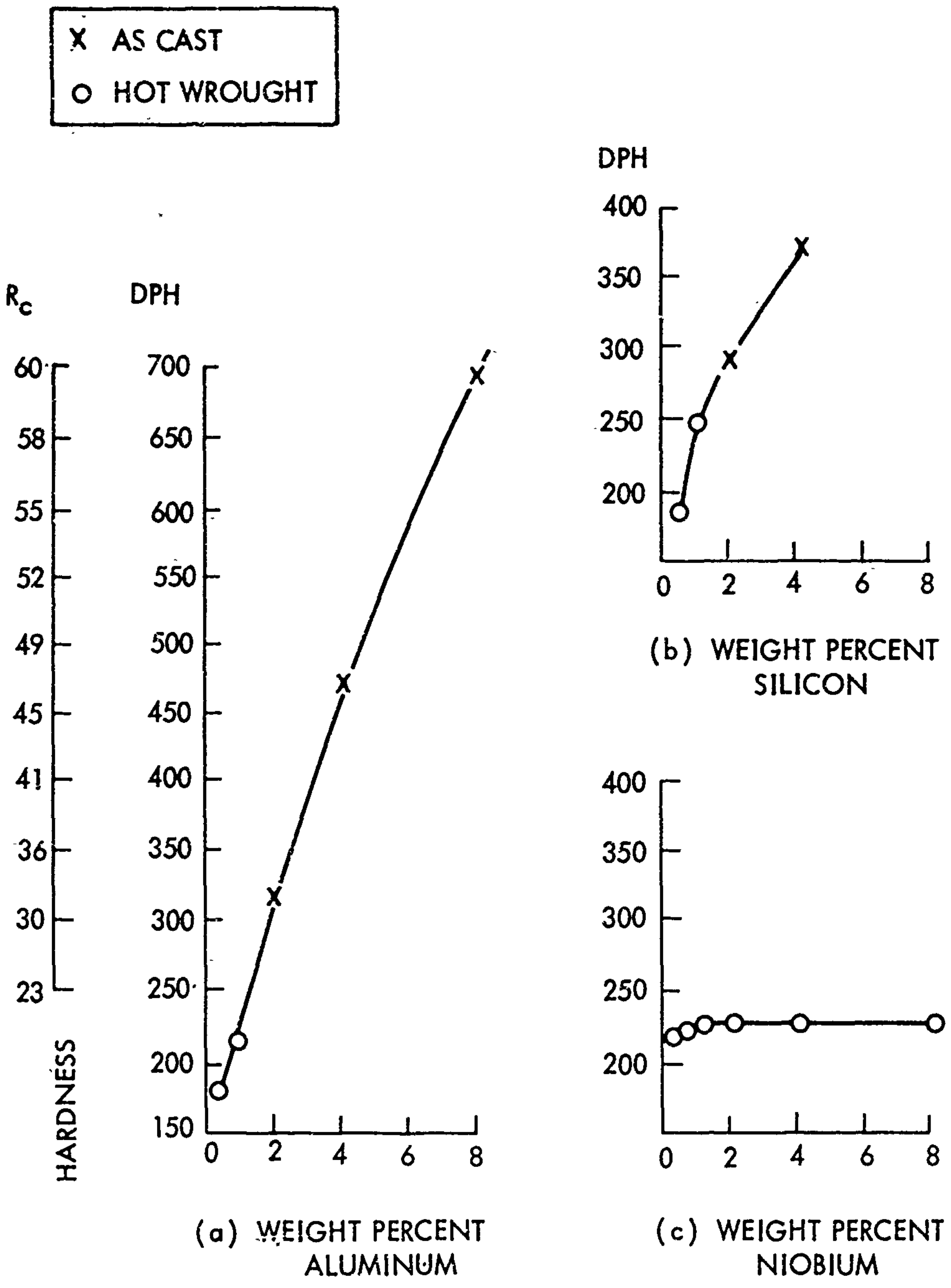
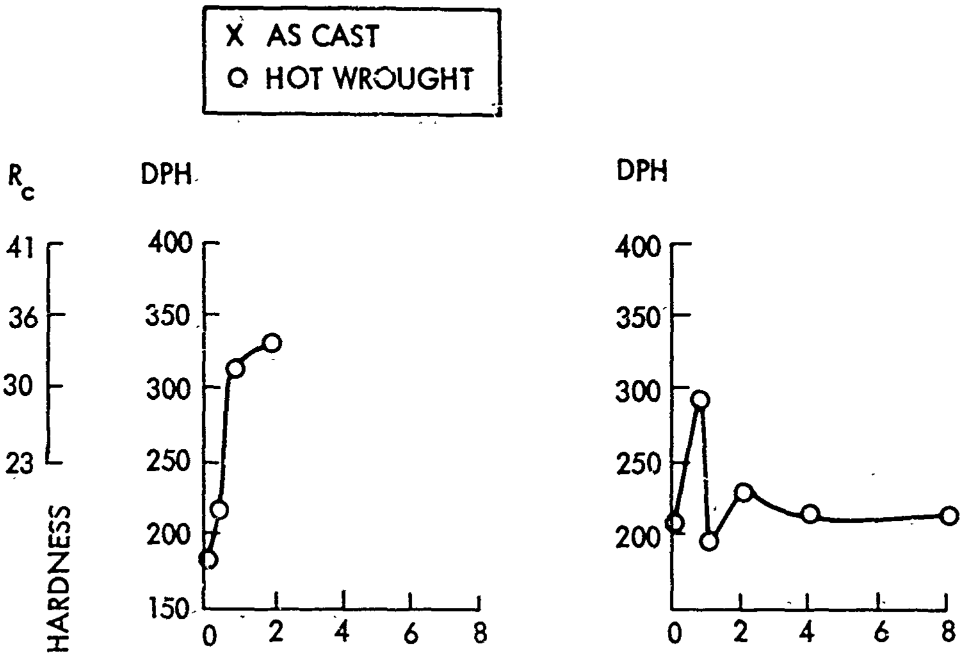
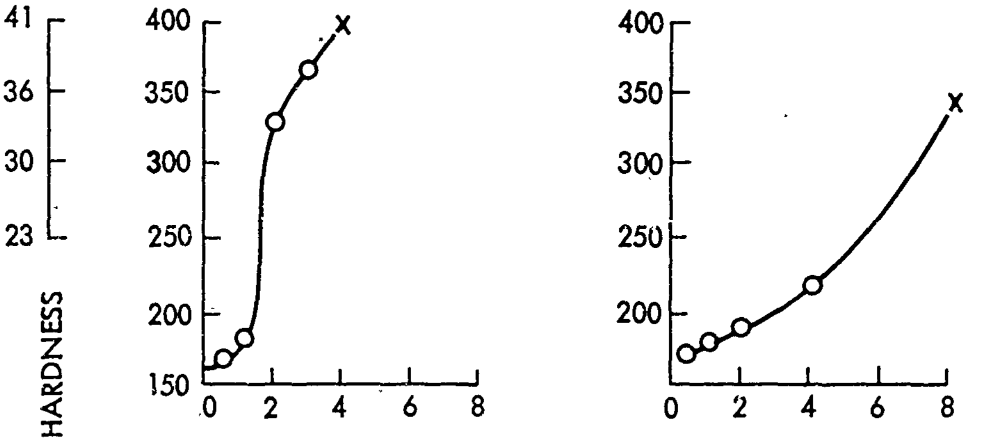


