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(54) TREATING HEAT-RECOVERABLE ALLOYS

(71) We, RAYCHEM CORPORATION, a body corporate organised according to the laws of the State of California, United States of America, of 300 Constitution Drive, Menlo Park, California 94025, United States of America, 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 heat-recoverable alloys and methods for treating them.

Metallic compositions, for example, alloys, which have the properties of being capable of undergoing reversible transformation from the austenitic to the martensitic state are known, and some of these may be formed into articles that are heat-recoverable. Such alloys, commonly known as heat-recoverable alloys or memory alloys, are, for example, 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 in British Patents Nos. 1,315,652; 1,315,653; 1,346,046 and 1,346,047 in the name of Fulmer Research Institute, which four patents are herein referred to as the 'Fulmer Patents'. The disclosures of all the patents mentioned above are incorporated herein by reference.

Such alloys are also disclosed in NASA Publication SP110, '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 likewise incorporated herein by reference.

These and other alloys have in common the feature of undergoing a shear transformation on cooling from a high temperature austenitic state to a low temperature or martensitic state. The terms 'martensite' and 'martensitic' being used herein to denote the low temperature state and the terms 'austenite' and 'austenitic' being used herein to denote the high temperature state from which the alloy is capable of undergoing a transformation on cooling which is known as a 'martensitic transformation'. Under certain conditions of composition and temperature, both transformable and non-transformable phases may co-exist; only those phases 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 undeformed state, producing a so-called shape memory effect. 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 deg C/min, rates of change of temperature of the sample. Similarly, the temperatures of beginning and end of the 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 can be equal to, lower than or higher than A_s, depending on the

alloy composition and also on the alloy's thermomechanical history. 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, 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 points 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, U.S. Patent No. 3,174,851. 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, i.e. by selecting the appropriate composition for the alloy, 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 of 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, the disclosures of which are incorporated by reference, 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 the mechanical properties of the austenite are superior), the M_s of the material is chosen to be below any which it may possibly reach in service, so that during service the material will remain at all times in the austenitic state. For this reason, after deformation 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 kept at a higher and more convenient temperature.

In our British Patent Specification No. 1,490,181 entitled 'Heat Treating Method', the disclosure of which is incorporated by reference, there is described a method by which the A_s of certain metallic compositions can be raised for one heating cycle. This method comprises first lowering the temperature of the composition from one at which it exists in the austenitic state to below its M_f temperature. Then the composition is heated to a temperature at which normally it would exist wholly in the austenitic state, i.e. above the A_f temperature. However, the transformation from martensite to austenite does not occur if the heating rate selected is a 'slow' one. The definition of a 'slow' heating rate is fully set forth in the copending application. Suffice it to say that it can vary depending upon the nature of the metallic composition but is easily determined by one skilled in the art having the benefit of the disclosure of that application.

If the composition is cooled after slow heating is complete and subsequently reheated at a rapid rate it does not begin to undergo a martensite to austenite transformation until approximately the temperature at which slow heating was terminated is reached. More importantly, if an article was made from the composition and deformed while in the martensite state either prior to, or after, slow heating is terminated, it will not begin to undergo recovery to the form in which it existed in the austenitic state until it reaches approximately the temperature at which slow heating was terminated. This process is referred to as 'thermal preconditioning'.

In our British Patent Specification No. 1,490,182 the disclosure of which is also incorporated herein by reference, there is explained how the tendency of some metallic compositions to lose martensite-austenite reversibility, e.g. particularly as occurs with some compositions with an M_s of 0°C or higher, can be inhibited. This method comprises 'aging' the composition by holding it at an elevated temperature, typically 50-150°C, in which it exists in the austenitic state prior to transforming it to the martensitic state. The aging temperature and the holding time required to inhibit loss of this reversibility vary according to the nature of the composition but may be readily determined by those skilled in the art having the benefit of the disclosure in the application.

As a result of these two discoveries, it has been found possible to prepare useful heat recoverable articles from metallic compositions which as a result of the treatment have a significantly reduced tendency to lose martensite-austenite reversibility and which also have an elevated A_s temperature. However, notwithstanding the many advantages of these

discoveries in order to elevate the A_s temperature for metallic compositions it is necessary that equipment capable of providing a controlled 'slow' heating rate be employed. Furthermore, it is necessary that some preliminary investigation be done with compositions other than those specifically described in order to determine the optimum slow heating rate. Finally, the 'slow' heating rate necessary to avoid the onset of recovery may necessitate an undesirably long preconditioning period to achieve the desired A_s. Therefore, it would be advantageous to have a method by which an elevated A_s can be imparted to metallic compositions capable of undergoing a reversible transformation between an austenitic state and a martensitic state that does not suffer these limitations.

