

PATENT SPECIFICATION

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(54) HEAT-TREATING METHOD

(71) We, RAYCHEM LIMITED, a British Company, of Moor House, London Wall, London, E.C.2, do hereby declare the invention, for which we pray that a patent may be granted to us, and the method by which it is to be performed, to be particularly described in and by the following statement:—

This invention relates to a method of improving the properties of certain heat-recoverable metal compositions and articles made from such compositions.

Such metallic compositions, which are usually alloys, have the property of being capable of undergoing reversible transformation from the austenitic to the martensitic state. Under particular consideration are those to which memory may be imparted. As will be described in more detail below, if they are deformed in the martensitic state they will return to their original configuration on heating to the austenitic state.

Such alloys are, for example, those disclosed in U.S. Patents Nos. 3,012,882; 3,174,851; 3,351,463; 3,567,523; 3,753,700; and 3,759,552; Belgian Patent No. 703,649 and British Patents Nos. 1,315,652; 1,315,653; 1,346,046 and 1,346,047 (Belgian Patents Nos. 749,851; 758,861 and 758,862) in the name of Fulmer Research Institute, the disclosure of each of which is incorporated herein by reference.

Such alloys are also disclosed in NASA Publication SP5110, "55-Nitinol—the alloy with a memory, etc." (U.S. Government Printing Office, Washington, D.C., 1972), N. Nakanishi et al, *Scripta Metallurgica* 5, 433—440 (Pergamon Press 1971), the disclosures of which are incorporated herein by reference.

These alloys have in common the feature of undergoing a shear transformation on cooling from a high temperature state to a low temperature state.

In this specification, "martensite" and "martensitic" are used to denote such an alloy in its low temperature state, while "austenite" and "austenitic" are used to denote the alloy at a high temperature and in a state capable of undergoing a transformation on cooling known as a "martensitic transformation". Under certain conditions of composition and temperature, both transformable and non-transformable phases may co-exist. Only those states capable of undergoing the transformation are martensitic or austenitic.

If an article made of such an alloy is deformed when in its martensitic state it will remain so deformed. If it is heated to return it to a temperature at which it is austenitic, it will tend to return to its underformed state. The transition from one state to the other, in each direction, takes place over a temperature range. The temperature at which martensite starts to form on cooling is designated M_s , while the temperature at which this process is complete is designated M_f , each of these temperatures being those achieved at high, e.g., 100°C per minute, rates of change of temperature of the sample, i.e., the "basic" M_s , etc. Similarly, the temperature of beginning and end of transformation to austenite are designated A_s and A_f . Generally, M_f is a lower temperature than A_s , M_s is a lower temperature than A_f , and M_s is equal to, lower than, or higher than A_s , for a given alloy. The transformation from one form to the other may be followed by measuring one of a number of physical properties of the material in addition to the reversal of deformation described above,

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for example, its electrical resistivity, which shows an anomaly as the transformations take place. If graphs of resistivity-v-temperature or strain-v-temperature are plotted, a line joining the point M_s , M_f , A_s , A_f , and back to M_s forms a loop termed the hysteresis loop. For many materials M_s and A_s are at approximately the same temperature.

One particularly useful alloy possessing heat recoverability or shape memory is the intermetallic compound TiNi, British Patent No. 1,020,872. The temperature at which deformed objects of the alloys return to their original shape depends on the alloy composition as disclosed in British Patent No. 1,202,404 and U.S. Patent No. 3,753,700 e.g., the recovery of original shape can be made to occur below, at, or above room temperature.