FIG. 5 HARDNESS AT ROOM TEMPERATURE AS A FUNCTION OF ALLOYING ADDITIONS.



(a) WEIGHT PERCENT IRON

(b) WEIGHT PERCENT VANADIUM



(c) WEIGHT PERCENT COBALT

(d) WEIGHT PERCENT MANGANESE

FIG.6 HARDNESS AT ROOM TEMPERATURE AS A FUNCTION OF ALLOYING ADDITIONS.

a linear correlation between hot hardness and the hot tensile and creep-rupture properties.

Drawing upon the above finding the less difficult hot hardness measurements were selected as a rapid means of evaluating the hot strengthening of the ternary addition elements. Using the hot hardness tester apparatus described in the early Nitinol work[1] and carefully prepared specimen surfaces, suitable hot hardness measurements were made with a 2 Kg load. Specimens were temperature equilibrated in the hot hardness tester for a minimum of 20 minutes prior to indentation.

Figure 7(a) shows a band of the hardness values of the 55.1-Nitinol control alloy vs temperature. An 800°F hot hardness value of 200 D.P.H. for the control alloy is noted by a triangular data point. This reference point is carried through on the subsequent hot hardness graphs. This enables rapid evaluation of the relative effect of the various alloying elements on the hot hardness of the 55.1-Nitinol base. For the ternary alloys selected on the basis of impact strength, deformation, and room temperature hardness data, a series of hot hardness curves are shown in Figures 7(b) through 11(c). In most cases the particular ternary alloy selected contained the maximum allowable amount of addition element while retaining ductility. Observing these graphical results it can be seen that in many cases the room and initial elevated temperature hardnesses were significantly higher than the binary control alloy but in every case a serious drop in hardness occurred near 1000°F. Secondary hardening, as in the case of Si, Al, Co, and V, which might have indicated potential precipitation strengthening was searched for by solution and aging treatments. None of these leads proved fruitful.

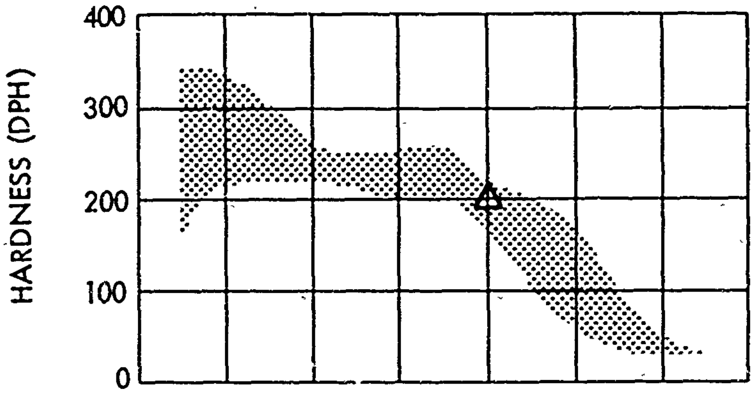
Figure 12 shows the effect of 10 wt % tungsten on the hot hardness. The solution of the tungsten was accomplished by melting mixed fine powders of Ni, Ti,and W in the proper ratio. This resulted in improved hot strength, but like the other elements added, was also unsatisfactory for use above about 1000°F.

2. Type 304 Stainless Steel

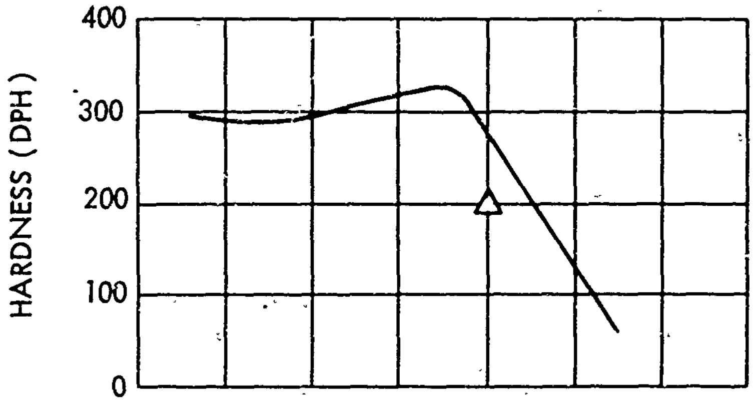
For further comparative purposes Figure 13 shows the hot hardness curve for an annealed 18-8 stainless steel, type 304. This is an example of an alloy with lower initial hot hardness, but which shows little sign of a rapid drop in hardness out to 1200°F.

