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THE DEVELOPMENT OF MELTING AND CASTING
PROCEDURES FOR NITINOL NICKEL-BASE
ALLOYS

Prepared by
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SANDIA LABORATORIES

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THE DEVELOPMENT OF MELTING AND
CASTING PROCEDURES FOR NITINOL
NICKEL-BASE ALLOYS

by

D. C. Drennen, C. M. Jackson, and H. J. Wagner

SUMMARY

A nickel-titanium alloy designated 55-Nitinol was developed several years ago by the U. S. Naval Ordnance Laboratory. This alloy, which contains nominally 55 weight percent nickel and 45 weight percent titanium, exhibits a rare ability to restore itself to a predetermined shape after being plastically deformed if it is reheated to a certain "transition" temperature. This transition temperature is a sensitive function of the chemical composition of the alloy and can range from below room temperature to above 250 F.

Nitinol alloys also possess certain other unusual physical and mechanical-property relationships. For example, below its transition temperature, Nitinol exhibits a very high damping capacity, whereas, above its transition temperature, the alloy shows a very low damping capacity.

Sandia Corporation is interested in utilizing the unusual features of Nitinol in the form of wire and strip. In view of the fact that Nitinol is still an experimental alloy and not yet commercially available, the Columbus Laboratories of Battelle Memorial Institute conducted a program to develop suitable melting and casting procedures which would lead to the preparation of large ingots of three alloys having transition temperatures of approximately 100, 200, and 300 F.

Fifteen heats of experimental Nitinol alloys were vacuum melted and cast during the course of the program. In addition to obtaining large ingots it was necessary to prepare a large number of heats in order to (1) determine whether losses of nickel or titanium occur when a particular melting practice is used and (2) to develop a curve relating the transition temperature to chemical composition.

Melting and casting experiments were conducted in thoria and in ATJ graphite crucibles. The results of the experiments using a thoria crucible were unsatisfactory. On the other hand, the results of the experiments utilizing the ATJ graphite crucible showed that Nitinol alloys can be vacuum melted and contained very well in this material. No problems were encountered during vacuum melting of the alloys that could be attributed to the ATJ graphite crucible.

A melting and casting procedure for Nitinol alloys was developed, and several large, high-quality ingots and smaller rod castings were prepared.

With very few exceptions, the analyzed titanium contents were within ± 0.3 percent of the intended amounts. Also, the carbon levels were relatively low (varying from 0.052 to 0.074 weight percent); little if any pickup from the crucible was indicated.

The results of the transition (shape recovery) temperature studies indicated that the experimental Nitinol alloys have transition temperatures ranging from approximately 55 to 278 F, depending on composition. Furthermore, the data confirm that the transition temperature is a very sensitive function of the titanium content of the alloy. A curve illustrating this relationship was developed. Also, the data show that it was possible to prepare alloys of the desired transition temperatures within reasonable limits. These alloys are Nos. 5, 2B, and 8A, which display transition temperatures of about 106, 210, and 260 F, respectively. Alloys 2B and 8A are available as large ingots; however, only a small rod casting of Alloy 5 was prepared.

Metallographic studies revealed that the experimental Nitinol alloys in the as-cast condition contained several different phases in addition to the matrix. Photomicrographs illustrating the different types of metallurgical structures of the alloys are presented in this report.

The ingots prepared on this program are considered to be prime material for working into strip and wire for research use.

INTRODUCTION

The U. S. Naval Ordnance Laboratory developed a nickel-titanium alloy (U. S. Patent No. 3,174,851) several years ago called 55-Nitinol. This alloy, which contains nominally 55 weight percent nickel and 45 weight percent titanium, exhibits certain unusual properties as a result of a martensitic transformation. The reverse transformation occurs over a range of temperature on heating; the temperature range is a sensitive function of the nickel:titanium ratio of the alloy. The upper limit of the range is called the "transition" temperature; it can be varied from well below room temperature to above 250 F by changing the chemical composition of the alloy.

55-Nitinol is a unique engineering material inasmuch as it possesses a so-called "shape memory" which enables it to return to a prefixed shape after being plastically deformed and then reheated to its transition temperature. Another feature of the 55-Nitinol alloy is that it possesses a very high damping capacity (similar to that of the better manganese-copper alloys) below its transition temperature, but an extremely low damping capacity (like a bell material) above this temperature.