In certain commercial applications employing heat recoverable alloys, it is desirable that A_s be at a higher temperature than M_s , for the following reason. Many articles constructed in the alloys are provided to users in a deformed condition and thus in the martensitic state. For example, couplings for hydraulic components, as disclosed in British Patents Nos. 1,327,441 and 1,327,442, are sold in a deformed (i.e., an expanded) state. The customer places the expanded coupling over the components (for example, the ends of hydraulic pipe lines) to be joined and raises the temperature of the coupling. As its temperature reaches the austenitic transformation range the coupling returns, or attempts to return, to its original configuration, and shrinks onto the components to be joined. Because it is necessary that the coupling remain in its austenitic state during use (for example, to avoid stress relaxation during the martensitic transformation and because its mechanical properties are superior), the M_s of the material is chosen to be below that which it may possibly reach in service. For this reason, it has to be kept in, for example, liquid nitrogen until it is used. If, however, the A_s which, as used herein, means that temperature which marks the beginning of a continuous sigmoidal transition, as plotted on a strain vs. temperature graph, of all the martensite capable of transforming to austenite to the austenitic state could be raised if only temporarily, for example for one heating cycle, without a corresponding rise in the M_s , then the expanded coupling could be maintained at a higher and more convenient temperature.

In copending Application No. 53243/72 (Serial No. 1,490,181), there is disclosed and claimed a heat-recoverable metallic composition having for at least one heating cycle an A_s higher than its M_s , or a raised A_s if the alloy already has an A_s higher than its M_s , and a method of raising the A_s of an alloy, at least temporarily, relative to the M_s of the alloy. Stated another way, that invention provides a means for retaining at least a useful portion of martensite at temperatures at which austenite would normally exist. Thus, the physical properties associated with martensite are retained at higher temperatures. The method is termed "preconditioning" and the resulting alloy is stated to be "preconditioned".

The parent application provides a method for raising for at least one heating cycle the A_s of a heat-recoverable alloy relative to its M_s which comprises slowly, e.g., less than 1 degree centigrade/min., heating the alloy from a temperature below its M_s to a temperature in the region where the A_s is desired. The alloy can then be cooled to any temperature below that to which it has been slowly heated or it can be held at that temperature. When the alloy is to be used, it is simply heated again at any convenient fast rate, e.g., 5 degrees centigrade/min. or greater; preferably 100 degrees C/min. or greater, and the A_s will be found to be approximately at the temperature to which it was heated slowly.

In principle, a composition may be transformed between martensite and austenite any number of times simply by raising and lowering its temperature in the appropriate range, i.e. the transformation is reversible. It has been found, however, that certain compositions may fail to make the transformation completely from martensite to austenite on heating; this characteristic, which is undesirable, is herein denoted as a "tendency to lose reversibility".

The present invention provides a metallic composition having a substantially reduced tendency to lose reversibility between its martensitic and austenitic state as compared with the tendency to do so of a material of the same composition as initially formed into the austenitic state.

It will be understood that where (as is usually the case, and as is described in the Examples below) austenitic material is produced at elevated temperatures and quenched, "initially formed" denotes such material when initially brought to ambient temperatures.

The present invention also provides a method of reducing loss of reversibility between the martensitic and austenitic states in metallic articles which reversal would

otherwise occur at ambient temperatures by holding the article at a temperature above the M_s temperature while in the austenitic state for a time sufficient to reduce the loss of reversibility.

For certain alloys in which quenching is required to ensure that the high temperature phase is austenitic, for example, β -brass in which quenching is necessary to ensure the β , rather than $\alpha+\beta$, configuration, it is preferred that the alloy initially be quenched from a high temperature (for example, about 800°C in the case of brasses) to a temperature at which it is still wholly austenitic. Reduction of loss of reversibility may be achieved by holding the alloy at the quenchant temperature or some moderately elevated temperature, e.g. 50°C to 100°C for about 10 minutes to 24 hours or even several days at the lower temperatures. The procedure is referred to as "aging", and aging as used in this specification is hereby defined as maintaining a material at a temperature above its M_s , and an "aged" material as one that has been maintained at a temperature above its M_s in the austenitic state.

It will be appreciated that there is an upper limit to the temperature range in which any given material may be aged. For example, as stated above, β -brass tends to change to an equilibrium mixture of α and β materials at elevated temperatures and those skilled in the art will be aware that in other materials other detrimental changes resulting in the material no longer being in the austenitic state may take place after long exposure to very high temperatures, which should therefore be avoided.

