United States Patent [19]

Goldstein et al.

[11] **4,283,233**

[45] **Aug. 11, 1981**

[54] **METHOD OF MODIFYING THE TRANSITION TEMPERATURE RANGE OF TINI BASE SHAPE MEMORY ALLOYS**

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[73] Assignee: **The United States of America as represented by the Secretary of the Navy**, Washington, D.C.

[21] Appl. No.: **128,326**

[22] Filed: **Mar. 7, 1980**

[51] **Int. Cl.**[3] **C22F 1/10**

[52] **U.S. Cl.** .... **148/11.5 R**; 148/11.5 F; 148/11.5 N

[58] **Field of Search** .... 148/11.5 N, 11.5 F, 148/11.5 R

[56] **References Cited**

U.S. PATENT DOCUMENTS

3,174,851	3/1965	Buehler et al.	75/170
3,753,700	8/1973	Harrison et al.	75/170
4,144,057	3/1979	Melton et al.	75/170

OTHER PUBLICATIONS

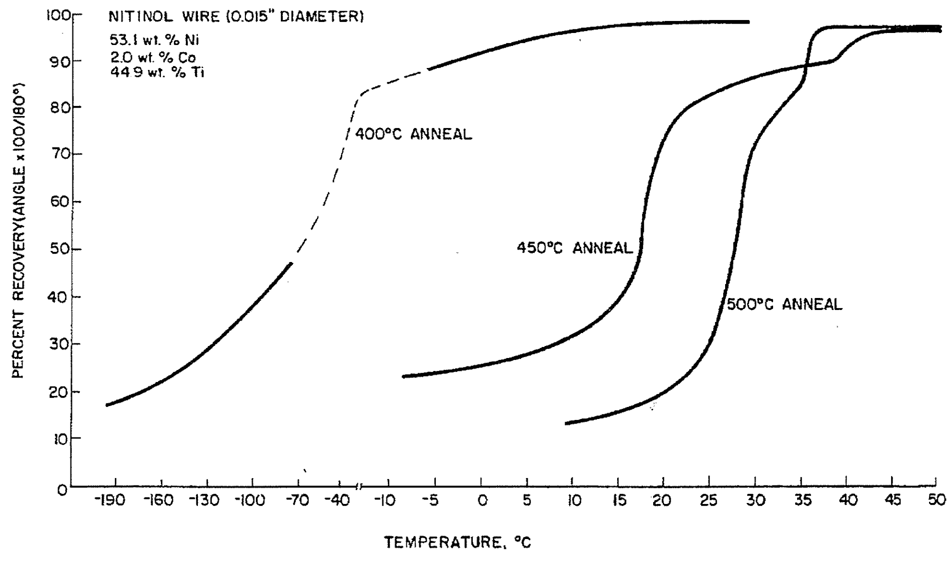
Buehler et al., 55–Nitinol, Unique Wire Alloy with a Memory, Wire Journal, Jun. 1969.

Primary Examiner—R. Dean
Attorney, Agent, or Firm—R. S. Sciascia; A. L. Branning; R. D. Johnson

[57] **ABSTRACT**

A method of changing the shape change transition temperature range (TTR) of an object made from a nickel-titanium based shape change memory alloy by selection of the final annealing temperature.