3. Quaternary Alloys

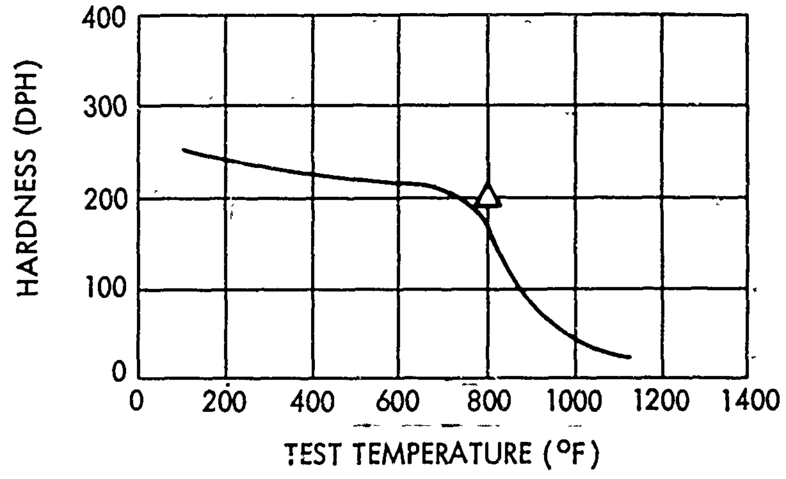
Quaternary alloys produced by combining varying quantities of both tungsten and molybdenum were also investigated. The starting materials were bulk master alloys of 50 wt % each of tungsten-molybdenum, and similarily molybdenum-titanium. Nickel was added in elemental form at the final melt. Upon comparison with the ternaries, these quaternaries showed similar drops in their sustained strength above about 1000°F, as shown in



(a) 55.1 NITINOL CONTROL ALLOY

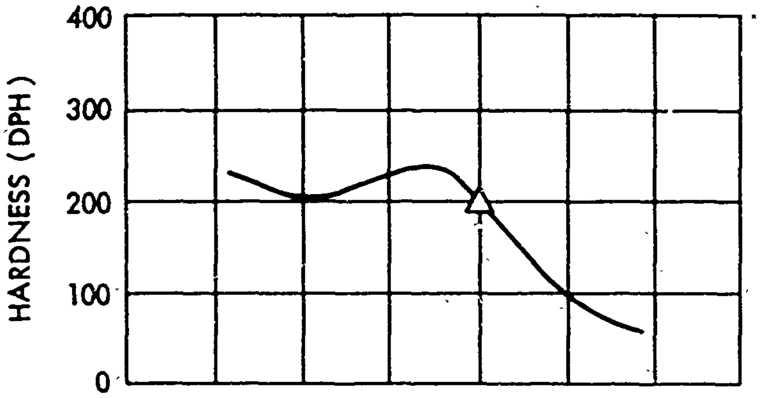


(b) 4 WEIGHT PERCENT COPPER-55.1 NITINOL

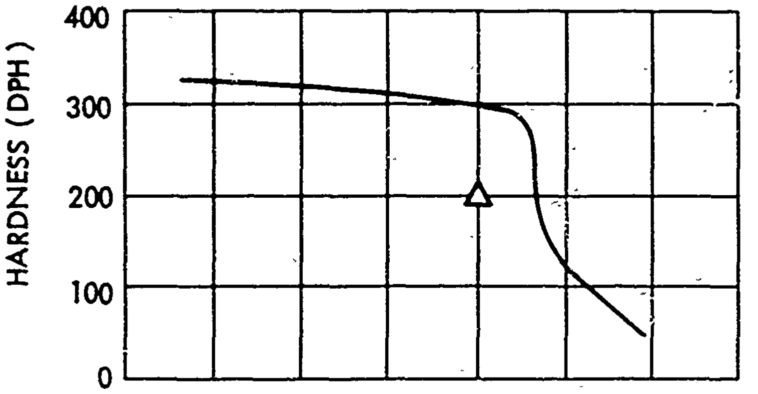


(c) 1 WEIGHT PERCENT TANTALUM - 55.1 NITINOL

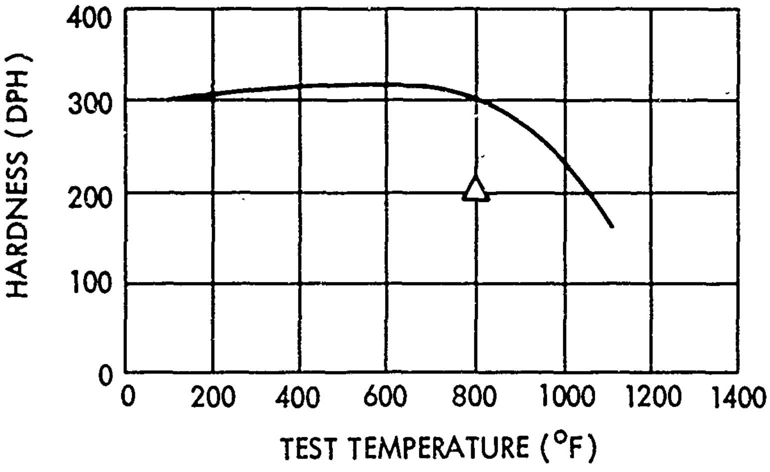
FIG. 7 HARDNESS AT ELEVATED TEMPERATURES FOR SELECTED 55.1 NITINOL TERNARY ALLOYS.