For alloys with a room temperature basic M_s , 20–50°C proves to be a convenient quenchant range of temperatures and 50–100°C a convenient aging temperature range. If the alloy has been quenched to a lower temperature (i.e., one at which transformation to the martensite does take place) it is then aged, i.e., preferably heated to a temperature at which the alloy is transformed to the austenite and held at such temperature for a suitable time. Preferably the aging process is carried out as soon as possible after quenching.

It has thus been found that this treatment of alloys above any temperature at which martensite exists can be employed to prevent or reduce loss of the reversible austenite/martensite transformation when the materials are stored. The higher the aging temperature, the shorter the treatment time needs to be.

When metallic articles are subjected to the process for inhibiting loss of reversibility according to the present invention their pseudo elasticity, i.e., their ability to transform from the austenitic to martensitic state with attendant deformation when subjected to stress and to revert to the austenitic state and recover their original shape, is improved.

Preferably, the metallic article is made of an alloy, and preferably the alloy is an intermetallic compound. Among suitable alloys there may be mentioned copper-zinc and copper-aluminum alloys in which zinc and aluminum may replace each other and which preferably contain relatively small proportions of silicon, tin, or manganese, or mixtures thereof, which alloys may contain up to about 20% or more weight percent (based on the weight of copper and zinc) of the third component or the total of the additional components. It will be appreciated that the proportion of metals other than copper and zinc affects the transition temperature and other properties of the alloys. Examples of suitable alloys for use in the present invention include 69.7% Cu, 26.3% Zn, 4% Al; 62.2% Cu, 37.3% Zn, 0.5% Al, and 80.5% Cu, 10.5% Al, 9% Mn. As examples in this specification, there will be discussed in some detail alloys having about 65% copper to 35% zinc, with optional additions of up to 2% silicon or up to 2 or 3% aluminum, these being weight percentages. It will be appreciated, however, that such alloys, having M_s temperatures very close to ambient, are discussed only as examples and that the processes of the invention are applicable to alloys having, for example, M_s temperatures lower than ambient, and to alloys, for example, those based on gold or silver, other than copper-based.

The following examples illustrate the invention:

EXAMPLE 1

A series of experiments was conducted to determine the degree of response of various compositions in the Cu–Zn–Si and Cu–Zn–Al systems to the thermal pre-conditioning process of this invention. Alloy samples were cast from melts having different ratios of copper, zinc, and either silicon or aluminium. The castings were hot-rolled into strips, cut into specimens about 37 mm × 3 mm × 0.75 mm. All specimens were heated until they entered the high-temperature, all-beta phase, then quenched into water. Half the samples were aged at 100°C for 10 minutes, the other half were not aged. All the samples were deformed by bending at –79°C to cause an outer fibre strain of 6%. After deformation, the samples were released and measured to

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determine how much strain was retained. Specimens from the aged and unaged groups were then heated according to one of the three following methods:

(1) heated rapidly by immersion in liquid at 40°C, cooled to room temperature and measured to determine how much strain was recovered, then heated rapidly by immersion in liquid at 200°C and again returned to room temperature to determine how much additional recovery of strain occurred;

(2) slowly heated at a rate of 0.25 deg. C per minute from -79°C to +40°C, cooled to room temperature, measured to determine how much strain was recovered, then heated rapidly by immersion in liquid at 200°C, cooled to room temperature and measured to determine how much additional recovery occurred; or

(3) treated as (2), except that the slow heating rate was 1 deg. C per 24 minutes, instead of 0.25 deg. C per minute.

