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ABSTRACT OF THE DISCLOSURE

Metal alloys of the formulas $TiNi_xCo_{1-x}$, $TiCo_xFe_{1-x}$,
wherein x is an integer from 0 to 1 undergo martensitic
transitions over a very wide temperature range from less
than 4° K. to 1000° K. The metal alloys are worked and
heat treated to effect a reversion back to an original con-
figuration as the result of the martensitic transition of the
alloys due to the heat treatment.

CROSS REFERENCES TO RELATED APPLICATIONS

This application is a continuation-in-part of application
Ser. No. 579,185, filed Sept. 9, 1966, now abandoned.

BACKGROUND OF THE INVENTION

This invention relates generally to structural alloys and
more particularly to alloys of an intermetallic compound
type characterized by a capability of effecting a marten-
sitic (diffusionless) transition at a predetermined tem-
perature.

A considerable amount of effort has been expended
heretofore in an attempt to develop a series of alloys
having the same unique properties as the near stoichio-
metric TiNi (disclosed in U.S. Pat. No. 3,174,851) where
TiNi denotes an alloy containing near equiatomic quanti-
ties of titanium and nickel, sometimes referred to as
Nitinol, and especially to develop alloys which exhibit a
unique martensitic (diffusionless) transition at any se-
lected temperature throughout a desired temperature range
without effecting any of the desirable attendant features
of the stoichiometer TiNi. Attempts to provide such a
series of alloys have heretofore met with little success,
probably because of a lack of a clear understanding of
the atomic structural transition associated with the un-
usual mechanical and physical properties found ni TiNi.

The TiNi-base alloys, particularly those near stoichio-
metric TiNi composition, are capable of performing
unique and heretofore unknown property feats. These
unusual propeties of mechanical memory, acoustic damp-
ing, energy conversion, etc., have opened an entirely new
area of potential applications. Currently such applica-
tions as self-erecting aerospace and hydrospace compo-
nents, low acoustic noise machine mountings and devices,
prestressed bindings and reinforcements, stored energy
tools, energy converters, temperature actuated devices
(switches, fire alarms, etc.), clock mechanisms, cryo-
genic components, are but a very few of the possible uses.

Near TiNi alloys, while efficient in the performance of
the above tasks, are limited by a somewhat narrow crit-
ical temperature range. Therefore if one wanted to use
materials in such a way as to fully utilize the martensitic
transition properties of alloys one was severely limited by
the temperature range of this transition. Thus, if one
wished to erect a structure on the ocean floor, where
the water temperature is around 271° K., one could not
use a TiNi alloy unless one were willing to continually
heat the alloy to maintain its transition temperature of

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around 439° K. so that the structure would maintain
its stiffness.

SUMMARY OF THE INVENTION

Accordingly, one object of this invention is to provide
a series of intermetallic alloys especially exhibiting the
unique properties of a mechanical memory, acoustic
damping, direct conversion of heat to mechanical energy,
and useful mechanical properties, e.g., strength, tough-
ness, etc.

Another object is to provide a series of alloys having
similar properties yet each alloy exhibiting an individual
martensitic transformation property at a diverse prede-
termined point in a desired temperature range.

A further object is to provide alloys which exhibit a
martensitic transition characteristic over an extended tem-
perature range.

Another object is to provide alloys which make use of
relatively inexpensive elements and which are readily
available for engineering structures.

These and other objects are attained by the formula-
tion of alloys that can undergo unique atomic structural
changes at any predetermined temperature from virtually
zero degrees Kelvin (−273° C.) to approximately 1000°
Kelvin (727° C.) said alloys represented by the follow-
ing structural formulas:

$$TiNi_xCo_{1-x} \quad TiCo_xFe_{1-x} \quad ZrRh_xRu_{1-x}$$

and

$$ZrPd_xRh_{1-x}$$

Especially preferred are the Ti systems and most preferred
is the $TiNi_xCo_{1-x}$ system.