4 Claims, 3 Drawing Figures



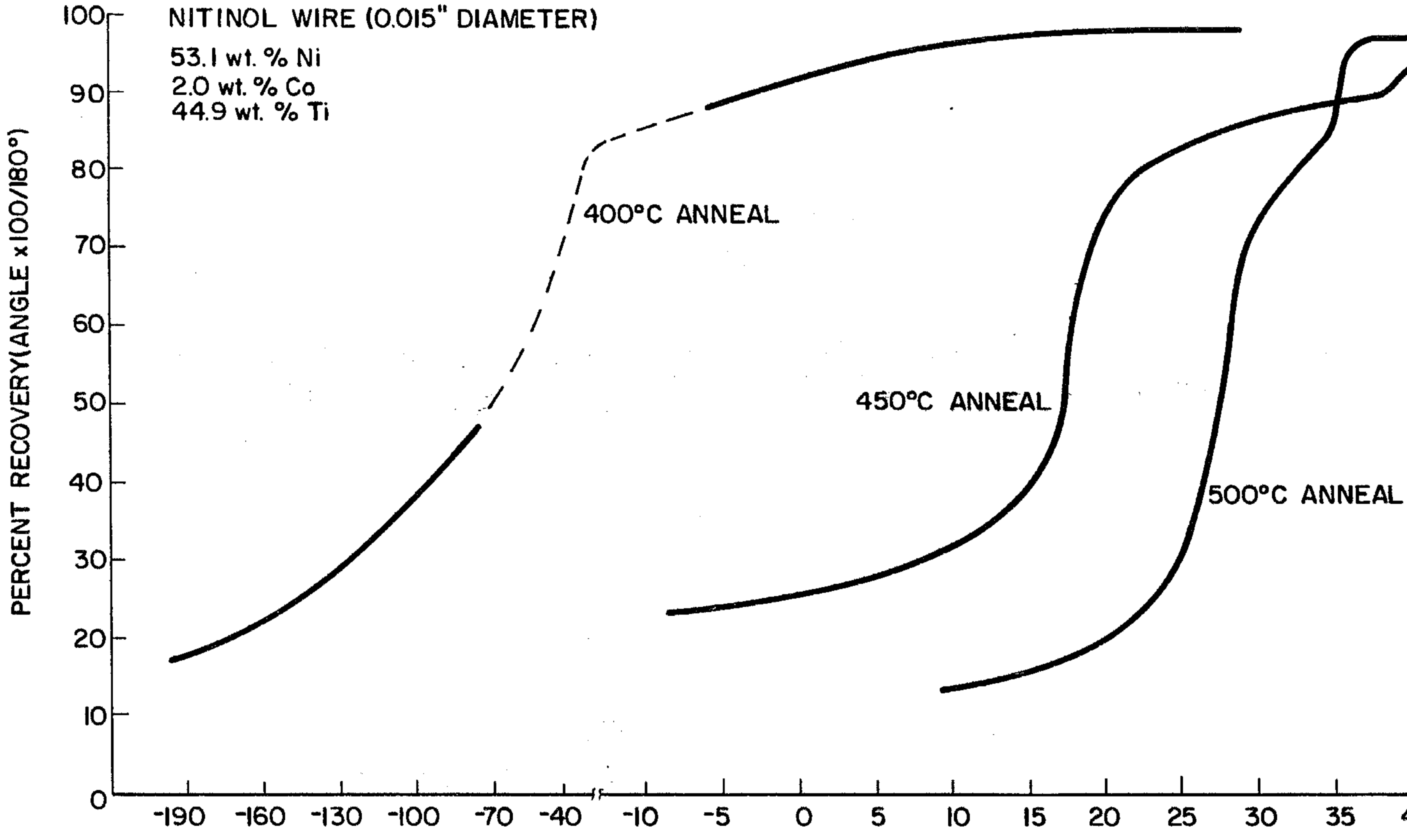

NITINOL WIRE (0.015" DIAMETER)
53.1 wt. % Ni
2.0 wt. % Co
44.9 wt. % Ti
400°C ANNEAL
450°C ANNEAL
500°C ANNEAL
PERCENT RECOVERY(ANGLE x 100/180°)
TEMPERATURE, °C