(a) 8 WEIGHT PERCENT TANTALUM - 55.1 NITINOL

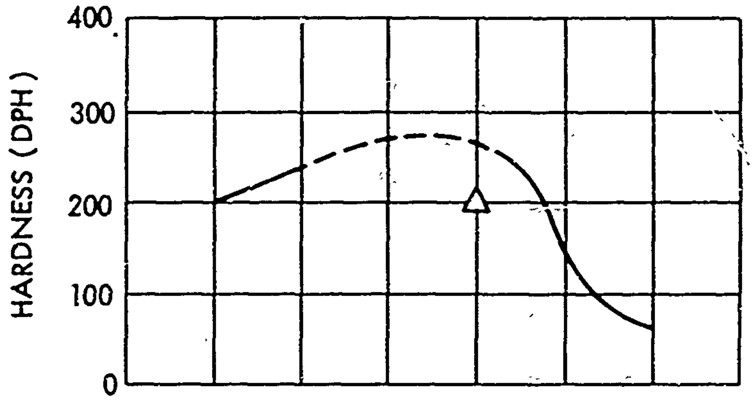


(b) 4 WEIGHT PERCENT MOLYBDENUM - 55.1 NITINOL



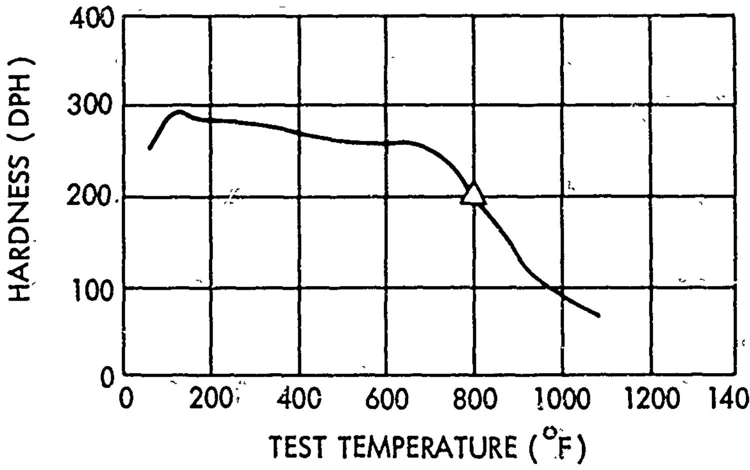
(c) 4 WEIGHT PERCENT CHROMIUM - 55.1 NITINOL

FIG. 8 HARDNESS AT ELEVATED TEMPERATURES FOR SELECTED 55.1 NITINOL TERNARY ALLOYS.



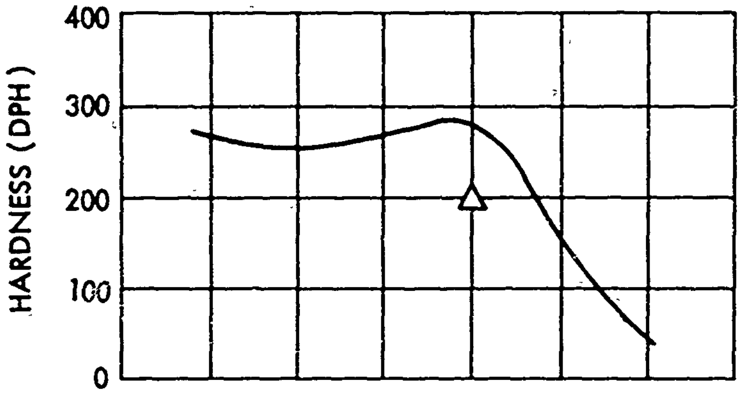
(a) 1 WEIGHT PERCENT ALUMINUM - 55.1 NITINOL

(b) 1 WEIGHT PERCENT SILICON - 55.1 NITINOL

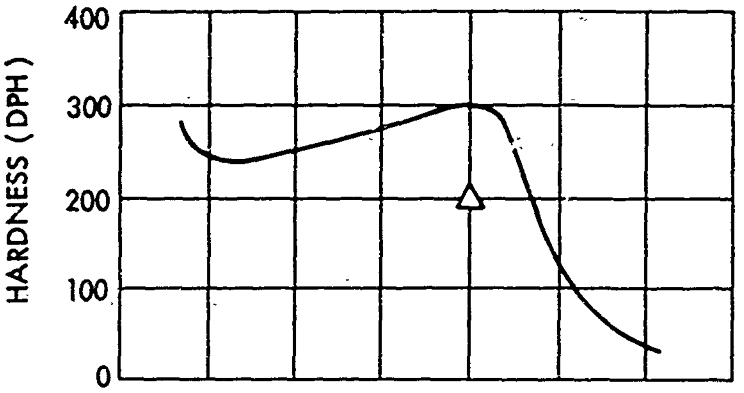


(c) 4 WEIGHT PERCENT NIOBIUM - 55.1 NITINOL

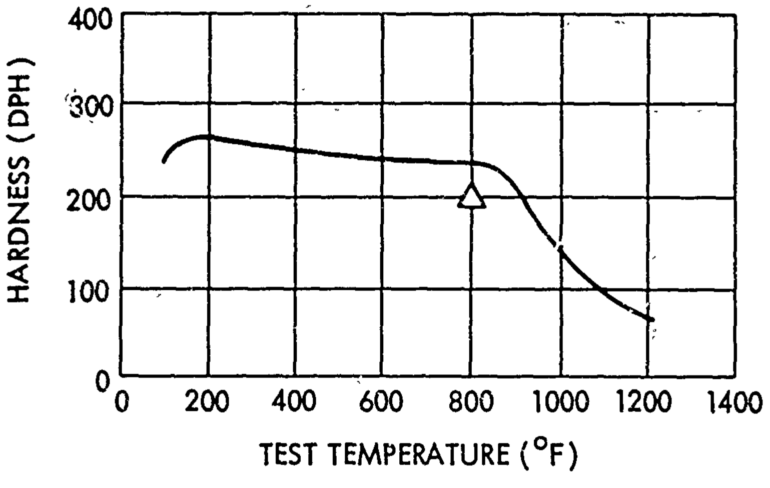
FIG. 9 HARDNESS AT ELEVATED TEMPERATURES FOR SELECTED 55.1 NITINOL TERNARY ALLOYS.