Some possible applications to utilize the "shape memory" of Nitinol include temperature-sensitive switches, mechanical-work devices, blind fasteners and self-erectable antennas for aerospace applications.

Sandia Corporation desires to investigate the unusual properties of Nitinol alloys and is interested in obtaining quantities of Nitinol wire and strip for experimentation. However, since Nitinol alloys are not available commercially, the Columbus Laboratories of Battelle Memorial Institute undertook a program to develop melting and casting procedures in order to produce large, high-quality ingots of three Nitinol alloys from which wire and strip could be fabricated. These alloys were to have transition temperatures of approximately 100, 200, and 300 F.

This report covers the development of melting and casting procedures for Nitinol nickel-base alloys, and the preparation of material with the transition temperatures desired by Sandia Corporation.

EXPERIMENTAL PROCEDURES AND RESULTS

Alloy Compositions

Table 1 lists the nominal compositions of the alloys prepared during this program. Although the objective of the program was to obtain only three alloys having different transition temperatures, a larger number of alloys was prepared. This was necessary because the transition temperature was known to be a very sensitive function of chemical composition, and it became important to learn (1) the closeness to which chemical composition had to be controlled and (2) the degree to which it could be controlled using the melting practices studied. Along this line, the published curve⁽¹⁾ which relates transition temperature (determined by damping experiments on as-cast samples) to chemical composition for nickel-titanium alloys proved to be too approximate for our use. In view of this unexpected fact, it was deemed necessary to develop our own curve on the basis of small preliminary heats. With respect to melting practice, it was difficult to forecast the exact percent recovery of the charge materials that could be realized using any particular melting practice until a number of heats were made.

Preparation of Experimental Alloys

Melting Stock

The melting stock used in preparing the experimental alloys consisted of electrolytic titanium crystal (sponge) and electrolytic nickel. The typical chemical compositions of these materials are presented in Table 2. In most of the melting experiments, the electrolytic nickel was used without any treatment other than degreasing. However, for Alloys 2A, 3A, 5, and 6, the nickel was vacuum degassed prior to melting; this was done by heating the nickel at 1800 F for one hour in vacuum at an ultimate pressure of 7.2×10^{-5} torr.

TABLE 1. NOMINAL COMPOSITIONS OF EXPERIMENTAL NITINOL ALLOYS

Number	Intended Composition, weight percent	
	Nickel	Titanium
1	54.00	46.00
2, 2A, 2B	54.50	45.50
3, 3A, 3B	55.00	45.00
5, 5B	55.25	44.75
6	55.50	44.50
7	54.25	45.75
8, 8A	53.50	46.50
9	53.00	47.00
10	55.10	44.90

TABLE 2. DESCRIPTION OF MELTING STOCK

Element	
Nickel	Electrolytic sheared metal ^(b) ; 99.95 Ni + Co - 0.01 to 0.04 Fe - 0.01 to 0.03 Cu - 0.0063 O ₂ - 0.00077 H ₂ - 0.0002 N ₂
Titanium	EL-90 grade, electrolytic titanium crystal (sponge) ^(c) ; 0.016 C - 0.005 Fe - 0.101 Cl - 0.004 Si - 0.040 O ₂ - 0.002 N ₂ ; Hardness = 86.6 BHN

(a) Compositions are in weight percent.

(b) International Nickel Company.

(c) Titanium Metals Corporation of America.

Melting Recovery Factors

Since the vapor pressures of nickel and titanium are about the same, recovery factors of 1.0 were used for both of these elements in the initial melts. Subsequent chemical analysis of several of the early melts indicated that the actual recoveries of the elements justified the continued use of the same recovery factors. Therefore, a recovery factor of 1.0 was used for the remainder of the alloys.

Selection of Materials for Melting Crucibles, Molds, and Thermocouple Protection Tubes

The materials for melting crucibles, molds, and thermocouple protection tubes were selected primarily on the basis that the material must not be readily reduced by the chemically active NiTi intermetallic compound. Other factors considered were availability and cost.