A "figure of merit" for the responsiveness of each composition tested to control of the recovery temperature range is obtained by expressing as a percent the recovery occurring above 40°C for slowly-heated specimens, less the recovery above 40°C for rapidly-heated specimens, divided by 5% (which is the ideal recovery after the elastic springback which accompanies release of the bending stress) i.e.,

$$\text{Figure of Merit} = 100 \times \frac{(\text{recovery above } 40^\circ\text{C in slowly heated specimens}) - (\text{recovery above } 40^\circ\text{C in rapidly heated specimens})}{5}$$

Compositions found especially suitable for use in the invention will now be described in greater detail with reference to the accompanying drawings, in which:

Fig. 1a is a small part of the copper-zinc silicon system, for unaged samples,

Fig. 1b is a small part of the same system, for aged samples,

Fig. 2 is a graph indicating the effect of different "slow" heating rates on the same system, for both aged and unaged samples,

Fig. 3 indicates the effect on the "Figure of Merit" of varying degrees of strain, for two samples of the system,

Figs. 4a and 4b correspond to Figs. 1a and 1b but for the copper-zinc-aluminium system, while

Fig. 4c illustrates the "Figure of Merit" for aged samples "slowly" heated to 100°C.

Referring now to Figs. 1a and 1b, the figure-of-merit is plotted versus composition in Figures 1a and 1b in a topographical format. Generally, the long axes of the zones of constant figure-of-merit are parallel to iso-transformation temperature contours. Compositions with lower transformation temperature are in the upper left while those with higher transformation temperatures are in the lower right of the figure. A distinct optimum appears in Figure 1 in the range 1.8 to 2.7 Si, 66.2 to 67.5 Cu, balance Zn. Comparison of Fig. 1a with 1b shows that aging 10 minutes at 100°C broadens the optimum from the same general centre point. The arbitrary selection of 40°C as the end of slow heating apparently disqualifies alloys whose usual transformation range lies above or partially above +40°C but it will be appreciated that a zero on the graph does not indicate unsuitability of the alloys for use in the invention, merely that a temperature of other than +40°C should be chosen. The choice of 40°C causes the iso-figure-of-merit zone to close toward the high transformation temperature side (lower right). Alloys in the lower right region are responsive to the process of this invention, as the CuZnAl data below indicate.

Sensitivity of the optimum region to the rate of slow heating was explored by testing samples of composition 66.5 wt. % Cu, 30.8 wt. % Zn, 1.96 wt. % Si, prepared as the samples above, but slowly heated at a range of different heating rates. The recovery which occurred during heating through the temperature interval from -79°C to +40°C versus heating rate is presented in Figure 2. Slow heating rates up to about 1 deg. C per minute are usable. Higher rates than 2 deg. C per minute lead to appreciable recovery during slow heating, indicating that about 2 deg. C per minute is the limit of "slow" heating for this system.

Sensitivity of the optimum region to the rate of strain of the tests above was explored using compositions 66.5 wt. % Cu, 30.8 wt. % Zn, 1.96 wt. % Si and 64.2 wt. % Cu, 34.8 wt. % Zn, 1.0 wt. % Si. One group of samples was treated according to the method above, except that 12% strain was introduced at -79°C. Another group was treated as above, but with zero strain before the slow heat step. After slow heating, the unstrained samples were strained 12% at room temperature, then all samples

5 were rapidly heated to +200°C. A figure of merit was determined for each by the sample method described above, except that 10% (assumed ideal recovery for 12% strain) is in the denominator rather than 5%. The results are illustrated in Figure 3. While twelve percent strain appears to be beyond optimum for 66.5 wt. % Cu, 30.8% wt. % Zn, 1.9% wt. % Si, it gives better response in the 64.2 wt. % Cu, 34.8 wt. % Zn, 1.0 Si than 0 or 6% strain.

5 A topographical presentation of the figure-of-merit results for the CuZnAl system appears in Figure 4. Again, the constant figure-of-merit zones lie parallel to the isotherm transformation contours. A more distinct optimum region was defined by the unaged samples, Figure 4a than for the aged, Fig. 4b.