(a) 2 WEIGHT PERCENT IRON - 55.1 NITINOL

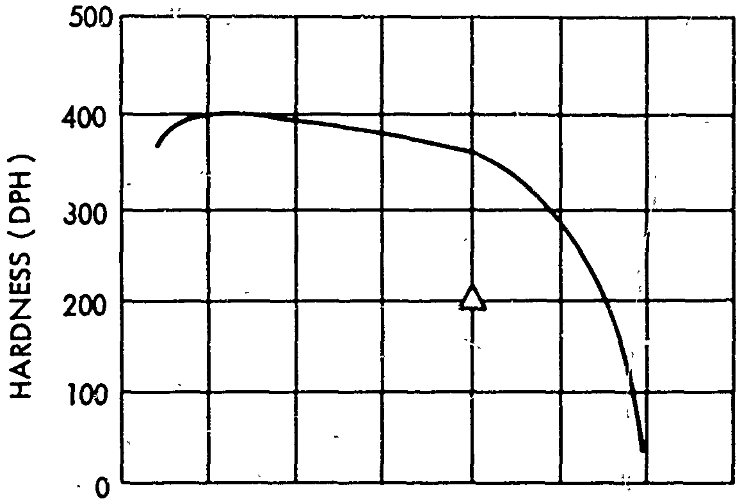


(b) 0.5 WEIGHT PERCENT VANADIUM - 55.1 NITINOL



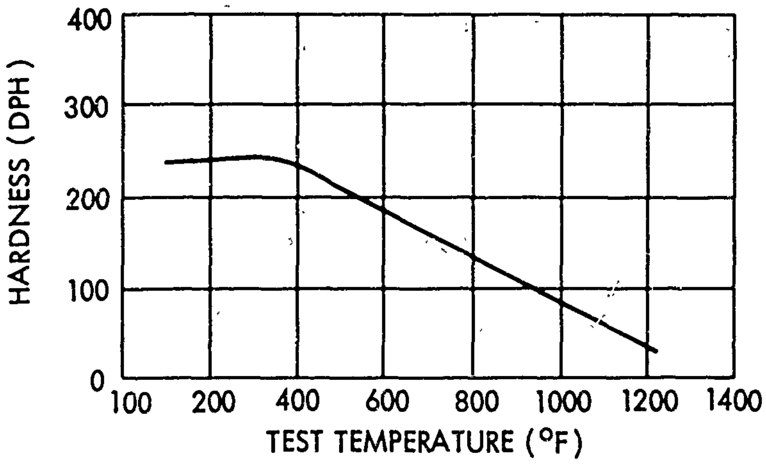
(c) 8 WEIGHT PERCENT VANADIUM - 55.1 NITINOL

FIG. 10 HARDNESS AT ELEVATED TEMPERATURES FOR SELECTED 55.1 NITINOL TERNARY ALLOYS.



(a) 2 WEIGHT PERCENT COBALT - 55.1 NITINOL

(b) 3 WEIGHT PERCENT COBALT - 55.1 NITINOL



(c) 4 WEIGHT PERCENT MANGANESE - 55.1 NITINOL

FIG. 11 HARDNESS AT ELEVATED TEMPERATURES FOR SELECTED 55.1 NITINOL TERNARY ALLOYS.

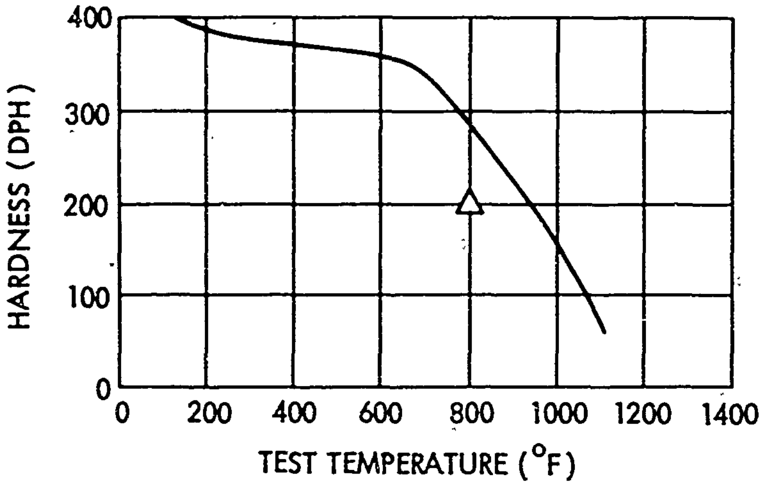


FIG. 12 HARDNESS AT ELEVATED TEMPERATURES FOR 10 WEIGHT PERCENT TUNGSTEN - 55.1 NITINOL TERNARY ALLOY.

