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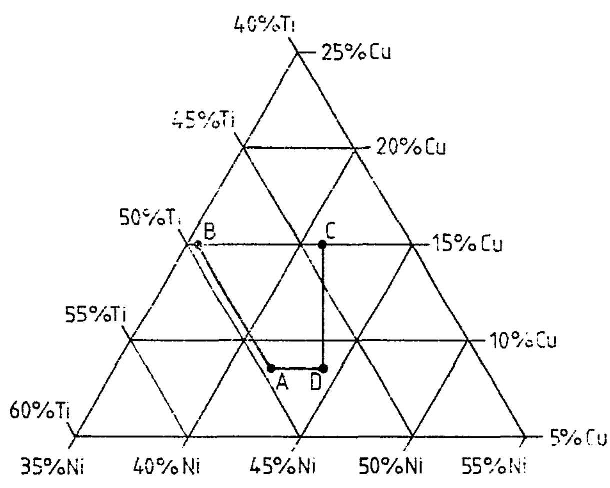
(54) **Nickel/titanium/copper shape memory alloys.**

(57) The invention relates to shape memory alloys consisting essentially of nickel, titanium, and copper. The alloys of this invention, which contain less than a stoichiometric amount of titanium, are capable of developing the property of shape memory at a temperature above 0°C. The presence of from 8.5 to 15 atomic percent copper stabilizes the alloys. Alloys according to this invention are particulary useful as switches and actuators.



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Nickel/Titanium/Copper Shape Memory Alloys

DESCRIPTION

This invention relates to shape memory alloys consisting essentially of nickel, titanium, and copper.

Alloys which exhibit the shape memory effect are now well-known, and include a number of alloys comprising nickel and titanium. See, e.g., U.S. Pat. Nos. 3,174,851; 3,351,463; and 3,753,700. A wide variety of useful articles, such as electrical connectors, actuators, and pipe couplings can be made from such alloys. See e.g. U.S. Pat. Nos. 3,740,839; 4,035,077; and 4,198,081.

Shape memory alloys also find use in switches, such as are disclosed in U.S. Patent No. 4,205,293, and actuators, etc. For such applications, it is generally desirable that the A_s temperature should be above ambient, so that the alloy element will remain in its martensitic state unless heated either externally or by the passage of an electric current through it. Because of the hysteresis of the austenite-martensite transformation, the desired M_{50} will generally be above 0°C for an A_s above, say, 20°C.

Especially in the case of switches, actuators, and heat engines, in which the shape memory alloy element may be subject to repeated cycling between the austenitic and martensitic states under load, shape memory "fatigue" may be a problem. Cross et al, NASA Report CR-1433 (1069), pp.51-53, discuss briefly this phenomenon, which they term "shape recovery fatigue", and indicate that there may be a significant loss in recovery at higher strain levels for binary nickel-titanium.

For shape memory applications in general, a high austenitic yield strength is desirable, as this minimises the amount of the somewhat expensive alloy required and the size of the article.

It has been generally accepted that shape memory alloys are unstable in the range of 100°C to 500°C if the titanium content is below 49.9 atomic percent (See Wasilewski et al., Met. Trans., v. 2, pp. 229-38 (1971).).

The instability (temper instability) manifests itself as a change (generally an increase) in M_s, the temperature at which the austenite to martensite transition begins, between the annealed alloy and the same alloy which has been further tempered. Annealing here means heating to a sufficiently high temperature and holding at that temperature long enough to give a uniform, stress-free condition, followed by sufficiently rapid cooling to maintain that condition. Temperatures around 900°C for about 10 minutes are generally sufficient for annealing, and air cooling is generally sufficiently rapid, though quenching in water is necessary for some of the low Ti compositions. Tempering here means holding at an intermediate temperature for a suitably long period (such as a few hours at 200 - 400°C). The instability thus makes the low titanium alloys disadvantageous for shape memory applications, where a combination of high yield strength and reproducible M_s is desired.

Two further requirements for these shape memory alloys should be noted. These are workability and machinability. Workability is the ability of an alloy to be plastically deformed without crumbling or cracking, and is essential for the manufacture of articles (including even test samples) from the alloy. Machinability refers to the ability of the alloy to be shaped, such as by turning or drilling, economically. Although machinability is not solely a property of the alloy, Ni/Ti alloys are known to be difficult to machine (see, e.g., Machining Data handbook, 2 ed. (1972) for comparative machining conditions for various alloys), i.e. they are expensive to shape, and a free-machining nickel/titanium shape memory alloy would be extremely economically attractive.