DESCRIPTION OF THE DRAWING

FIG. 1 is a graphical representation of the unique
martensitic transition temperature range (° C.) of TiNi
as a function of the atomic (and weight) percent of Ni;

FIG. 2 is a graphical representation of the logarithm
of the unique martensitic temperature (° K.) as a junc-
tion of the "free" electron concentration of the ternary
alloys $TiNi_xCo_{1-x}$ and $TiCo_xFe_{1-x}$; and

FIG. 3 is a graphical representation of the unique mar-
tensitic transition temperature (° K.) as a function of
the "free" electron concentration of $TiNi_xCo_{1-x}$ and
$TiCo_xFe_{1-x}$.

DESCRIPTION OF THE PREFERRED EMBODIMENTS

The unique martensitic transition which the alloys of
the instant invention undergo is effected merely by caus-
ing the alloys to be deformed at a temperature below their
critical temperature (which is hereinafter defined) and
thereafter heating these alloys to or above their critical
temperature. Thus, these alloys will, when heated to their
critical temperature, revert back to a predetermined or
original configuration. This original configuration will
be the configuration of the alloy as it is cooled down below
its critical temperature. For example one can cast a
straight rod of the alloy, cool it down below the critical
temperature, deform it and then heat it to the critical
temperature whereupon the rod will revert back to its
original configuration (i.e., a straight rod). Similarly a
wire can be made so that it is curled, the temperature can
be lowered below the critical temperature, the wire can
be straightened out and then heated to the critical tem-
perature whereupon the original curled configuration is
returned to the wire.

The term "critical temperature" as hereinbefore and
hereinafter used, refers to the temperature at which the
alloy under consideration exhibits a martensitic (diffu-
sionless) transition. Near stoichiometric TiNi and the

related alloys of this invention exhibit unusual overt properties as a function of deformation and temperature. The near TiNi alloys are capable of transforming heat energy directly and efficiently into mechanical energy. The near TiNi composition composition alloys have a latent heat near 6 calories per gram at the "critical temperature." Also acoustic damping, and both elastic and mechanical properties (particularly yield strength) change drastically in the temperature range covered by the critical temperature. The critical temperature associated with the atomic structure transition varies drastically with minor variations in composition. The alloys recorded show the temperature maximum of 439° K. (166° C.) for stoichiometric TiNi and falling to well below 273° K. (0° C.) for slightly Ni-rich variations on the TiNi composition as shown in the graph of FIG. 1, wherein the martensitic transition temperature range of TiNi is shown plotted as a function of the atomic percent composition of Ni (remainder essential Ti) and also plotted with the corresponding weight per cent composition thereof on the same axis.

While this temperature range of martensitic transition is impressive and useful based upon normal ambient temperature conditions, even exceedingly minor amounts of excess Ni in these binary alloys tend to cause the formation of a second phase of $TiNi_3$. A very minor quantity of the second phase $TiNi_3$, like the normal nonmetallic impurities Ti_4Ni_2O, Ti_4Ni_2NTiC, etc., can be tolerated, but these insoluble impurities tend to reduce the efficiency of TiNi to perform in a manner as stated above.

A desire to provide alloys with the unique overt properties of near stoichiometric TiNi alloys at any desired temperature from essentially absolute zero (0° K.) up to and in excess of 439° K. (166° C.) is accomplished without damaging the efficiency of the overt properties required by the careful and thoughtful alloying with other elements as shown in Table I.

FIG. 2. These graphical data, on the alloys formed from the elements of the first long period when combined in the proper ratio, immediately indicate that progressively lower critical temperatures are possible by increased substitution of Co for Ni ($TiNi_xCo_{1-x}$) on an atom for atom basis. This substitution does not in any way alter the Ti content of the ternary alloys of this series.