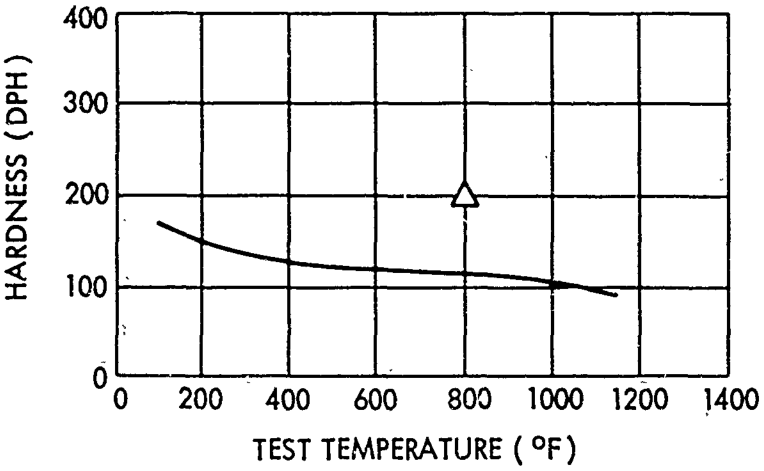


FIG. 13 HARDNESS AT ELEVATED TEMPERATURES FOR ANNEALED STAINLESS STEEL TYPE 304.

Figures 14(a) and (b). They are unique from the ternaries however in that their matrix phases are not TiNi. Figure 15(a) shows that as little as 0.6 wt % of combined tungsten and molybdenum produces a far greater change in the microstructure than does any single ternary addition. Figure 15(b), which shows a 7 wt % total tungsten and molybdenum addition is also unique, with large grains and a continuous second phase in the grain boundaries.

An X-ray diffraction pattern confirmed that neither of these quaternaries are of the TiNi type crystal structure. Both quaternaries can be cold rolled with intermediate anneals, although the 3W - 4Mo - TiNi is harder (R_c 34) than the 0.2 W-0.4 Mo - TiNi (R_B 96).

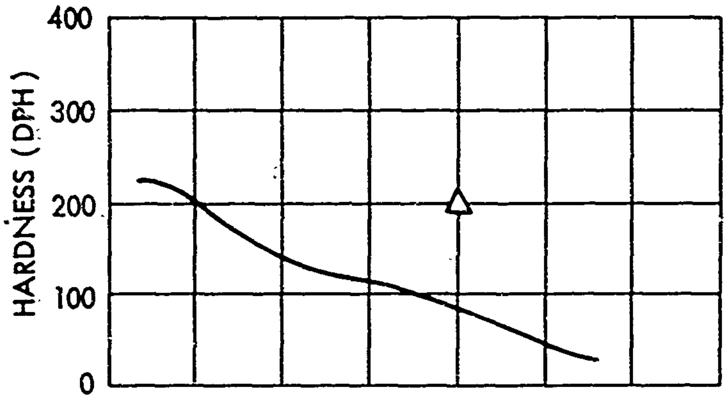
NITINOL-TUNGSTEN COMPOSITES

In an earlier section of this report it was noted that bulk pieces of tungsten did not dissolve readily in 55.1-Nitinol. A radiograph of such a melt is shown in Figure 16, in which the 1/8" charged rods of tungsten are clearly visible (as indicated by the arrow) with sharp edges, despite repeated melting. Further, it was discovered that the button illustrated in Figure 16 was capable of being hot deformed at 900°C without fracture. Based upon these observations it became readily apparent that a very limited surface solubility occurred at the 55.1-Nitinol-tungsten interface and that an unexpected excellent compatibility during deformation existed between these materials.

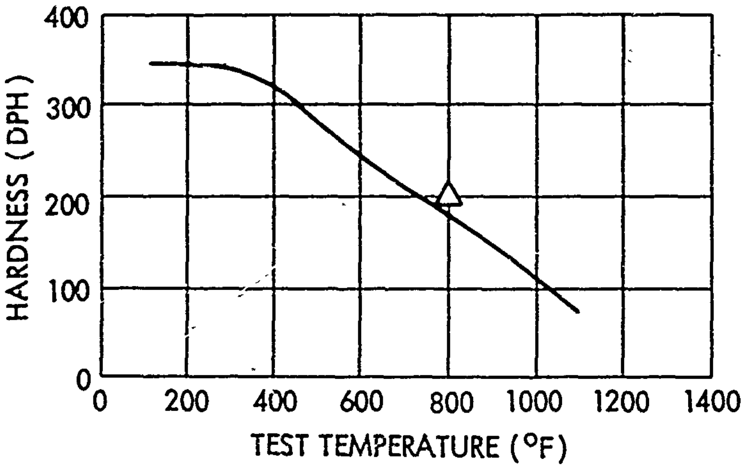
From this phenomenon then arose the possibilities of a metal-metal composite of tungsten fibers in a Nitinol matrix. This was sufficiently promising to warrant immediate further investigation. Accordingly, appropriate ingots embedding 0.040 inch diameter wires of tungsten in 55.1-Nitinol were made. This was accomplished by arc-melting the 55.1-Nitinol around the W wires. A typical arc-cast composite is shown in Figure 17. To confirm the deformation compatibility between these bonded materials a 3-3/8" portion of one arc-cast composite was hot swaged at 900°C to a length of 6-3/4 inches (see Figure 18). The tungsten wires not only deformed without fracture but were reduced in diameter in proportion to the overall diameter reduction of the arc-cast bar. Swaging at 900°C was continued until the rod measured 17.5 inches in length. Even at this vast (over 500%) elongation the tungsten wire filaments remained continuous, also experiencing over a 500% increase in length.

One swaged rod with tungsten filaments embedded was sectioned and micro-hardness measurements were made. Observing Figure 19 it can be seen that the diffusion zone between the tungsten (48 R_c) and the base 55.1-Nitinol is very narrow.