FIG. 1

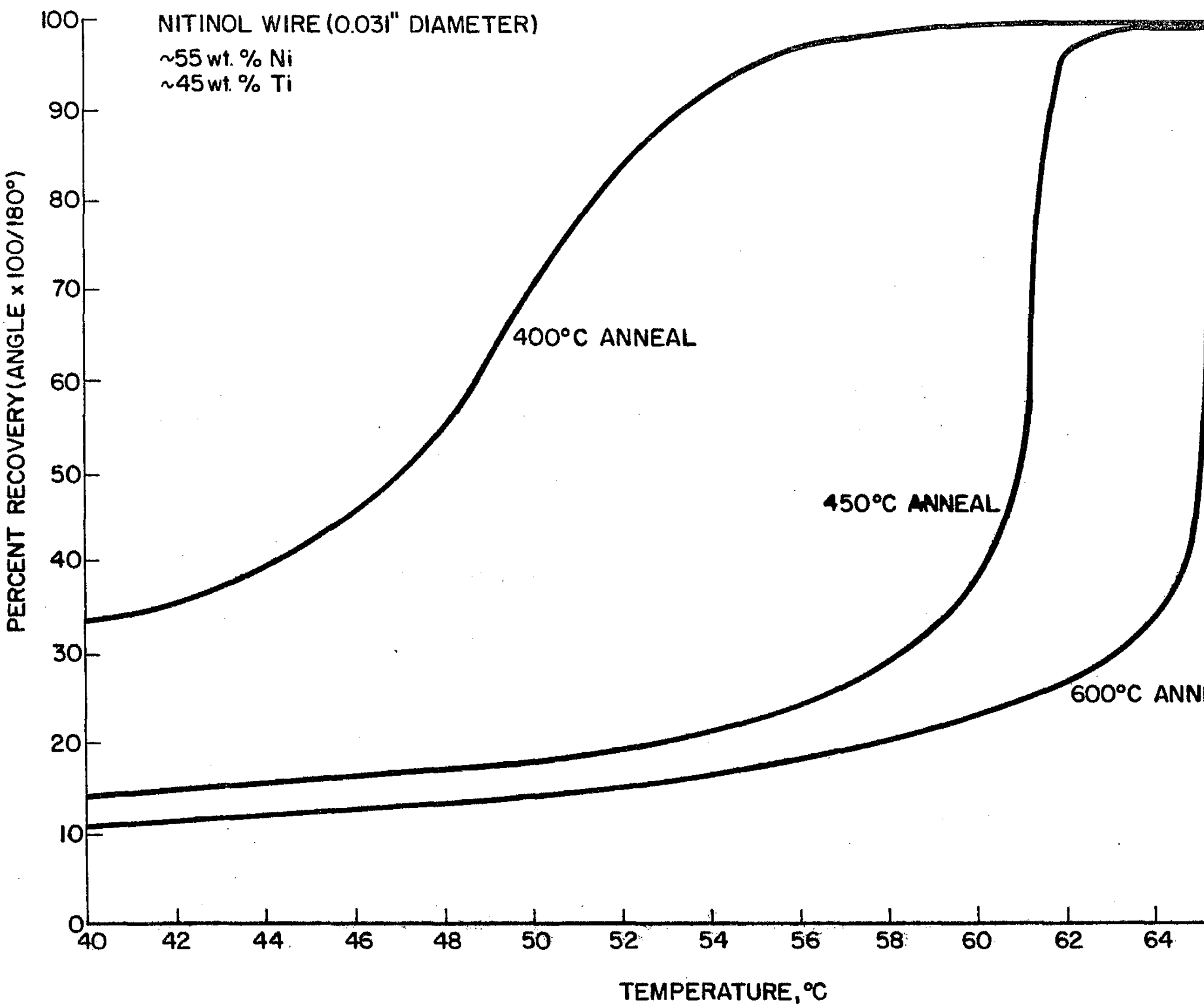
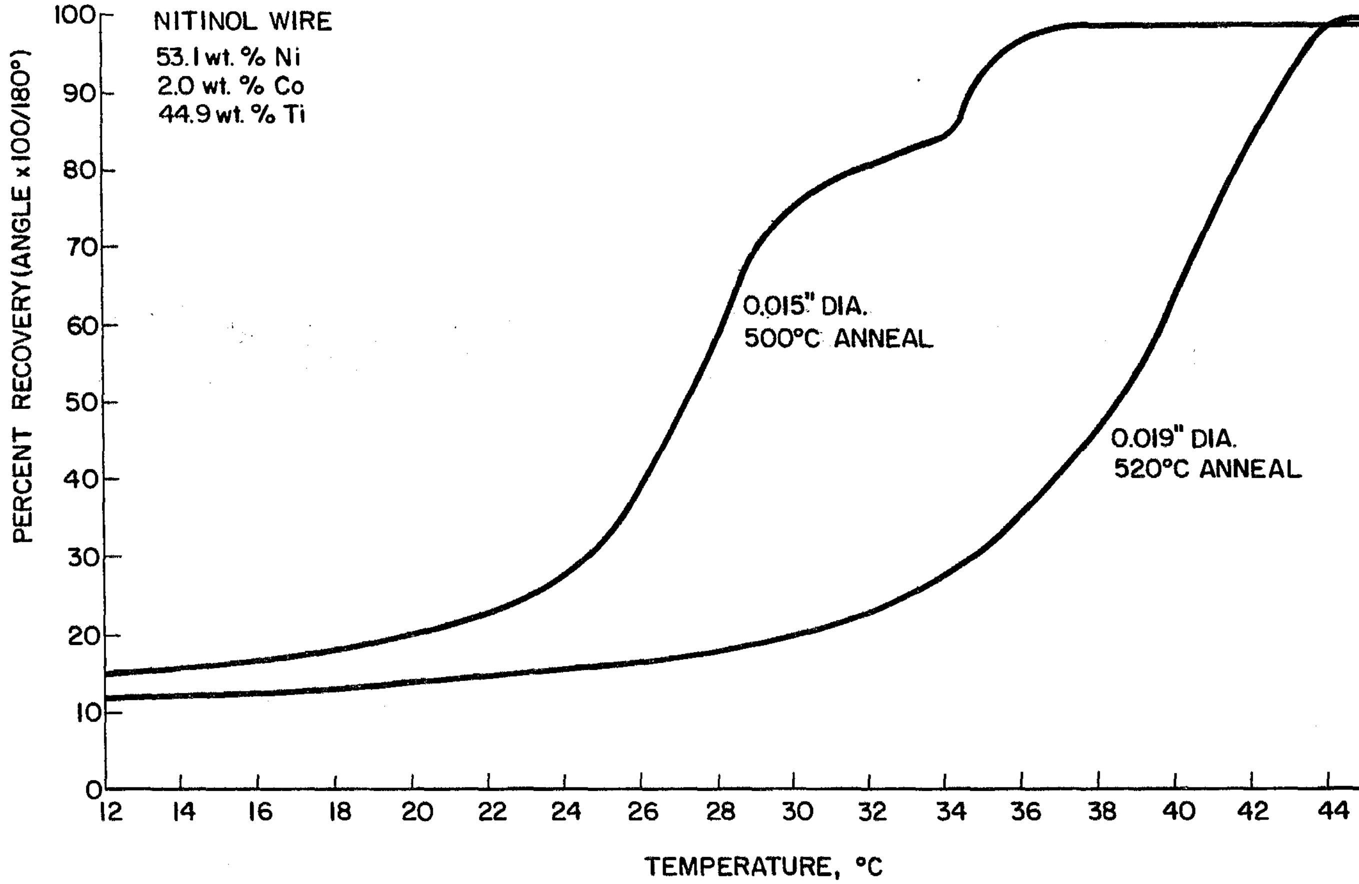