In U.S. Patent No. 4337090 it is disclosed that the addition of copper to nickel/titanium alloys having a low transition temperature (an A_{50} in the range of from -50°C to -196°C) provides a significant improvement in machinability and temper stability, enabling the production of high yield strength, low M_s alloys.

We have discovered that the addition of appropriate amounts of copper to nickel/titanium shape memory alloys having an M_s above 0°C can significantly improve the machinability and temper stability of the alloy and enable the manufacture of shape memory alloy has generally desired combination of high yield strength and high M_s.

In one aspect, this invention provides a shape memory alloy consisting essentially of nickel, titanium and copper within an area defined on a nickel, titanium, and copper ternary phase diagram by a quadrilaterial with its first vertex at 42 atomic percent nickel, 49.5 atomic percent titanium, and 8.5 atomic percent copper; its second vertex at 35.5 atomic percent nickel, 49.5 atomic percent titanium, and 15 atomic percent copper; its third vertex at 41 atomic percent nickel, 44 atomic percent titanium, and 15 atomic percent copper, and its fourth vertex at 44.25 atomic percent nickel, 47.25 atomic percent titanium, and 8.5 atomic percent copper. The alloys according to the invention advantageously display the properties of high strength and an M_{50} (138 MPa)(20 ksi) temperature above 0°C. The alloys also display unexpectedly good temper stability, workability and machinability.

In a preferred embodiment the shape memory alloy consists essentially of from 40.5 to 41.5 atomic percent nickel, from 48.5 to 49.5 atomic percent titanium and from 9.5 to 10.5 atomic percent copper.

Shape memory alloys according to the invention may conveniently be produced by the methods described in, for example, U.S. Pats. No. 3,753,700 and 4,144,057. The following example illustrates the method of preparation and testing of samples of memory alloys.

EXAMPLE

Commercially pure titanium, carbonyl nickel, and OFHC copper were weighed in proportions to give the atomic percentage compositions listed in Table 1 (the total mass for test ingots was about 330 g). These metals were placed in a water-cooled copper hearth in the chamber of an electron beam melting furnace. The chamber was evacuated to 10^{-5} Torr and the charges were melted and alloyed by use of the electron beam.

The resulting ingots were hot swaged and hot rolled in air at approximately 850°C to produce strip of approximately 0.5 mm (0.025 ins) thickness. After de-scaling, samples were cut from the strip and vacuum annealed at 900°C.

The annealed samples were cooled and re-heated while the change in resistance was measured. From the resistance-temperature plot, the temperature at which the martensitic transformation was complete, the M_f temperature, was determined. The transformation temperature of each alloy was determined as the temperature at which 50% of the total deformation had occurred under 138 MPa (20 ksi) load, referred to as the M_{50} (138 MPa)(20 ksi) temperature.

After tempering each sample for two hours at 400°C, the tests were repeated. The average of the temperature shift of the resistivity change and of M_{50} (138 MPa)(20 ksi) was used as an index of instability: the greater the absolute value of the index, the greater the instability. The yield strength of annealed samples was measured at temperatures high enough to avoid the formation of stress-induced martensite i.e. at 80°C above M_s. Values for M_{50} (138 MPa)(20 ksi), the instability index, the yield strength and the workability are listed in Table 1. On the basis of these data, the preferred composition limits for this invention have been defined.

Table 1. Properties of Nickel/Titanium/Copper Alloys

Composition Atomic Percent Ni	Ti	Cu	M_{50}(20 ksi), (138 MPa) °C	Yield Strength MPa(ksi)	Instability Index	Workability
43.0	49.0	8.0	-5	552 (80)	-2	
42.0	50.0	8.0	64	227 (33)	-4	
44.0	46.0	10.0	-45	758(110)	4	
43.0	47.0	10.0	11	544 (79)	2	
42.0	48.0	10.0	27	675 (98)	-1	
41.0	49.0	10.0	11	599 (87)	-1	
40.5	49.5	10.0	-	-	-	No
40.0	50.0	10.0	-	-	-	No
43.0	45.0	12.0	-23		1	
42.0	46.0	12.0	11	709(103)	0	
41.0	47.0	12.0	15	675 (98)	0	
40.0	46.0	14.0	5	724(105)	1	
39.0	45.0	16.0	-	-	-	No
38.0	46.0	16.0	-	-	-	No
37.0	47.0	16.0	32	648 (94)	0	
36.0	48.0	16.0	-	-	-	No
34.0	50.0	16.0	-	-	-	No