10 Five alloy compositions having a normal A_1 at or above 40°C were used to test the mobility of the recovery range at higher temperatures. Again, the same general test procedure was used, but slow heating was continued to +100°C rather than stopping at +40°C. Results for aged samples appear in Figure 4c; the new optimum lies parallel to that in Fig. 4b, but shifted as would be expected toward compositions with higher transformation temperature. Although the recovery range is mobile in CuZnAl, the mobility seems more limited than in CuZnSi.

15 As the unaged CuZnAl samples lost their memory properties as a consequence of slow heating to 100°C, but the aged samples did not, it is apparent that the aging treatment is successful in preserving reversibility of the transformation in the higher temperature range.

20 It will be appreciated that the aging periods and conditions selected for Figs. 1b and 4b result in certain compositions having optimum properties and that other aging periods and conditions result in different compositions having the same or broadly similar optimum properties. The aged alloys within the areas bounded by lines 40, 60 and 80 in Fig. 1b and line 20 in Fig. 4b are novel, and are especially suited for the process of the invention, and the present invention accordingly provides aged alloys, preferably aged as described above, as novel alloys.

25 The purpose of this Example is to show how an optimum composition can be selected, given a desired set of characteristics. Examples to follow will show how characteristics can be changed to optimize movement of the recovery range for the case of a fixed alloy composition. For example, the optimum range of Example 1 may give too low ductility or too low electrical conductivity for specific applications.

EXAMPLE 2

35 Several specimens of an alloy of composition, by weight, of 64.5% copper, 34.5% zinc, 1.0% silicon were quenched after 5 minutes at 860°C into water at 20°C, and then aged at 50°C for times up to 1 week. After cooling to below M_s , the specimens were reheated at a rate of 10 to 20 degrees C/minute. Little transformation of martensite to β -phase (as measured by changes in resistivity) occurred during heating of the specimen aged for 5 minutes. Some transformation took place in the specimen aged for 45 minutes; the specimens aged for 90 minutes or over transformed completely. Other specimens of the same alloy were given the same heat treatment and after aging were deformed in tension at -50°C and reheated. The amount of heat-recovery was approximately proportional to the amount of martensite which had transformed in the resistivity tests on undeformed specimens. Hence, using the process of the invention by aging at least 45 minutes allowed heat-recoverable properties to be imparted to this alloy.

40 After aging 5 minutes at 20°C before cooling to -50°C, the heat recoverable strain was 2.30%. After 45 minutes, at +50°C before cooling to -50°C, the heat recoverable strain was 6.20%. This slowly increased after longer aging times to 6.50% after 3 hours and 7.0% after 1 week.

EXAMPLE 3

45 Several samples of an alloy of composition by weight of 66.50% copper, 31.75% zinc and 1.75% silicon were also quenched after 5 minutes at 860°C into water at 20°C. They were then aged at 50°C for times up to 1 week. After 5 minutes at 50°C, the heat recoverable strain was 0.1%. After 45 minutes at 50°C, this remained at 0.1% and after 90 minutes had only increased to 0.55%. Three hours increased the heat recovery strain to 0.70%, 1 day to 1.0%, and 2 days to 3.9%. Thus, the increased silicon content can be seen to require much longer aging time to produce improved recovery.

EXAMPLE 4

50 The alloy described in Example 2 was also used in this Example. Its basic A_1

was about 15 to 25°C, and normally about 75% of any heat recovery has taken place by 75°C. A sample was heat treated and quenched in the manner described in Example 1 and aged for about 5 minutes at ambient temperature. It was then cooled to below M_s to the martensitic state, then heated at between 0.75 and 1.0 degree C per minute to 75°C, and then cooled to -50°C (i.e., below its M_s of about -20°C). The sample was then deformed to impart 8% strain at -50°C. Approximately half the deformation strain was recovered on heating to above A_1 . Recovery was 4%, about 0.8% taking place below, and 3.2% above, 75°C.

EXAMPLES 5 to 8

Samples of the same alloy used in Example 2 were heat treated and quenched to 20°C, and aged for 2 days at 50°C. They were then cooled to -50°C and deformed. Samples were then heated to 75°C at the same slow rate as in Example 4, and cooled again to 20°C. Different samples were then stored for different periods, and heated at 50 to 200°C/minute (i.e., rapidly) to cause recovery.