All ternary phases, $TiNi_xCo_{1-x}$ and $TiCo_xFe_{1-x}$ formed by replacing Ni with Co, and Co with Fe, have crystal structures similar to the basic binary TiNi compound. The crystal structure of TiNi has been determined through single crystal and powder X-ray defraction studies and the existence of a martensitic transition (without a first order crystallographic transformation) has been confirmed. Assuming the number of "free" electrons contributed by Ti, Fe, Co and Ni in their alloys to be 4, 8, 9 and 10 (number of electrons beyond the closed shell) respectively, the transition temperature, plotted as a function of the "free" electron concentration (number of "free" electrons per atom) in these alloys, is a smooth curve as shown in FIG. 3. This curve indicates that the martensitic type transition observed in TiNi is not unique to this compound alone, but is prevalent also in those binary compounds of TiCo and TiFe and in the ternary combinations of these elements as stated above.

In the case of the ternary alloys formed from Ti with selective variations of Ni, Co and Fe it is possible to attain any desired critical temperature from virtually zero degrees Kelvin to 439° Kelvin. Selected ternary combinations of Ti, Ni, Co have been compounded, in the ratio of $TiNi_xCo_{1-x}$, and processed into test specimens. These ternary systems have exhibited all the same unique overt properties as TiNi (critical temperature 439° Kelvin) but at a lower temperature dependent upon the amount of Co substituted for Ni.

Further observing Table I, it becomes apparent that the intermetallic compounds ZrRu, ZrRh and ZrPd should

TABLE I.—DATA ON ELEMENTS AND INTERMETALLIC COMPOUND PRODUCTS FORMED FROM THESE ELEMENTS

	Atomic radius, A.	Atomic radius ratio [1]	Valence electrons	Compound formed	Crystal structure	Electron concentration, e./a.	"critical transition temperature" K.
		1st Long Period (Periodic Table)					
Element:							
Ti	1.45+		4				
Fe	1.24	1.17	8	TiFe	Complex [3]	6.0	<4
Co	1.25+	1.16	9	TiCo	Complex [1]	6.5	35
Ni	1.25−	1.16	40	TiNi	Complex [2]	7.0	439
		2nd Long Period (Periodic Table)					
Zr	1.59		4				
Ru	1.32	1.20	6	ZrRu	Complex [4]	6.0	40
Rh	1.35	1.18	9	ZrRh	do.[4]	6.5	653
Pd	1.37	1.16	10	ZrPd	do.[4]	7.0	1,000
		3rd Long Period (Periodic Table)					
Hf	1.56		4				
Os	1.33	1.17	8	HfOs	Complex [4]	6.0	[5]
Ir	1.35	1.16	9	HfIr	do.[4]	6.5	[5]
Pt	1.39	1.12	10	HfPt	do.[4]	7.0	[5]

[1] Ratio obtained in each period by dividing $\frac{Ti(Radius)}{Fe\ or\ Co\ or\ Ni(Radius)}$, $\frac{Zr(Radius)}{Ru\ or\ Rh\ or\ Pd(Radius)}$, etc.

[2] a_s=9A.; a_{sub}=2.98 A.
[3] a_s=9A.; a_{sub}=2.99 A.
[4] a_s=9.6 A.; a_{sub}=3.2 A.
[5] To be determined.

Observing the data given in Table I, certain basic structural similarities are evident. These similarities exist mainly in the atomic radius ratios and valance electrons of the corresponding metallic elements and the crystal structures and electron concentrations of their intermetallic compound products. In this table consideration has been given to the first, second and third long periods of the Atomic Periodic Table. Plotting the natural logarithm of the transition temperatures (critical temperatures) for the first long period compounds, TiNi, TiCo and TiFe as well as intermediate ternary alloy compositions, e.g., $TiNi_xCo_{1-x}$ and $TiCo_xFe_{1-x}$, as a function of "free" electron concentration, a smooth linear curve is obtained as shown in