NITINOL WIRE (0.031" DIAMETER)
~55 wt. % Ni
~45 wt. % Ti
PERCENT RECOVERY (ANGLE x 100/180°)
TEMPERATURE, °C
400°C ANNEAL
450°C ANNEAL
0
10
20
30
40
50
60
70
80
90
100
40
42
44
46
48
50
52
54
56
58
60
62
64

FIG. 2



NITINOL WIRE
53.1 wt. % Ni
2.0 wt. % Co
44.9 wt. % Ti
PERCENT RECOVERY (ANGLE x 100/180°)
100
90
80
70
60
50
40
30
20
10
0
0.015" DIA.
500°C ANNEAL
0.019" DIA.
520°C ANNEAL
12
14
16
18
20
22
24
26
28
30
32
34
36
38
40
42
44
TEMPERATURE, °C

FIG. 3

METHOD OF MODIFYING THE TRANSITION TEMPERATURE RANGE OF TINI BASE SHAPE MEMORY ALLOYS

BACKGROUND OF THE INVENTION

This invention relates to metal alloys and more particularly to nickel-titanium base metal alloys which have shape change

The Nitinol alloys are nickel-titanium-base metal alloys having shape change memories. The general method for using the memory properties of these alloys is to:

(1) shape the alloy into a permanent form at a temperature below the temperature transition range (TTR);

(2) constrain the alloy in this shape;

(3) anneal the alloy at 500° C.;

(4) cool the alloy to a temperature below the TTR;

(5) remove the constraint; and

(6) shape the alloy into an another form.

The alloy can then be converted from its other shape to its permanent shape by heating it to a temperature above the TTR. An excellent discussion about the theories and properties of Nitinol is given by William J. Buehler and William B. Cross, "55-Nitinol: Unique Wire Alloy with a Memory," *Wire Journal,* June 1969. Methods of preparing Nitinol are disclosed in U.S. Pat. No. 3,174,851, entitled "Nickel-Base Alloys," which issued to Buehler and Wiley on Mar. 23, 1965. The shape change memory properties of nickel-titanium alloys containing from 53.5 to 56.5 weight percent nickel, the remainder being titanium, are disclosed in U.S. Pat. No. 3,403,238 entitled "Conversion of Heat Energy to Mechanical Energy," which issued to William J. Buehler and David M. Goldstein on Sept. 24, 1968.