Accordingly, it is an object of this invention to provide a further method for imparting an elevated A_s for at least one heating cycle to metallic compositions that undergo a reversible transformation between an austenitic state and a martensitic state.

The present invention provides a method for treating an article made from a memory which is capable of undergoing a reversible transformation between austenitic and martensitic states, the method comprising holding the article in a deformed configuration under constraint at a temperature above M_s for a time sufficient to cause at least a portion of the deformation to be retained when the constraint is removed. The present invention also provides an article treated by said method.

The method of the present invention may be termed 'mechanical preconditioning'. The holding period for a given alloy may be determined by routine experiment. In general, the minimum useful period to obtain the effects desired will depend on the holding temperature, but may be, for example 10 seconds at 200°C, 10 minutes at 100°C, and one hour at room temperature. The amount of deformation retained is a function *inter alia* of the temperature at which the composition is held and the duration of the holding step.

An article made of the compositions under consideration can initially be deformed while in the austenitic state. Normally, however, this requires a great deal of force. Accordingly, it is preferred initially to deform the composition while it is in the more workable condition that occurs near or within the M_s-M_f range and then to raise its temperature while it is still under constraint to the desired holding temperature above M_s.

After the treatment the article may be cooled to below M_s, preferably to a temperature below the M_s-M_f range, in order to render it heat-recoverable. This is preferably done before the constraint is removed.

A mechanically preconditioned heat-recoverable article so produced will when heated to a fast rate recover at least partially to its initial configuration.

It is known that the application of a load or stress to an article of a metallic composition in the austenitic state, for example by applying tension, compression or tension or by bending the sample, can result in an introduction of strain in the sample by means of a stress induced transformation of a portion of the austenite to martensite. This strain, which disappears when the load is removed, is referred to as 'pseudoelastic strain' because its effects differ from those of normal elastic behaviour in that strain does not vary linearly with stress. See H. Pops, *Met. Trans.* 1 (1) 251-58 (1970). The strain disappears because the transformation to martensite induced by the applied stress is reversed back to austenite in an elastic, but non-Hookeian, manner. Generally, there exists a maximum temperature up to which stress induced martensite formation will occur. This temperature, which varies with the metallic composition, is usually and herein referred to as M_d.

The reversibility between stress induced pseudoelastic martensite and the austenitic state is a phenomenon that is superficially similar to the shape emory effect observed when a sample of a metallic composition that has been deformed while in a low temperature stable martensitic state undergoes a return to its original configuration when heated to a temperature range over which the martensite reverts to austenite. The major differences between this phenomenon and that associated with pseudoelastically produced martensite are that, in the latter, the formation of martensite is localized at the area of stress and the transition from martensite to austenite, as well as the reverse, is an isothermal one.

For the latter reason, reversible pseudoelastic strain, while of theoretical interest, does not lend itself to the practical applications that are possible when utilization is made of the thermally recoverable strain achieved by deforming a sample of a metallic composition below its M_f and holding it there until it is desired to recover the strain. However, as pointed out below, this latter process will frequently require that the sample be kept at a relatively low temperature; i.e. below A_s, to prevent recovery until desired unless the temperature at which the onset of the transition to austenite normally occurs (A_s) can be advanced sufficiently to allow the sample to be kept and handled without recovery at ambient temperature. The only method other than by the present invention by which this has been possible is the hereinabove discussed method of 'thermal preconditioning'.

By using the 'mechanical preconditioning' method of the present invention the reversion (or recovery) of a deformed metallic article to its original configuration in the austenitic state

is prevented from occurring until it reaches a temperature above the normal A_s, i.e. the normal reversion temperature associated with the given metallic composition. This is achieved by deforming the article from an original configuration and holding it in that deformed condition at a temperature above M_s, but, preferably, below M_d, for a period of time sufficient that it retains at least a portion of the originally imparted strain when the holding stress is released. Subsequent fast heating of the article, i.e. at a rate that precludes further elevation of A_s by thermal preconditioning, normally and preferably 100°C/min or greater, will result in the recovery of at least a portion of that retained strain. Thus the metallic composition from which the article is made has an A_s-A_f range that is elevated in comparison to the A_s-A_f range normally associated with it and its hysterises loop is thereby expanded.