Some room temperature swaging of the tungsten-Nitinol composite material was done and monitored by X-ray radiography. Again, as in the case of the hot deformation, no apparent break occurred in the embedded tungsten filaments. This latter experiment indicates the possible use of Nitinol as a medium for working tungsten metal at room temperature, a goal which

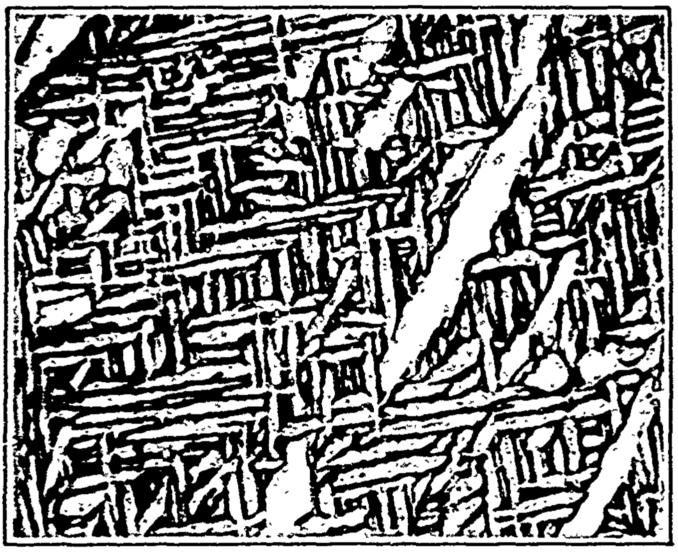


(a) 0.2 WEIGHT PERCENT TUNGSTEN, 0.4 WEIGHT PERCENT MOLYBDENUM, BALANCE 55.1 NITINOL

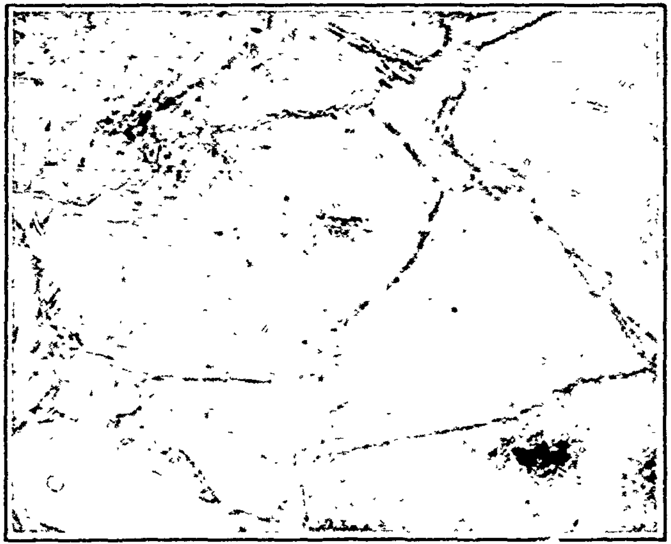


(b) 3 WEIGHT PERCENT TUNGSTEN, 4 WEIGHT PERCENT MOLYBDENUM, BALANCE 55.1 NITINOL

FIG. 14 HARDNESS AT ELEVATED TEMPERATURES FOR QUATERNARY ALLOYS OF TUNGSTEN AND MOLYBDENUM WITH A 55.1 NITINOL BASE.



(a) 0.2 WEIGHT PERCENT TUNGSTEN, 0.4 WEIGHT PERCENT MOLYBDENUM, BALANCE 55.1 NITINOL. HOT WROUGHT AT 900°C.



(b) 3 WEIGHT PERCENT TUNGSTEN, 4 WEIGHT PERCENT MOLYBDENUM, BALANCE 55.1 NITINOL. HOT WROUGHT AT 900°C.

FIG. 15 PHOTOMICROGRAPHS OF WROUGHT NITINOL BASE TUNGSTEN-MOLYBDENUM QUATERNARIES. 710 MAGNIFICATIONS.

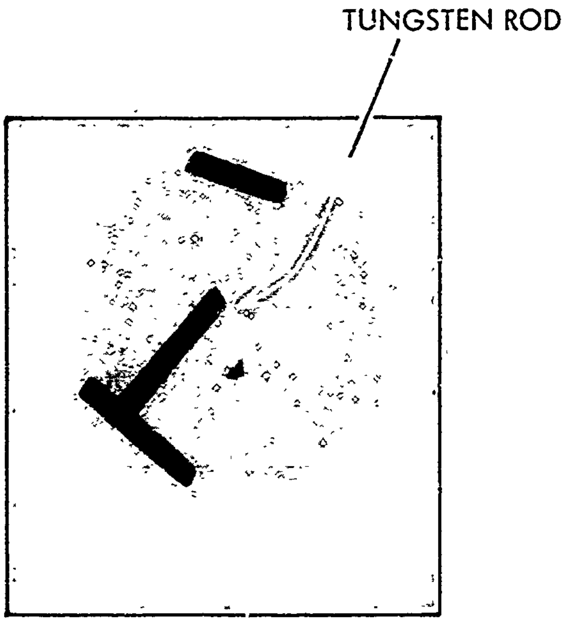


FIG. 16 RADIOGRAPH SHOWING UNDISSOLVED TUNGSTEN IN TiNi BUTTON. BUTTON DIAMETER 2 INCHES.

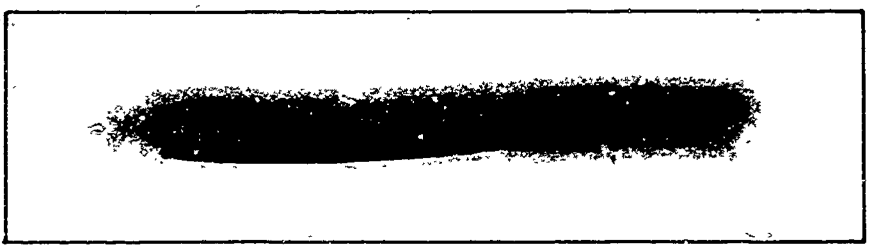


FIG. 17 X-RAY RADIOGRAPH SHOWING 0.040 INCH DIAMETER W WIRE EMBEDDED IN AN ARC - CAST 55.1 - NITINOL MATRIX.