The composition of the alloy of this invention can be described by reference to an area on a nickel, titanium, and copper ternary composition diagram. The general area of the alloy on the composition diagram is shown by the small triangle in Figure 1. This area of the composition diagram is enlarged and shown in Figure 2. the compositions at the points, A, B, C, and D, are shown in Table II below.

Table II. Atomic Percent Composition

Point	Nickel	Titanium	Copper
A	42.00	49.50	8.50
B	35.50	49.50	15.00
C	41.00	44.00	15.00
D	44.25	47.25	8.50

The lines AB and BC correspond approximately to the workability limit these alloys, while the lines CD and DA correspond approximately to an M_{50} (133 MPa)(20 ksi) of 0°C.

As the extent of thermally recoverable plastic deformation (shape memory) that can be induced in these alloys decreases with decreasing titanium content, the particularly preferred alloys of this invention will lie nearer line AB (the high titanium line) of the quadrilateral ABCD of Figure 2.

The alloys of this invention also exhibit a greater resistance to shape memory fatigue than binary alloys. For example, a copper alloy showed less than half the loss of recoverability of an equivalently processed binary after 1000 cycles of fatigue testing at about 276 MPa (40 ksi) load.

It has been found that the alloys of this invention possess machinability which is unexpectedly considerably better than would be predicted from similar Ni/Ti alloys. While not wishing to be held to any particular theory, it is considered that this free-machining property of the alloys is related to the presence of a second phase, possibly $Ti_2(Ni,Cu)_3$, in the TiNi matrix. It is therefore considered that this improved machinability will manifest itself only when the titanium content is below the stoichiometric value and the Ti:Ni:Cu ratio is such as to favour the formation of the second phase.

In addition to the method described in the Example, alloys according to the invention may be manufactured from their components (or appropriate master alloys) by other methods suitable for dealing with high-titanium alloys. The details of these methods, and the precautions necessary to exclude oxygen and nitrogen either by melting in an inert atmosphere or in vacuum, are well known to those skilled in the art and are not repeated here.

Alloys obtained by these methods and using the materials described will contain small quanities of other elements, including oxygen and nitrogen in total amounts from about 0.05 to 0.2 percent. The effect of these materials is generally to reduce the martensitic transformation temperature of the alloys.

The alloys of this invention possess good temper stability, are hot-workable, and are free-machining; in contrast to prior art alloys. They are also capable of possessing shape memory, and have a M_{50} (138 MPa) (20 ksi) temperature above 0°C.

CLAIMS:

1. A shape memory alloy consisting essentially of nickel, titanium and copper within an area defined on a nickel, titanium, and copper ternary phase diagram by a quadrilaterial with its first vertex at 42 atomic percent nickel, 49.5 atomic percent titanium, and 8.5 atomic percent copper; its second vertex at 35.5 atomic percent nickel, 49.5 atomic percent titanium, and 15 atomic percent copper; its third vertex at 41 atomic percent nickel, 44 atomic percent titanium, and 15 atomic percent copper, and its fourth vertex at 44.25 atomic percent nickel, 47.25 atomic percent titanium, and 8.5 atomic percent copper.

2. A shape memory alloy according to claim 1 which consists essentially of from 40.5 to 41.5 atomic percent nickel, from 48.5 to 49.5 atomic percent titanium, and from 9.5 to 10.5 atomic percent copper.

3. An article possessing the property of shape memory which is made from an alloy as defined in claim 1 or 2.

Fig. 1.