For the initial small-scale melting and casting experiments, thoria was selected as the crucible and thermocouple protection tube material. Other refractories, e.g., magnesia and alumina, were considered. However, thoria was selected because it is more stable thermodynamically than magnesia or alumina and is less apt to be reduced by the Nitinol alloys. Furthermore, Hume-Rothery⁽²⁾ verified experimentally that thoria is not reduced by molten NiTi.

We were able to obtain two small thoria crucibles having a capacity of about 3 pounds of Nitinol, and one thermocouple protection tube of the desired size. The crucible was rammed in a vacuum-furnace box.

For the large-scale melting and casting experiments, we selected ATJ graphite, a high-density, low-porosity graphite, for the crucible and thermocouple protection tube material. ATJ graphite was also selected as the mold material for both the small- and large-scale experiments.

ATJ graphite was chosen on the basis of the experience of Mr. W. J. Buehler of the Naval Ordnance Laboratory, the developer of Nitinol, who has successfully melted and cast small-scale heats of Nitinol alloys in this material for a number of years. Both Mr. Buehler and other investigators⁽³⁾ have reported that NiTi does not have any appreciable solubility for carbon. It should be noted, however, that special charging procedures had to be employed to ensure that neither molten nickel nor molten titanium came in contact with the crucible. These procedures are discussed later.

Design of Graphite Crucibles and Molds

For the large-scale melting, a melting crucible with a 100-pound capacity was designed. The crucible and pouring lip were mechanically joined together so that the molten alloy never contacted any material other than graphite during the melting and pouring.

A large mold was designed to produce a tapered round ingot weighing about 50 pounds with an additional tapered round hot top weighing about 17.5 pounds. The ingot is 14-1/4 inches long; its diameter is 5 inches at the top and 3-1/2 inches at the bottom. The hot top is 5-1/4 inches in diameter at the top, 4-3/4 inches at the bottom, and 4-1/2 inches long. The tapered ingot was designed to obtain properly controlled directional solidification and avoid secondary pipe, which can occur when untapered ingots are cast.

In addition, a small graphite mold was designed to produce three 5-inch-long tapered round rods measuring 3/8 inch at the bottom and 5/8 inch at the top with a tapered rectangular hot top serving all three rods. The total weight of Nitinol required to fill this mold is about 3 pounds. This type of mold was selected so that the cast rods could be hot swaged directly to rods for subsequent use in studies to determine the transition (shape recovery) temperature range of each alloy.

Photographs of the ingots and rods produced in the two types of graphite molds are shown in a later section of this report (Figures 1 and 2).

Melting and Casting

Small Heats. Heats of Alloy 1 (54.00 w/o Ni-46.00 w/o Ti) and Alloy 2 (54.50 w/o Ni-45.50 w/o Ti), each weighing 2.5 pounds, were vacuum-induction melted in a fused thoria crucible and cast in the ATJ graphite rod molds which were described in the previous section. The pressure in the melting chamber was about 7×10^{-3} torr (7 microns).

The results of these initial melting experiments using the thoria crucible discouraged any further use of thoria. Although the thoria crucible did not appear to have reacted with the molten Nitinol alloys, it cracked severely, presumably from thermal shock, during the melting cycle. The cracks were large enough that the molten metal leaked out and reacted with the magnesia backup refractory behind the crucible.

A second problem encountered during the melting was with the thoria topping mix which was used around the top of the crucible and also as the pouring lip. This mix consisted of pure fused thoria grog and a binder which is normally recommended for use with thoria. However, the binder was apparently chemically reduced by the molten Nitinol alloys. Thus, gas (presumably oxygen) was evolved and the unbonded thoria grog fell into the melt.

This problem with the thoria grog could probably be eliminated by utilizing an oversized crucible with an integral pouring lip; in this manner, the molten Nitinol would always be in contact with pure fused thoria containing no binder. Such a crucible would have to be designed and slip-cast especially for this work, and would be very expensive. The crucible we used was the only one that was available as an off-the-shelf item from commercial manufacturers of thoria crucibles.

A third problem occurred with the fused thoria tube used to protect the immersion thermocouple. Although the tube was preheated to about 1800 F, it cracked apart from thermal shock when it was immersed in the molten Nitinol.