Generally speaking, the method of this invention is applicable to the wide variety of metallic compositions that undergo reversible austenite-martensite transformations. It is particularly suited to metallic compositions that are alloys, and more particularly, to alloys that form electron compounds. Preferred electron compounds are those corresponding to the Hume-Rothery designation for structurally analogous body-centered cubic phases (e.g. ß-brass) or electron compounds that have ratios of about 3 valence electrons to 2 atoms. See *A.S.M. Metals Handbook*, Vol. 1, 8th Ed. (1961) at p.4.

Among suitable alloys may be included ß phase alloys, for example, those typified by the copper-zinc and copper-aluminum alloys that form ß alloys of the body-centered cubic type associated with ß-brass. Among these are those alloys of copper zinc or copper aluminum in which zinc and aluminum may at least partially replace each other and which themselves can be partially replaced by other alloying elements for example, silicon, tin, manganese or mixtures thereof. Some alloys within this description are discussed in detail in our aforementioned copending application disclosing the thermal preconditioning process. Preferred alloys include those containing (apart from incidental impurities) from about 60-85 wt. % copper with varying amounts of zinc and/or aluminum, advantageously, in combination with silicon, manganese or mixtures thereof, for example, alloys that form body centred cubic type structures having up to 40 wt. % zinc, and/or up to about 14 wt. % aluminum together with 0 to about 5 wt. % silicon, and/or to about 15 wt. % manganese. Ternary, quaternary, and more complex alloys of copper can be used. In the Examples, a number of specific alloys that fall within these limits will be discussed in greater detail. However, it shuld be understood that the method of this invention may be applied beyond the limits of the preferred embodiments. For example, it is within the scope of this invention to apply the method of the present invention to alloys based on metals other than copper.

Alloys of this type are obtained in a ß-phase by methods well known to the art. Usually the ß-phase is obtained by rapidly quenching the alloy from an elevated temperature at which it exists in substantial part as a stable ß-phase to a temperature at which it will exist as a metastable ß-phase. If the quenching rate is too slow, extensive amounts of a second phase may form which does not undergo the reversible austenite-martensite transformation. However, an alloy that is at least substantially in the ß-phase, e.g. over 70% beta, may still possess to a substantial extent the same useful properties as the pure ß-phase structure.

If the alloy is quenched to below its M_s temperature, the ability to be subsequently rendered heat recoverable can be adversely affected. Accordingly, it is desirable to quench the alloy to a temperature above M_s at a rate such that no significant α-phase formation will result. For alloys with an M_s below about 0°C, a quenchant temperature of about 20°C is satisfactory. This can be achieved, for example, by quenching the alloy in water at 20°C.

The chosen alloy employed is fabricated into an article having the shape desired after heat recovery. The deformation of the article into the configuration from which heat recovery is desired, i.e. a configuration which will ultimately be that of the heat unstable (i.e. heat recoverable) state, is preferably accomplished at temperatures below the M_d temperature. For example, the deformation can be accomplished while the article is in the austenitic state whereby the initial strain introduced into the article will be of the 'pseudoelastic' type since its unduly rapid release would result in the deformation undergoing the previously described isothermal recovery. Nevertheless, by holding the article in the deformed condition for a suitable length of time, at least a portion of the originally 'pseudoelastic' strain will be converted into strain that is retained after the stress is removed. That portion of the originally pseudoelastic strain that is not retained can be referred to as 'springback'.

To recover the retained strain, the sample having been returned to the martensitic state is rapidly heated, as hereinbefore described, through the temperature range in which the transformation to austenite occurs. Any portion of the retained strain that does not recover, a not uncommon occurrence in the case of martensite-austenite transformation, is referred to as 'non-recoverable strain'. The rate of heating necessary to recover the strain must be sufficiently 'fast' to avoid the effect of 'thermal preconditioning' as previously described because if an article is heated unduly slowly recovery will not occur. Since a suitable rate will vary according to the nature of the alloy, it is not possible to specify absolute rates of heating

which would qualify as 'slow' or 'fast' for all alloys. However, the significance of these terms will be clear from the previous discussion herein and from a consideration of our copending application relating to 'thermal preconditioning', the disclosure of which has been incorporated herein by reference. With that information, a rate of heating qualifying as 'fast' is readily ascertained.