behave in a similar manner. Also the compounds of HfOs, HfIr and HfPt of the third long period are candidates for the same atomic structural behavior. Experimental evidence has confirmed these latter two series compounds also to have critical temperatures and exhibit the same unique behavior as was found in the TiFe-FiCo-TiNi series. Further, ternary substitution, e.g., $ZrPd_xRh_{1-x}$ and $HfPt_xIr_{1-x}$, etc., should be permissible to yield intermediate critical temperatures. As the table indicates, the compounds of Zr, Hf and their intermediate ternary alloys provide higher critical temperatures for the atomic structural transition to occur. As a result, from a practical standpoint, the critical temperature has been extended

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from absolute zero (zero degrees K.) to approximately 1000° K. (717° C.).

Both the yield strength and the elastic modulus (Young's modulus) increase significantly above the critical temperature. To take advantage of the increased "stiffness" above the critical temperature it is necessary to tailor alloys that have critical temperatures below the operating environment range for a particular application. This would be particularly significant in self-erectable structures for both hydrospace and aerospace applications. In order that structures may self-erect, anywhere, such for example as in sea-water, it is necessary to provide self-erecting alloys with critical temperatures well below the minimum sea water temperature of minus 2° C. (271° K.). To accomplish this and to provide efficient mechanical memory, etc., cobalt substituted alloys ($TiNi_xCo_{1-x}$) could be invaluble.

Obviously, numerous modifications and variations of the present invention are possible in the light of the above teachings. It is therefore to be understood that within the scope of the appended claims the invention may be practiced otherwise than as specifically described herein.

What is claimed as new and desired to be secured by Letters Patent of the United States is:

1. A method of effecting a reversion back to an original configuration by means of a martensitic transition of a metal alloy at a predetermined critical temperature from about 35° K. to about 439° K., said alloy having the formula

$$TiNi_xCo_{1-x}$$

wherein

Ti denotes titanium and constitutes approximately 50 atomic percent of the composition, and the term Ni_xCo_{1-x} denotes nickel and cobalt respectively and make up the remaining approximately 50 atomic percent of the composition, and

x is a factor which varies from greater than 0 to less than 1 whereby the relative percentage of nickel and cobalt varies inversely from less than 100 percent to more than 0 percent with respect to each other on an atom for atom exchange basis as the martensitic transformation temperature varies correspondingly from about 439° K. to about 35° K. in a nonlinear manner which comprises the steps of:

(1) subjecting said alloy while in said original configuration to deformation at a temperature below

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the critical temperature to change the shape thereof and

(2) thereafter heating said alloy to or above said critical temperature to effect said reversion back to said original configuration.

2. A method of effecting a reversion back to an original configuration by means of a martensitic transition of a metal alloy at a predetermined critical temperature from about 4° K. to about 35° K., said alloy having the formula

$$TiCo_xFe_{1-x}$$

wherein

Ti denotes titanium and constitutes approximately 50 atomic percent of the composition, and the Co_xFe_{1-x} term denotes cobalt and iron respectively and make up the remaining approximately 50 atomic percent of the composition, and

x is a factor which varies from 1 to 0 whereby the relative percentage of cobalt and iron varies inversely from 100 to 0 percent with respect to each other on an atom for atom exchange basis as the martensitic transformation temperature varies correspondingly from about 35° K. to about 4° K. in a nonlinear manner which comprises the steps of:

(1) subjecting said alloy while in said original configuration to deformation at a temperature below the critical temperature to change the shape thereof and

(2) thereafter heating said alloy to or above said critical temperature to effect said reversion back to said original configuration.

References Cited

UNITED STATES PATENTS

| 1,337,276 | 4/1920 | Scheuch | 75—170 |
| 3,174,851 | 3/1965 | Buchler et al. | 75—170 |

OTHER REFERENCES

Journal of Metals, September 1950, pp. 1173–1176.
Physical Review, vol. 126, No. 5, June 1, 1962, pp. 1746–1748.

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