The rods cast from the small-scale heats of Alloys 1 and 2 were obviously contaminated by the loose thoria grog which fell into the melts and was probably trapped in the pouring stream. Therefore, these rods were not considered to be good material and were excluded from further characterization.

In view of the unsatisfactory results obtained with the small-scale melting experiments in the thoria crucible, we discontinued any additional experiments using thoria crucibles and proceeded to the large-scale melting using ATJ graphite crucibles.

Large Heats. In general, the large-scale melting involved the vacuum-induction melting of 70- to 80-pound heats of the experimental alloys and the pouring of an ingot and a rod casting. In some cases, a 70- to 80-pound master heat was melted and an ingot and/or a rod casting was poured, after which supplementary amounts of nickel or titanium, or both, were added to the melt in order to obtain ingots or castings of other compositions.

The ATJ graphite was found to work extremely well as a crucible material to melt and contain the molten Nitinol alloys. No erosion or other problems were encountered with the ATJ graphite. Furthermore, chemical analyses, which are discussed later, confirmed that molten Nitinol does not pick up any appreciable amount of carbon even with relatively long holding times in the crucible.

Several different melting procedures were employed during the course of this investigation. However, the following one was considered the best, and enabled us to prepare high-quality ingots of the Nitinol alloys:

- (1) A 5- to 10-pound piece of a previously melted Nitinol alloy with a known composition was placed in the crucible.
- (2) The nickel and titanium additions were mixed together and placed in the charging cups in the tower of the vacuum furnace. In the cases where only titanium was to be added, it was also placed in the charging cups.
- (3) The vacuum furnace was pumped down to an ultimate pressure of 1 to 10 microns.
- (4) The initial piece of Nitinol in the crucible was melted.
- (5) The chamber was blanked off from the vacuum pumps and backfilled with high-purity argon to a pressure of 1/6 atmosphere.

- (6) The nickel and/or titanium additions from the charging tower were made to the melt at a rate about equal to their dissolution rate.
- (7) After melting was completed, the pressure in the chamber was again gradually lowered to an ultimate level of about 1 to 12 microns in order to allow the melt to outgas gently.
- (8) The temperature of the melt was measured by means of an immersed platinum-platinum + 10 percent rhodium thermocouple sheathed with an ALJ graphite protection tube. The melt was maintained between temperatures of 2550 and 2680 F.
- (9) The vacuum furnace was blanked off.
- (10) If both a rod casting and an ingot were to be poured, the rod casting was poured first.
- (11) Approximately 5 to 10 pounds of metal were left in the crucible or poured into another graphite mold for use as a starting charge for subsequent melting.

Figures 1 and 2 are photographs of an ingot and a rod casting, respectively, of experimental Nitinol alloys. The excellent surface of the ingot is evident.

Several observations regarding some of the large-scale melting and casting experiments leading up to the development of the procedure just described are worthy of discussion. For example, we found that if the melt-down of the titanium and nickel (untreated or vacuum degassed) was conducted under a full vacuum in the order of 10 microns, the evolution of gas, especially from the nickel, was extremely violent and tended to blow the molten metal out of the crucible and onto the upper part of the crucible. Since the upper portion of the crucible was relatively cold, a large buildup of metal occurred around it. Although vacuum degassing the nickel reduced the gas evolution considerably, there was still more gas evolution and splattering than could be tolerated.

The use of an argon backfill to 1/6 atmosphere enabled us to add undegassed nickel and titanium rapidly with very little, if any, observable evolution of gas and concomitant splattering. Although heavy smoke, presumably a chloride that remained from the refining operations, was given off from the titanium as it melted, this caused no problems other

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FIGURE 1. PHOTOGRAPH OF 65-POUND INGOT OF NITINOL NICKEL-BASE ALLOY

42953

FIGURE 2. PHOTOGRAPH OF ROD CASTING OF ALLOY 3

than making it difficult to observe the melt through the sight port. However, as soon as the vacuum furnace was pumped down again, the heavy smoke was drawn off by the pumps and good visibility was restored.