If held long enough in the deformed state essentially all the original strain will be retained when the stress is removed. The length of time necessary to have significant retained strain at a given temperature varies according to the compositon and the thermomechanical history of the alloy. Generally speaking, for a given alloy the length of the necessary holding time decreases as the holding temperature increases. Nevertheless, there may be a penalty incurred if the holding temperature is too high as a significant portion of the retained strain may be rendered non-recoverable. However, 'mechanical preconditioning' has been carried out at temperatures as high as about 200°C. From this discussion, it will be apparent that the optimum combination of holding temperature and period of constraint, i.e. the period during which the article is under stress, will depend on the alloy but that this combination can be readily ascertained. In an optimum case up to about 10% heat recoverable strain is achievable with articles treated by the method of this invention.

In the case of 'thermal preconditioning', the temperature of the elevated A_z, referred to as A_{se}, is often approximately at the temperature where the slow heating is terminated. This is not the case with the 'mechanical preconditioning' method of this invention. It can be below, at or above the holding temperature. In general, it increases as the length of the holding time is increased. Routine experiment with a given alloy will make it possible to determine the amount of preconditioning necessary to achieve the desired elevation in A_s. Storage at ambient temperature after mechanical preconditioning may result in a loss of some heat recoverability but does not affect the elevated A_s temperature.

As indicated above, in a presently preferred embodiment of this invention, the article is deformed from its original configuration while in the austenitic state, i.e. under conditions where the initial strain induced in the article may be regarded as essentially 'pseudoelastic'. However, metallic compositions suitable for use in this invention are usually more easily deformed as their temperature is lowered from the holding temperature, e.g. until near, within or below the M_s-M_f range. Accordingly, it is within the scope of this invention initially to lower the temperature of the article, for example, to below the M_s-M_f range, to facilitate its deformation, deform it and then to heat it while using constraining means to keep it deformed while the desired holding temperature above the normal A_s-A_f range is reached, and maintained for the required time.

In contradistinction to the situation with the 'thermal preconditioning' process, the rate of heating to reach the elevated holding temperature need not be a 'slow' one, as heretofore defined, as recovery for the deformation is prevented by the constraining means. However, certain advantages accrue from the use of a controlled 'slow' heating rate to reach the elevated temperature. One advantage is that damage to the article caused by the force exerted against the constraining means during fast heating as the article attempts to recover is avoided or minimized because stresses occasioned by the onset of recovery are substantially diminished. Secondly, it is possible to precondition alloys in this way that are only marginally suited to purely thermal or mechanical preconditioning. In view of the fact that stress induced martensite forms locally, it is also within the scope of this invention to impart to an article an elevated A_s by mechanical preconditioning and then cool the article to below its normal M_s, and deform it again giving it a dual A_s. The second A_s can be advanced by thermal preconditioning to a temperature below that of the A_s imparted by mechanical preconditioning.

Although the constraining means can be removed at the holding temperature, two advantages flow from the additional step of cooling the deformed article to a lower temperature prior to such removal. The first is that cooling, for example, to the M_s-M_f range or below, may reduce the work needed to remove the constraining means. Secondly, by cooling the article under constraint from the holding temperature to a lower temperature, an additional increment of heat recoverable strain can be imparted to the article. After the constraining means has been removed, this increment of strain is usually recovered during a subsequent 'fast' heating step over the temperature interval defined by the temperature at which the constraining means is released and the holding temperature. This additional increment of strain has its own A_s temperature. In other words, the article has a 1st A_s below the A_s (2nd A_s) imparted by mechanical preconditioning. As a result, a two stage heat recovery can be obtained.

As explained in our British Patent Specification No. 1,490,182, some metallic compositions also respond better to thermal and mechanical preconditioning if aged while in the austenitic state in that a higher portion of the retained strain is heat recoverable. However, if the mechanical preconditioning conditions are the same, the A_s temperature imparted to an

unaged sample is often somewhat higher than that of an aged sample of the same composition. For those beta phase alloys of copper containing varying amounts of zinc, aluminum, silicon, manganese and combinations thereof having an M_s temperature below room temperature aging at from about 50°C to 125°C for a time ranging from about 5 minutes to 3 or 4 hours is usually adequate. For other compositions, the time and temperature that will produce the optimum results may vary but is readily ascertained by comparing the amount of heat recoverable strain retained by samples of the same composition aged under different conditions.