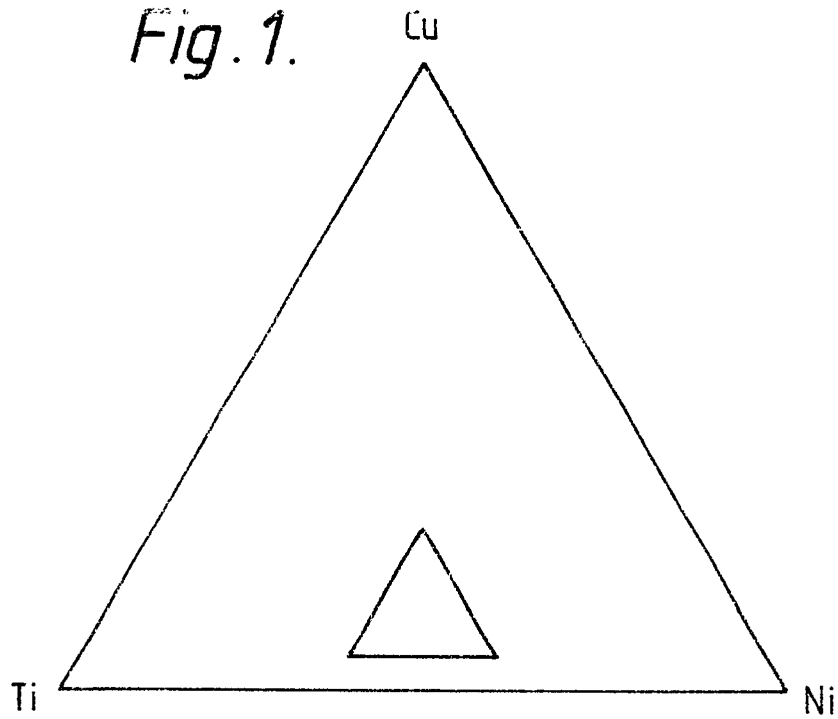
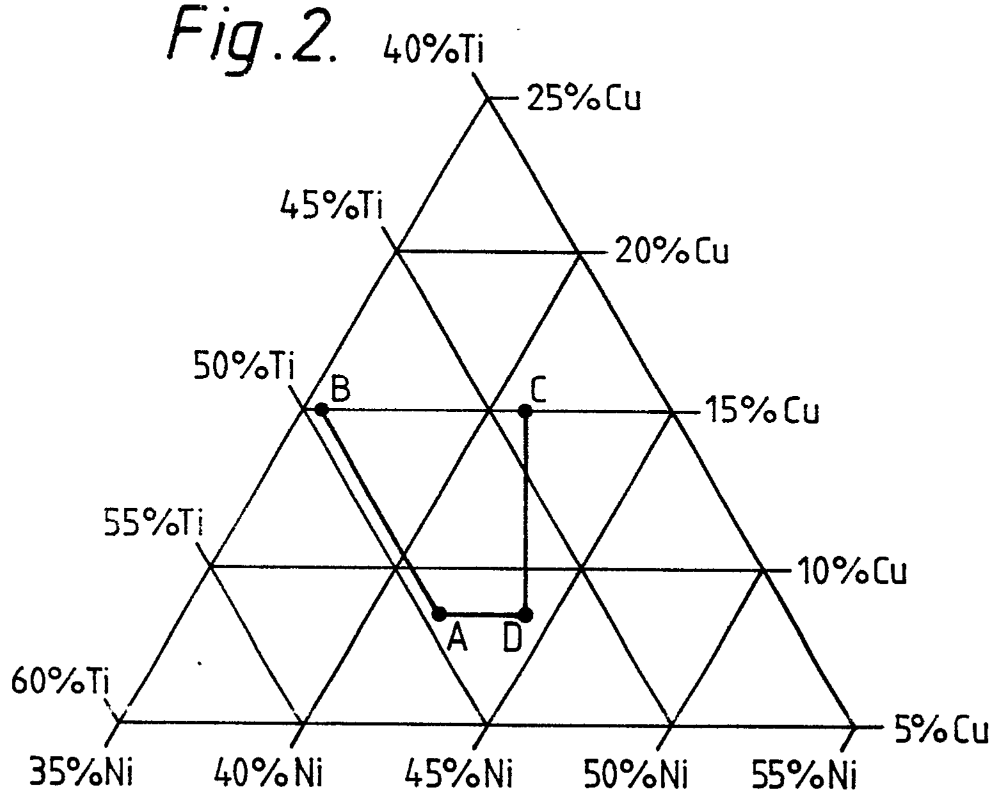

Cu
Ti
Ni

Fig. 2.


40%Ti
25%Cu
45%Ti
20%Cu
50%Ti
B
C
15%Cu
55%Ti
10%Cu
A
D
60%Ti
5%Cu
35%Ni
40%Ni
45%Ni
50%Ni
55%Ni