An alternate meltdown procedure was employed for the melting of Alloy 3B and could be substituted for Steps 1 through 6 of the preferred melting procedure previously listed if a piece of Nitinol alloy were not available for the initial meltdown. This alternate meltdown procedure was, in general, as follows:

- (1) A piece of 93-mil-thick Nickel 200 sheet was placed on the bottom of the crucible.
- (2) A formed tube of 93-mil-thick Nickel 200 sheet measuring 6 inches in diameter by 12 inches high was placed on top of the piece of nickel in the crucible.
- (3) Alternate layers of titanium and nickel were charged into the nickel cylinder. The remainder of the additions were placed in the charging cups in the tower of the vacuum furnace.
- (4) The furnace was pumped down to an ultimate pressure of about 1×10^{-2} torr (10 microns).
- (5) The vacuum chamber was blanked off and backfilled with high-purity argon to a pressure of 1/2 atmosphere (1/6 atmosphere would have been sufficient).
- (6) The initial charge in the crucible was melted, after which the remaining nickel and titanium additions were made to the melt at a rate about equal to their dissolution rate.

This charging method, rather than simply charging nickel and titanium together into the crucible, was used in order to avoid having molten nickel or titanium in contact with hot graphite.

Characterization of Experimental Nitinol Alloys

Radiographic Examination

Radiographic inspection of the large ingots 2A, 2B, 3, 3B, 5B, 8A, and 10 revealed no porosity or secondary pipe. Furthermore, in almost all cases the primary pipe was completely restricted to the hot top.

Chemical Analyses

In general, a cast rod of each of the experimental alloys was chemically analyzed for titanium only. However, in some cases, oxygen and carbon analyses as well as spectrographic analyses for minor constituents were performed.

The general procedure used for the titanium analysis was as follows:

- (1) Dissolve the Nitinol sample in an $\text{HNO}_3\text{-HCl}$ solution
- (2) Cool the solution
- (3) Add Cupferron reagent to promote the precipitation of titanium cupferrate
- (4) Filter and wash the precipitate
- (5) Ignite to TiO_2
- (6) Weigh the residue.

Using this technique the accuracy of the chemical analysis was believed to be within ± 0.5 percent of the actual amount of titanium present.

The results of the chemical analyses are given in Table 3. These data indicate that, in most cases, the analyzed titanium contents are reasonably close (± 0.3 percent) to those intended. The largest difference was obtained in Alloy 6, where the analyzed titanium content was 2.2 percent lower than intended. The carbon analyses varied from 0.052 to 0.074 percent. This carbon level is considered quite satisfactory especially in view of the required holding time of the melt in the ATJ graphite crucible. The actual oxygen content, which, if too high, can have a detrimental effect on the fabrication behavior of the Nitinol alloys, was, in general, about 1000 to 1900 ppm. The unusually high (3700 ppm) oxygen content of Alloy 3 was caused by having to open the vacuum furnace during the melting cycle because of a mechanical malfunction.

Transition Temperature Studies

The transition (shape recovery) temperature, i.e., the temperature to which plastically deformed Nitinol must be heated in order for it to return completely to its original shape, was determined on flattened

TABLE 3. CHEMICAL ANALYSES OF EXPERIMENTAL NITINOL ALLOYS

Alloy Number	Intended		Chemical Composition, weight percent										
			Analyzed										
	Ni	Ti	Ni	Ti	C	O	Si	Fe	Mg	Cu	Mn	Cr	Co
2A(a)	54.50	45.50	Balance	46.2	0.074	0.1645	0.003	0.01	<0.001	0.03	0.01	0.01	0.02
2B(a)	54.50	45.50	Balance	45.5	0.065	0.1900	0.001	0.005	<0.001	0.03	0.005	0.01	0.02
3(a)	55.00	45.00	Balance	43.6(b)	0.052(c)	0.3700(d)	0.001	0.005	<0.001	0.03	0.005	0.01	0.02
3A	55.00	45.00	Balance	45.4	-	-	-	-	-	-	-	-	-
3B(a)	55.00	45.00	Balance	45.1	0.072	0.1060	0.003	0.02	<0.001	0.03	0.02	0.01	0.02
5	55.25	44.75	Balance	45.1	-	-	-	-	-	-	-	-	-
5B(a)	55.25	44.75	Balance	45.5	-	-	-	-	-	-	-	-	-
6	55.50	44.50	Balance	42.3	-	-	-	-	-	-	-	-	-
7	54.25	45.75	Balance	47.4	-	-	-	-	-	-	-	-	-
8	53.50	46.50	Balance	46.7	-	-	-	-	-	-	-	-	-
8A(a)	53.50	46.50	Balance	46.2	-	-	-	-	-	-	-	-	-
9	53.00	47.00	Balance	46.7	-	-	-	-	-	-	-	-	-
10(a)	53.10	44.90	Balance	44.8	-	-	-	-	-	-	-	-	-

(a) A large ingot of this alloy was prepared.