The end use to which the article is put will determine its recovered and recoverable configuration. The deformation force applied to the preconditioned article can be any of a variety of types including bonding, twisting, compressing and expansion forces and may employ any convenient constraining means. In this way, articles that recover from an L to an I shape and vice versa can be obtained. Articles that lengthen or shorten are also possible. Hollow articles, particularly cylindrical ones, that expand to a larger diameter or that contract to a smaller diameter are readily made by the process of this invention. As a result of the fact that mechanical preconditioning occurs in the area of the stress it is possible to precondition a portion only of the article. This allows a series of deformations to be built into the article which can recover at different temperatures.

The following Examples illustrate the invention:

Example 1

A 38 mm x 5 mm x 0.75 mm strip of brass containing 64.6 wt. % Cu-34.4 wt. % Zn-1.0 wt. % Si was betatized at 800°C, then water quenched. After this treatment, the M_s was at +20 and the strip was pseudoelastic at room temperature, that is, the A_s and A_f were below room temperature.

The strip was bent into a loop at room temperature (outer fibre strains 7%) and clamped for one hour. Upon release, the loop remained bent (retained outer fibre strain ~5%). When heated to 200°C, the strip became straight again.

Example 2

A 14 cm length of 0.9 mm diameer wire made up of 70 wt. % Cu-26 wt. % Zn-4 wt. % Al was betatized at 700°C for three minutes, then water quenched. After this treatment, the wire was pseudoelastic at room temperature and had an M_s at −3°C.

The sample was bent so as to have an outer fibre strain of 4.3% and constrained in this configuration at room temperature. From time to time, the constraining means was released, the retained strain measured, then the wire was returned to its constraint. Retained strain increased as follows:

Days	*Retained Strain %*
0	0
3	1
18	1.4
193	2.8
252	2.9

After the last measurement, the bent wire was immersed in oil at 200°C. It straightened immediately. This example demonstrates the effect on the retained strain of prolonging the holding time.

Example 3

Samples were cut from 0.76 mm sheets of the alloy compositions listed below. The strips were betatized at 800°C and water quenched. All were pseudoelastic at room temperature, as their low M_s temperatures would suggest. The samples were bent and constrained at room temperatures so as to cause an outer fibre strain of 4.25%. The samples and constraining fixtures were transferred to a bath at 200°C and held for 72 hours. Next, the constrained samples were cooled to room temperature. Virtually no springback occurred as the samples were removed from the constraining means. The samples were then rapidly heated. Both the heat recoverable strain and the temperature range over which it occurred are listed in the table below:

Composition % by weight	M_s	Elevated HRS	A_s	A_f
74Cu 18Zn 7Al 1Mn	—40°C	0.5%	375°C	500°C
76Cu 12Zn 8Al 4Mn	—44°C	2.3%	375°C	525°C
77.5Cu 9.5Zn 9Al 4Mn	—40°C	2.75%	350°C	525°C
77.75Cu 8.25Zn 9Al 5Mn	—28°C	2.3%	300°C	500°C
79.1Cu 5.9Zn 10Al 5Mn	—40°C	3%	350°C	525°C
79Cu 4Zn 10Al 7Mn	—40°C	2.2%	350°C	525°C
77.5Cu 7.5Zn 9Al 6Mn	—50°C	1.6%	375°C	525°C
78.25Cu 5.75Zn 9Al 7Mn	0°C	1.7%	400°C	525°C

This example demonstrates that the A_s temperature imparted to the alloy is not dependant upon the temperature at which the preconditioning is accomplished.

Example 4

In that a number of variables are important to successful mechanical preconditioning, an experiment was designed to test several variables simultaneously. Five variables were tested at each of two levels, thus the experimental design was 2^5 factional. The variables were:

	Betatization	Cooling Rate	Strain	Holding Temp.	Holding Time
high level	650°C - 5 min.	Air Cool	7.10%	125°C	150 min.
low level	575°C - 5 min.	Water quench and age 50°C-5min.	4.53%	50°C	15 min.