Example No.	Strain	Recovery on Slow Heat to 75°C	Storage Time at 20°C	A_{50} , °C	Recovery on Fast Heat to 75°C	Total Recovery on Fast Heat %
5	7.40	0.95	5 min.	85	0	5.30
6	6.80	1.20	90 min.	86	0	4.40
7	7.65	1.60	16 hrs.	85	0	4.30
8	7.30	1.60	168 hrs.	86	0	3.60

From Examples 4 to 8 it can be seen that the alloys may be deformed either before or after slow heating.

EXAMPLE 9

Sixteen samples of (80.8 wt. % Cu, 10.5 wt. % Al, 8.7 wt. % Mn) were austenitized at 800°C or 900°C for 3 minutes or 6 minutes then quenched into room temperature water. Half the samples were aged for 10 minutes at 100°C, the others were not aged. All samples were deformed by bending at -79°C to give an outer fibre strain of 6%, then the stress was relaxed. Half the samples were heated to 100°C at 1/4 deg C per minute, cooled to room temperature, then heated rapidly to 200°C. The other half were heated rapidly to 100°C, cooled to room temperature, then heated rapidly to 200°C. The rate of rapid heating was greater than 100 deg. C per minute.

The test conditions are summarized at follows:

Sample	Austenitization Temp.	Time	Treatment Post-quench	Heating Rate to 100°C
1	800 c	3 min	aged	fast
2	800 c	3 min	aged	slow
3	800 c	3 min	non-aged	fast
4	800 c	3 min	non-aged	slow
5	800 c	6 min	aged	fast
6	800 c	6 min	aged	slow
7	800 c	6 min	non-aged	fast
8	800 c	6 min	non-aged	slow
9	900 c	3 min	aged	fast
10	900 c	3 min	aged	slow
11	900 c	3 min	non-aged	fast
12	900 c	3 min	non-aged	slow
13	900 c	6 min	aged	fast
14	900 c	6 min	aged	slow
15	900 c	6 min	non-aged	fast
16	900 c	6 min	non-aged	slow

An analysis of the strain which was recovered during rapid heating to 200°C (EHRS) versus the controlled variables showed significance only for rapid heating to 100°C vs. 1/4 deg. C per minute heating to 100°C, i.e., non-preconditioned versus preconditioned.

Averaged Effects	
Percent Strain Recovered Above 100°C	
Fast Heated	0.39%
Preconditioned	1.89%

5 The experiment was repeated on an alloy containing 80.49 wt. percent Cu, 10.5 wt. percent Al, 9.01 wt. percent Mn. Analysis of the strain which was recovered during rapid heating to 200 degrees C versus the controlled variables showed significance for aging versus no aging and for non-preconditioned versus preconditioned. 5

Average Effects	
Percent Strain Recovered Above 100°C	
Un-Aged	1.00
Aged	0.36
Fast heated	0.15
Preconditioned	1.21