(b) A check analysis indicated 43.9 percent titanium.

(c) A check analysis indicated 0.059 percent carbon.

(d) The unusually high oxygen content resulted from opening the vacuum furnace during the melting cycle because of a mechanical malfunction.

rod samples of the experimental Nitinol alloys. In general, the following procedure or slight modifications of it was used to determine the transition temperature of the alloys:

- (1) After soaking one hour at 1475 F, a cast rod of each alloy was swaged at this temperature to 1/4-inch-diameter rod.
- (2) A length, approximately 2-1/2 inches, of one or both ends of the hot-swaged 1/4-inch-diameter rods was forged flat at 1475 F to a thickness of about 0.075 to 0.085 inch.
- (3) The rods were allowed to cool to room temperature.
- (4) The rods were "memory heat treated" at 930 F for 30 minutes and air cooled.
- (5) The flattened ends of the rods of all of the alloys except 3, 5B, and 6 were bent about 45 degrees at room temperature over a 1-inch-diameter mandrel. The ends of the rods of Alloys 3, 5B, and 6 were bent 45 or 90 degrees over a 1-inch mandrel while submerged in an acetone-dry ice mixture, because they could not be bent at room temperature. These samples were kept in the acetone-dry ice mixture until the recovery test was completed.
- (6) With the exception of Alloy 5B, a 10-mil wire was fastened to the bent end of the flattened rods. The rod of Alloy 5B was attached to a metal plate on which reference marks were scribed to facilitate observation of any movement of the bent end.
- (7) The bent end of the rods of Alloys 2A, 2B, 3A, 3B, 5, 7, 8, 8A, 9 and 10 were suspended in a bath of glycerin, and the wire was attached to a dial gage. The bent end of the rod of Alloys 3 and 6 was suspended in a acetone-dry ice mixture. The metal plate holding the rod of Alloy 5B was suspended in the acetone-dry ice mixture.
- (8) For all of the alloys except No. 5B the movement of the dial gage indicator was observed as the temperature of the glycerin or the acetone-dry ice mixture was slowly increased. For Alloy 5B, the shape of the bent portion of the rod was observed while the temperature of the acetone-dry ice mixture was increased.

- (9) The temperature at which the dial gage indicator moved, or in the case of Alloy 5B the temperature at which the shape of the bent end began to change, was noted; this indicated the start of the transition.
- (10) The temperature at which the dial gage indicator stopped moving, or for Alloy 5B the temperature at which the last change in shape occurred, was observed; this signalled the completion of the transition.

The results of the recovery tests are summarized in Table 4. It should be emphasized that the transition temperature range was determined for material 75 to 85 mils thick. According to W. J. Buehler of the U.S. Naval Ordnance Laboratory, this temperature may be expected to decrease somewhat as the material is reduced to smaller sizes, but will stabilize at some intermediate gauge.

The transition temperature ranges as listed in Table 4 are quite broad and should not be taken as an indication of the optimum ranges for these alloys. This is particularly true inasmuch as the samples were hot-formed rather than cold-formed immediately prior to the memory anneal. In order to determine the optimum recovery response and range for each alloy, it would be necessary to study the effect of (1) the degree of plastic deformation prior to the memory heat treatment and the state of stress and temperature during that deformation, (2) the temperature and time of the memory heat treatment and the applied stress during that treatment, and (3) the degree of deformation given the sample after the memory heat treatment and the state of stress and temperature during that deformation.

It is well worth noting that other work⁽⁴⁾ has shown that more than 80 percent of the plastic shape recovery can occur over a very narrow temperature range (10 degrees F), even though the range from start to completion may be large (50 degrees F). Figure 3, for example, shows that the shape recovery temperature range depends on the amount of initial deformation, and also illustrates that under conditions (4 and 8 percent prior strain for the alloy shown) the range can be very narrow.