The experimental design was exercised using four alloys:

Weight Percent

Cu	Al	Mn	Air Cooled	WO + 5 min. 50°C
79.2	10.0	10.8	—10C	—32C
78.9	10.0	11.1	—41	—45
79.04	9.86	11.1	—30	—47
79.07	10.13	10.8	—14	—32

Samples were prepared by air-melting the compositions above, coasting and rolling the 0.76 mm sheet. Strips were cut from the sheet, and betatized by heating 5 minutes at 575°C or 650°C. Next, the samples were water quenched and aged 5 minutes at 50°C or air cool. All the samples were cooled to −60°C then deformed and constrained either 4.53 or 7.1% by bending the samples around a mandrel and placing them in a clamping fixture. The samples and their constraining fixtures were transferred to baths at 50°C or 125°C and held for 15 minutes or 150 minutes. After the holding process, the samples and constraining fixtures were cooled to −80°C, the constraints were removed and the retained strain measured. The unconstrained samples were transferred to a bath at 0°C, and again the retained strain was measured. This procedure was repeated with baths at 20°C, 50°C, 100°C and 400°C. The resulting strain measurements were analyzed to determine the magnitude of the main effects and interactions with respect to the ranges over which the variables were exercised.

The strain which was heat recoverable in the temperature range aboe 50°C was taken as a measure of performance. Statistical analysis indicated significance for the main effect of *strain* average 1.95%, and hold temperature, average 1.65%. The other main effects and interactions were not significant in this experiment.

Within this experimental design, the best conditions were 7.1% strain at a holding temperature of 125°C. This gave an average of 3.81% heat recoverable strain above 50°C.

Example 5

An alloy containing 64 wt. % copper, 35 wt. % zinc and 1 wt. % silicon was studied. This alloy has an M_s temperature of −40°C.

Specimens were betatized for 5 minutes at 860°C, quenched into water at 20°C, and then aged for different times in the metastable beta phase, which in this series of experiments was performed at 50°C. After insertion in the tensile loading device (approximately 5 minutes to set up at ambient temperature) the specimens were cooled to −65°C and deformed 8% in tension. After deformation, a constraint was applied to the tensile rig so that no contraction could take place, but the specimens were free to undergo a spontaneous expansion if one occurred. The constrained specimen was placed in water at +40°C, which provides a very fast heating rate, and was held at that temperature for different times before re-cooling to below the M_f. Specimens came free of the constraint during cooling with a slight expansion compared with the original set after deformation. The constraint was removed from the apparatus so that specimens, now in their 'preconditioned' state, could heat recover freely when reheated at a 'fast' rate in a furnace set at 600°C.

The A_s temperatures and heat-recoverable strains were measured as a function of the two main variables, aging time at 50°C before deformation and the time held under constraint at 40°C.

Results of 'mechanical preconditioning' are shown in Table 1. For each aging time at 50°C some specimens have also been fast heated directly after deformation at −65°C, in order to compare the effect of 'mechanical preconditioning' on the A_s temperature.

Table 1 shows clearly the trend that the 2nd A_s temperature was raised as the holding time at 40°C was increased and in many cases exceeded the temperature of 40°C. On the other hand, the total heat-recoverable strain (i.e. 1st A_s to A_f) was reduced with increased holding time at 40°C, and this loss in recovery occurred mainly in that portion of heat-recoverable strain between the 2nd A_s and A_f.