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WHAT WE CLAIM IS:—

- 15 1. A metallic composition having a substantially reduced tendency to lose reversibility between its martensitic and austenitic states as compared with the tendency to do so of a material of the same composition as initially formed into the austenitic state. 15
- 20 2. A method of reducing the loss of reversibility between the martensitic and austenitic states in a metallic composition which would otherwise occur at or near ambient temperature comprising holding said composition at a temperature above the M_s temperature while in the austenitic state for a time sufficient to reduce said loss at said ambient temperature. 20
- 25 3. The method of claim 2 wherein, prior to said holding step, said composition is heated to a temperature substantially above room temperature and is then quenched. 25
- 25 4. The method of claim 3 wherein said quenching temperature is a temperature at which the composition is wholly in the austenitic state. 25
- 30 5. The method of claim 2, carried out substantially as described in any one of the examples herein.
- 30 6. A copper-silicon-zinc composition as claimed in claim 1 which, apart from incidental impurities, lies within the area bounded by the line designated 40 on the accompanying Fig. 1b. 30
- 35 7. A copper-silicon-zinc composition as claimed in claim 1 which, apart from incidental impurities, lies within the area bounded by the line designated 60 on the accompanying Fig. 1b.
- 35 8. A copper-silicon-zinc composition as claimed in claim 1 which, apart from incidental impurities, lies within the area bounded by the line designated 80 on the accompanying Fig. 1b. 35
- 40 9. A copper-aluminium-zinc composition as claimed in claim 1 which, apart from incidental impurities, lies within the area bounded by the line designated 20 on the accompanying Fig. 4b. 40
- 40 10. A copper-aluminium-zinc composition as claimed in claim 1 which, apart from incidental impurities, lies within the area bounded by the line designated 20 on the accompanying Fig. 4c.
- 45 11. A copper-aluminium-zinc composition as claimed in claim 1 which, apart from incidental impurities, lies within the area bounded by the line designated 40 on the accompanying Fig. 4c. 45
12. A composition as claimed in claim 1 substantially as described in any one of Examples 2 to 9 herein.



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Averaged Effects
Percent Strain Recovered Above 100°C
Fast Heated 0.39%
Preconditioned 1.89%

5 The experiment was repeated on an alloy containing 80.49 wt. percent Cu, 10.5 wt. percent Al, 9.01 wt. percent Mn. Analysis of the strain which was recovered during rapid heating to 200 degrees C versus the controlled variables showed significance for aging versus no aging and for non-preconditioned versus preconditioned.

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10 Average Effects
Percent Strain Recovered Above 100°C
Un-Aged 1.00 Fast heated 0.15
Aged 0.36 Preconditioned 1.21

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WHAT WE CLAIM IS:—

15 1. A metallic composition having a substantially reduced tendency to lose reversibility between its martensitic and austenitic states as compared with the tendency to do so of a material of the same composition as initially formed into the austenitic state.

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20 2. A method of reducing the loss of reversibility between the martensitic and austenitic states in a metallic composition which would otherwise occur at or near ambient temperature comprising holding said composition at a temperature above the M_s temperature while in the austenitic state for a time sufficient to reduce said loss at said ambient temperature.

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25 3. The method of claim 2 wherein, prior to said holding step, said composition is heated to a temperature substantially above room temperature and is then quenched.

4. The method of claim 3 wherein said quenching temperature is a temperature at which the composition is wholly in the austenitic state.

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5. The method of claim 2, carried out substantially as described in any one of the examples herein.

30 6. A copper-silicon-zinc composition as claimed in claim 1 which, apart from incidental impurities, lies within the area bounded by the line designated 40 on the accompanying Fig. 1b.

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35 7. A copper-silicon-zinc composition as claimed in claim 1 which, apart from incidental impurities, lies within the area bounded by the line designated 60 on the accompanying Fig. 1b.

8. A copper-silicon-zinc composition as claimed in claim 1 which, apart from incidental impurities, lies within the area bounded by the line designated 80 on the accompanying Fig. 1b.

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40 9. A copper-aluminium-zinc composition as claimed in claim 1 which, apart from incidental impurities, lies within the area bounded by the line designated 20 on the accompanying Fig. 4b.

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10. A copper-aluminium-zinc composition as claimed in claim 1 which, apart from incidental impurities, lies within the area bounded by the line designated 20 on the accompanying Fig. 4c.

45 11. A copper-aluminium-zinc composition as claimed in claim 1 which, apart from incidental impurities, lies within the area bounded by the line designated 40 on the accompanying Fig. 4c.

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12. A composition as claimed in claim 1 substantially as described in any one of Examples 2 to 9 herein.

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13. A composition as claimed in claim 1 substantially as described in Example 1 herein.

14. An article comprising a composition as claimed in any one of claims 6 to 13 or 1.

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15. A heat recoverable article, comprising a composition as claimed in any one of claims 6 to 13 or 1.

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