TABLE 4. TRANSITION TEMPERATURE RANGES OF EXPERIMENTAL NITINOL ALLOYS

Alloy Number	Titanium Content, weight, percent		Transition Temperature Range, F ^(a)	
	Intended	Analyzed	Start	Finish
2A	45.50	46.2	88	276
2B	45.50	45.5	98	210
3	45.00	43.6, 43.9	-85	76
3A	45.00	45.5	102	135
3B	45.00	45.1	85	165
5	44.75	45.1	90	106
5B	44.75	45.5	25	55
6	44.50	42.3	-7	64
7	45.75	47.4	154	214
8	46.50	46.7	163	278
8A	46.50	46.2	214	260
9	47.00	46.7	162	248
10	44.90	44.8	120	174

(a)

The transition temperature ranges shown in this table are quite broad; they should not be considered to be the narrowest ranges obtainable with these alloys. In order to narrow the ranges, it would be necessary first to study the effect of various factors (noted in the second paragraph on page 18) on the transition temperature range.

FIGURE 3. RECOVERY OF BENT WIRE AS A FUNCTION OF TEMPERATURE (BUEHLER AND CROSS(3))

The recovery data on Alloys 2A through 10 indicate that Nitinol alloys having transition temperatures ranging from approximately 55 to 280 F can be produced by following the detailed procedures given in this report. Furthermore, the data indicate that the transition temperature of several pairs of the alloys, e.g., 3B and 5, 2B and 5B, and 8 and 9 were quite different even though the analyzed compositions of each pair were identical. As will be shown, the agreement was better when intended compositions were considered.

Curves relating the transition temperature to composition were constructed from the data in Table 4 and are presented in Figures 4 and 5. These curves illustrate that the transition temperature is very sensitive to titanium content. Because of this sensitivity, the limitations in the accuracy of the chemical analysis techniques certainly overshadow the effects being studied. Furthermore, even if the analyses give a true indication of the actual titanium content, the total titanium content may not be a meaningful measure of transition temperature if part of the titanium is tied up in a phase that does not contribute or enter into the "shape memory" behavior of the alloy. Since there are two or more phases in the Nitinol alloys as discussed in the following section, the possibility of matrix composition (rather than overall composition) being the controlling factor should be investigated in future work.

Thus, with the above in mind the curve in Figure 4 (intended composition vs. transition temperature) shows a better correlation between composition and transition temperature, than the curve in Figure 5 which is based on the analyzed composition.

A study of the data in Table 4 will show that we prepared experimental Nitinol alloys having transition temperatures reasonably close to the desired temperatures of 100, 200, and 300 F. These alloys are Nos. 5, 2B, and 8A which exhibit complete recovery at 106, 210, and 260 F, respectively.

FIGURE 4. RELATIONSHIP BETWEEN INTENDED COMPOSITION AND TRANSITION TEMPERATURE OF EXPERIMENTAL NITINOL ALLOYS

FIGURE 5. RELATIONSHIP BETWEEN THE INTENDED AND ANALYZED COMPOSITIONS AND THE TRANSITION TEMPERATURE OF EXPERIMENTAL NITINOL ALLOYS

Microstructure

Metallographic studies were conducted on a sample taken from the top of a rod of each rod casting with the exception of Alloy 3. In the case of Alloy 3, a sample was taken near the bottom of the large ingot.

The microstructures of Alloys 2B, 5, 5B, and 8A in the as-cast condition are illustrated in Figure 6 and are typical of the metallurgical structures observed in the other alloys. In general, the alloys contained one or more of the following types of metallurgical structures in addition to the TiNi matrix:

- Type 1: Clusters of large globular, pinkish particles (Figures 6c, 6d)
- Type 2: Small randomly dispersed globular, pinkish particles (Figures 6a, b, c, d)
- Type 3: Large angular, whitish particles (Figure 6c)
- Type 4: A fine eutectic structure (Figure 6b)
- Type 5: A coarse, whitish eutectic structure (Figure 6d).

The clusters of the large globular phase have the usual pink color of titanium carbonitrides, but not the angular shape that is usually observed when this phase is present in nickel- and iron-base alloys. However, the extremely high hardness (2932 Knoop hardness with a 50-gram load) of this phase suggests that it is titanium carbonitride even though it does not have the usual morphology.