Table I

Aging Time	Pre-cond. Holding Time at 40°C	Strain Per Cent	A_s Temp. °C 1st	A_s Temp. °C 2nd	Recovery above 2nd A_s per cent strain	Total Recovery per cent strain
	No Precond.	7.05	—50—		—	6.50
5 mins	10 secs	6.90	—43—	4	5.65	6.80
at R.T.	30 secs	7.10	—37	31	4.15	5.65
	1 min.	6.90	—40	19	4.80	5.90
	5 min.	7.65	—37	59	2.90	3.95
	10 min.	6.95	—17	23	2.80	3.55
	1 hr.	7.10	—45	19	3.10	4.00
	No Precond.	7.25	—33—		—	6.95
45 mins	10 secs	6.75	—49—	9	5.30	6.55
at 50°C	30 secs	6.35	—52	4	4.40	5.85
	1 min.	7.10	—43	23	4.45	5.70
	5 min.	7.35	—40	20	5.60	7.00
	10 min.	7.20	—51	19	3.65	5.15
	1 hr.	7.55	—44	54	2.65	4.20
	No Precond.	7.00	—32—		—	6.75
3 hrs.	10 secs	7.25	—41—	4	5.75	7.00
at 50°C	30 secs	7.20	—32	15	4.15	5.65
	1 min.	7.05	—30	19	5.65	6.85
	5 min.	6.85	—47	13	4.80	6.20
	10 min.	7.20	—32	29	5.65	6.65
	1 hr.	7.30	—37	38	4.15	5.25
	5 hrs.	7.15	—44	44	5.60	6.75
	16 hrs.	7.50	—39	80	3.75	5.25
	No Precond.	7.20	—27—		—	6.70
24 hrs.	10 secs	7.05	—37—	4	5.85	6.55
at 50°C	30 secs	7.25	—42—	5	5.80	7.25
	1 min.	7.45	—43	0	5.70	6.95
	5 min.	7.50	—35	24	5.75	6.70
	10 min.	7.50	—42	35	5.85	7.25
	1 hr.	7.80	—34	29	4.70	5.80
	5 hrs.	7.40	—34	35	5.05	5.95
	16 hrs.	7.15	—47	69	2.90	4.70
	No Precond.	7.10	—33—		—	6.80
1 wk	10 min.	7.00	—28	33	5.60	6.45
at 50°C	1 hr.	7.25	—37	47	5.20	6.20
5 hrs.	7.45	—37	40	5.15	6.70	
16 hrs.	7.55	—40	33	5.60	6.70	

Increasing the aging time at 50°C, in metastable beta phase, greatly improved the overall heat-recoverable strains (HRS's) but had only a slight effect in reducing the 2nd A_s temperature.

The effect of storage at room temperature was also examined. After the mechanical preconditioning treatment specimens were cooled and the constraint removed, as previously. Instead of directly heating at a fast rate, the specimens were allowed to warm to room temperature (20°C ± 2) at which temperature they were stored for up to three weeks. After storage, specimens were replaced into the testing rig, and heated directly from room temperature to above the A_f temperature.

As an example, one specimen was aged 1 week at 50°C and held in restraint for 16 hours at 40°C (the last result in Table 1) The efficiency of heat recovery when directly heated from the M_f after releasing the constraint was 74%. This value fell to 57.4% after storage for two days, 47.8% after one week, and 46.4% after three weeks at 20°C. The second A_s temperature remained constant at about 35°C.

Example 6

An alloy containing 63.5 wt. % copper, 35.5 wt. % zinc and 1.0 wt. % aluminum was studied. Experimental conditions for 'mechanical preconditioning' of this alloy were exactly the same as described in Example 5, except the deformation temperature which was −50°C. The alloy had an M_s approximately −248C. Specimens were again aged in metastable beta phase at 50°C, and held under constraint at 40°C.

For specimens aged 3 hours at 50°C, and immediately fast-heated after deformation at −50°C, 1st A_s = −13°C, but no 2nd A_s was observed, HRS=7.20% (94% efficiency). Results of a specimen aged 3 hours at 50°C and mechanically preconditioned are shown in Table II. Compared with the previous example of a copper-zinc-silicon alloy, the rise in 2nd A_s temperature is not as high in this alloy.

Table II

Aging Time	Pre-Cond. Holding Time	Strain per cent	A_s temp. °C 1st	2nd	Recovery above 2nd A_s percent strain	Total Recovery percent strain
3 hrs at 50°C	10 secs	7.75	—35	—1	6.0	7.10
	30 secs	7.60	—13	40	5.45	6.40
	1 min	7.95	—32	—5	5.60	5.90
	5 min	8.40	—19	14	6.80	7.45
	10 min	7.65	—24	17	6.00	6.60
	1 hr	8.10	—15	34	5.05	6.45
	5 hr	7.60	—22	20	5.55	6.45
	16 hr	8.00	—24	25	5.90	6.55

Example 7

An alloy containing 65.75 wt. % copper, 32.25 wt. % zinc and 2.00 wt. % aluminum having an M_s of approximately −25°C was studied.

This alloy was treated in the same way as the previous alloy, and was aged at 50°C prior to deformation and held at 40°C under constraint in the mechanical preconditioning treatment. Table 3 shows the results for this alloy when aged for 3 hours at 50°C.