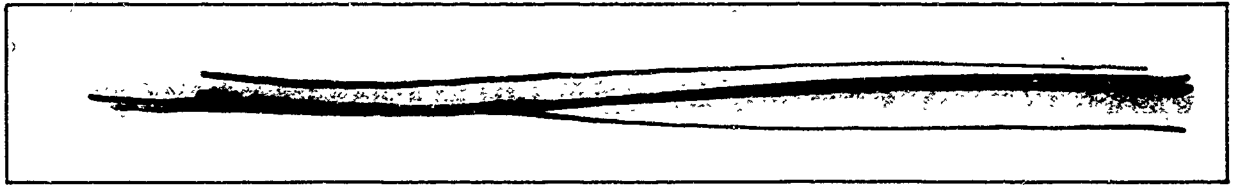


FIG 18 X-RAY RADIOGRAPH SHOWING THE ABOVE COMPOSITE (FIG. 17) HOT SWAGED AT 900°C, ELONGATING TUNGSTEN WIRES 100%.

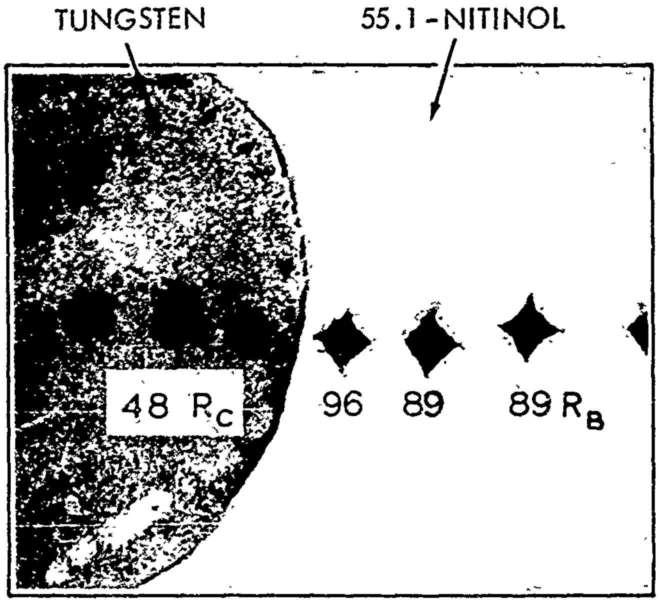


FIG. 19 PHOTOMICROGRAPH SHOWING HARDNESS VARIATION IN TRANSVERSE - SECTIONED TUNGSTEN FILAMENT EMBEDDED IN A 55.1 - NITINOL MATRIX. HARDNESS GIVEN IN ROCKWELL VALUES. 210 MAGNIFICATIONS.

has been long sought. This would place the deformation well below the currently accepted brittle-to-ductile transition temperature.

CONTINUING INVESTIGATIONS

The high temperature strengthening of the Nitinol-base alloys appears unlikely through ternary alloying alone. However, the chief result of this investigation has been the discovery of the unique compatibility of Nitinol with both tungsten and molybdenum. It is now desirable to consider the further work which should be done to explore this potential composite of tungsten and/or molybdenum with Nitinol. Several areas of investigation are currently underway. These include:

1. High strength composite structures incorporating refractory metal filaments in a Nitinol matrix.

2. Improved methods of plastically deforming refractory metals and their alloys.

3. A high temperature silver-free braze alloy for joining refractory metals.

4. A possible improved oxidation resisting coating for the oxidation-sensitive refractory metals.

All of the above and other by-product investigations are currently being worked on as a continuing effort.

CONCLUSIONS

1. It has been determined that 55.1-Nitinol is insufficiently hardened (strengthened) by alloying to be a structurally useful material for service at temperatures above 800°F. However, it can be significantly hardened (strengthened) by alloying with a wide range of elements for use up to this temperature.

2. Of the elements evaluated, chromium and vanadium are most readily dissolved in TiNi without the formation of a second phase, while molybdenum and silicon are the least soluble.

3. The presence of a similar appearing second phase, regardless of absence or presence of minor amounts of ternary additions, lends further weight to the presumption that such second phases are O_2, H_2, or N_2 interstitials.

4. Rather substantial amounts of the selected elements added to this binary compound did not affect the non-magnetic nature of the TiNi.

5. Room temperature hardness is improved most efficiently by silicon, aluminum, iron, or cobalt.

6. Hot hardness of the alloys tested decreases sharply, in the manner of titanium, as the testing temperature approached 1000°F. As a comparison to these ternaries, data are presented for type 304 stainless steel. Although not possessing the room temperature hardness of Nitinol, this stainless steel maintains its hardness as the temperature exceeds 1000°F.

7. Quaternary alloying using molybdenum and tungsten with TiNi has great effect on the TiNi microstructure, but does not improve its high temperature performance.

8. TiNi possesses a unique interfacial compatibility with bulk tungsten offering considerable promise as a means of working tungsten below the presently accepted tungsten working temperatures.

9. By utilizing their interfacial compatibilities the capability of producing a ductile TiNi-tungsten metal-metal composite has been shown.

ACKNOWLEDGMENT

Appreciation for the careful and extensive melting and fabrication of the numerous specimens involved in this program is extended to H. E. Eberly. Credit is also due E. F. Heintzelman for his excellent metallography and hardness testing. Further, the authors wish to acknowledge Dr. F. E. Wang's helpful discussions on TiNi structure theory and on the X-ray diffraction patterns obtained.

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