The small pinkish particles have not been identified, but may be Ni_3Ti or titanium carbonitride.

The large angular phase has the same appearance as one which the U.S. Naval Ordnance Laboratory⁽⁵⁾ has observed in Nitinol alloys melted in the presence of oxygen. NOL found that the phase had roughly the nickel:titanium ratio of $\text{Ti}_4\text{Ni}_2\text{O}$ and tentatively identified the phase as that compound. However, based on Rostoker's⁽⁶⁾ study of the Ti-Ni-O phase diagram, it appears that the phase NOL observed and that is present in several of our alloys (illustrated in Figure 6c) may be oxygen-stabilized Ti_2Ni that may not contain enough oxygen to conform to stoichiometric $\text{Ti}_4\text{Ni}_2\text{O}$. The Knoop hardness of this phase in Alloy 3 was 1098 with a 25-gram load.

500X

$95\text{H}_2\text{O}-3.5\text{HNO}_3-1.5\text{HF}$
2 3
a. Alloy 2B: Ni-45.5 w/o Ti

3D802

(TYPE 2)

500X

$82\text{H}_2\text{O}-14\text{HNO}_3-4\text{HF}$
2 3
b. Alloy 5: Ni-45.1 w/o Ti

6D074

(TYPE 4)

(TYPE 2)

FIGURE 6. MICROSTRUCTURES OF AS-CAST NITINOL ALLOYS

FIGURE 6. (CONT'D.)

The fine eutectic structure in the matrix has been tentatively identified by Buehler⁽⁷⁾ as alternate layers of Ti_4Ni_2O and $TiNi$.

The coarse eutectic which appears in most of the alloys that contain more than 46 percent titanium has not been positively identified. However, based on the nickel-titanium phase diagram, it is likely that it consists of Ti_2Ni and $TiNi$.

DISCUSSION AND CONCLUSIONS

The main objective of this program was achieved; that is, suitable melting and casting techniques were developed which yielded two large, high-quality Nitinol ingots (Alloys 2B and 8A) having transition temperatures of 210 and 260 F, and a rod casting with a transition temperature of 106 F. If desired at a later date, there is no reason why a large ingot of this latter alloy could not be made.

As a result of melting and casting a number of alloys, we developed a curve relating the transition temperature to the chemical composition of the Nitinol alloys. This curve indicates that the transition temperature is ultra-sensitive to titanium content. In fact, the transition temperature appears to be so sensitive to titanium content that the present limitations of the chemical analysis makes it difficult, if not impossible, to assess the true effect of titanium content on the transition temperature. The problem is further complicated by the likelihood that all of the titanium is not involved in the "shape memory" performance of the alloys since there are two or more phases in each alloy.

It appears from the curves (Figure 5) showing transition temperature as a function of the intended composition and the analyzed composition that by choosing a composition based on the "intended composition" curve, a desired transition temperature could readily be obtained within about 35 degrees F. This assumes that the procedures developed are followed carefully, since the curve represents the data from "good" heats, i.e., it omits data from Heat 3 wherein excess oxygen was present.

An important point to bear in mind is that the transition temperatures of all alloys were determined on a hot-flattened 1/4-inch rod that had been "memory heat treated" at one temperature. It is not at all likely that this

is either the optimum forming condition or the optimum memory heat treatment temperature for all the alloys and, furthermore, according to W. J. Buehler, the entire temperature range will probably shift after the material is made into wire or strip. Thus, the curve presented in Figure 4 (and also Figure 5) must be taken as conditional.

Obviously, much remains to be learned about the Nitinol alloys, in particular the influence of chemical composition on physical and mechanical properties, transition temperature, and transition temperature range. Nevertheless, a sufficient number of high quality ingots has been cast to indicate the feasibility of preparing Nitinol in semi-production quantities. Such ingots can be fabricated into wire and strip using modifications of procedures utilized in the commercial mechanical working of nickel-base alloys.

RECORDS

Data upon which this report is based may be found in Battelle Laboratory Record Book Nos. 25667 and 26325, Pages 1 through 100 and 1 through 39, respectively.

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