In the prior art, the usual method of changing the TTR was to change the ratio of nickel to titanium or to substitute cobalt or iron for nickel. A limitation of this previous method of alloying, has been the requirement to prepare by melting a different composition of alloy for each different transition temperature desired. This limitation presents significant economic disadvantages to the manufacturer of these alloys. In addition to an infinite number of TTR possibilities, it is difficult to precision alloy to control to a pre-selected composition. For example, a shift in total cobalt on the order of 0.2% of the total composition can change the midpoint (50% recovery) of the TTR by 8° C., an unacceptable amount in many applications. Even worse from the standpoint of reproducibility, a shift of 0.2 weight percent nickel can shift the midpoint of the TTR by 25° C.

Hence the alloy manufacturer may find it necessary to remanufacture the alloy or to prepare several melts of slightly different compositions to achieve his intended final composition. Normal melting losses make it exceedingly difficult to anticipate the final composition with adequate precision. The alloy manufacturer can encounter high scrap losses.

U.S. Pat. No. 4,144,057, entitled "Shape Memory Alloys," issued on Mar. 13, 1979, to Keith Melton and Olivier Mercier, discloses Nickel—the use of from 0.5 to 30 weight percent of copper and from 0.01 to 5 weight percent of at least one element selected from the group consisting of aluminum zirconium, cobalt, chrome, and iron in nickel-titanium alloys. They report that the transition temperatures in these alloys are less sensitive to compositional changes. The use of copper, however, is not desirable in some cases. Therefore, it is desirable to have another method of adjusting the TTR. Moreover, even when copper is used, it is desirable to have means of further fine tuning the TTR.

SUMMARY OF THE INVENTION

Accordingly, one object of this invention is to provide a new method of changing the temperature transition range (TTR) of a nickel-titanium alloy having a shape change memory (Nitinol).

Another object of this invention is to provide a method of changing the TTR of a nickel-titanium alloy (Nitinol) having a shape change memory without changing the composition of the alloy.

Still another object of this invention is to provide an easier method of obtaining a nickel-titanium shape change memory alloy (Nitinol) having a given TTR.

Yet another object of this invention is to reduce the amount of waste occurring in the production of a nickel-titanium shape change memory alloy having a specific TTR.

A further object of this invention is to provide a method of providing a nickel-titanium shape change memory alloy (Nitinol) having a more accurate TTR.

These and other objects of this invention are accomplished by providing:

in the process of forming an article with a shape change memory from a nickel-titanium based shape memory alloy by annealing the object at a temperature above the transition temperature range (TTR) while the object is restrained in its permanent shape and then reshaping the object into its intermediate shape at a temperature below the transition temperature range, the improvement comprising:

selecting the annealing temperature to obtain a desired transition temperature range.

BRIEF DESCRIPTION OF THE DRAWINGS

A more complete appreciation of the invention and many of the attendant advantages thereof will be readily appreciated as the same becomes better understood by reference to the following detailed description when considered in connection with the accompanying drawing wherein:

FIG. **1** contains three plots of percent shape recovery versus temperature for 3 Nitinol wires having the same composition of nickel, titanium, and cobalt but which have been anealed at 400° C., 450° C., and 500° C., respectively;

FIG. **2** contains 3 plots of percent shape change versus temperature for 3 Nitinol wires having the same composition of nickel and titanium but which are annealed at 400° C., 450° C., and 500° C., respectively; and

FIG. **3** contains 2 plots of percent shape change versus temperature for 2 Nitinol wires having the same composition as the wires in FIG. **1**, one of the wires was annealed at 500° C. and the other at 520° C.

DETAILED DESCRIPTION OF THE PREFERRED EMBODIMENT

The present invention provides a method by which the shape change temperature range (TTR) of Nitinol (nickel-titanium based) alloys can be varied by selecting the final annealing conditions. Broadly, the method may be applied to all nickel-titanium based alloys which possess shape change memory properties. U.S. Pat. No. 4,144,057 discloses shape memory alloys which may be

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