Results for an unconditioned sample of this alloy, aged 3 hours at 50°C and immediately fast heated after deformation at −50°C were:

1st A_s = −35°C, no 2nd A_s, HRS = 7.10 (98% efficiency).

As shown in Table III below the 2nd A_s temperatures in this alloy were not raised as much as the previous alloy containing 1% aluminum, but correspondingly the heat recoverable strains are very high.

Table III

Aging Time	Pre Con. Holding Time at 40°C	Strain per cent	A_s Temp. 1st	C. 2nd	Recovery above 2nd A_s percent strain	Total Recovery percent strain
3 hrs at 50°C	10 secs	6.60	—47	—10	5.85	6.30
	30 secs	7.50	—40	—8	6.85	7.35
	1 min	6.85	—19	15	5.75	6.50
	5 min	7.10	—34	—9	5.95	6.60
	10 min	7.10	—22	11	5.45	6.75
	1 hr	7.70	—24	21	5.25	7.30
	5 hr	7.75	—19	8	5.65	6.65
	16 hr	7.65	—25	19	6.40	7.20

It should be pointed out that the aluminum-containing alloy of this example and that of Example 6 could not readily be treated to have a raised A_s temperature by thermal preconditioning, as it was not possible in practice to prevent heat recovery during slow heating to the preconditioning temperature.

The same alloy was also aged in the beta phase at 100°C and held at 40°C, and aged at 50°C and held under constraint at 80°C. The results from these treatments are shown in Table IV, for specimens aged 3 hours at the appropriate temperature and held for different times in the stress-induced martensite state.

Table IV

Aging Time	Pre Con Holding Temp (°C)	Pre Con Holding Time	Strain per cent	A106s Temp 1st	C 2nd	Recovery above 2nd A_s per cent strain	Total Recovery percent strain
3 hrs at 100°C	40	10 mins	7.15	—40	—6	5.65	6.50
		1 hr	7.70	—33	—2	5.75	6.60
		5 hrs	6.10	—28	23	4.35	5.35
		16 hrs	7.35	—29	20	5.70	6.65
3 hrs at 50°C	80	10 min	7.80	—33	43	4.85	6.10
		1 hr	6.75	—32	53	3.40	5.10
		5 hr	8.25	—26	102	1.90	3.30

The overall effect of the higher aging temperature is to reduce the raised A_s temperature and increase heat recoverable strains.

The increase in preconditioning temperature from 40°C to 80°C has a much greater effect than the aging temperature on the raised A_s temperature. As shown in Table IV increasing the holding time at 80°C from 10 minutes to 5 hours raises the preconditioned (2nd) A_s from 43°C (i.e. less than the holding temperature). Heat recovery is correspondingly reduced as the 2nd A_s temperature increases.

Example 8

An alloy containing 62.2 wt % copper, 37.3 wt % zinc and 0.5 wt. % aluminum having an M_s of −33°C and an alloy containing 67.5 wt. % copper, 29.5 wt. % zinc and 3.0 wt. % aluminum having an M_s of −30°C were studied. These alloys were treated in the manner as described for the other copper-zinc-aluminum alloys in Examples 6 and 7. Results of mechanical preconditioning after aging in the beta-phase for three hours at 50°C and holding under constraint for different times at 40°C, are shown in Table 5. Under the same experimental conditions the heat recoverable strains between the 2nd A_s temperature and A_f are greater in the 3% aluminum alloy than in the alloy with 0.5% aluminum.

Table V

Alloy	Aging Time	Pre Cond. holding time (40°C)	Strain per cent	A_s Temp 1st	C 2nd	Recovery above 2nd A_s per cent strain	Total Recovery percent strain
62.2% Cu	3 hrs at 50°C	10 mins	8.20	—41	24	3.15	4.10
		1 hr	8.35	—39	34	3.80	4.80
		5 hr	7.90	—44	12	4.90	5.95
		16 hr	8.15	—47	29	4.25	5.30
67.5% Cu	3 hrs at 50°C	10 mins	6.65	—27	8	5.75	6.40
		1 hr	7.25	—40	24	5.35	6.60
		5 hr	7.15	—33	11	6.05	6.60
		16 hr	7.60	—21	26	5.15	6.60

WHAT WE CLAIM IS:

1. A method for treating an article made from a memory metal composition which is capable of undergoing a reversible transformation between austenitic and martensitic states, the method comprising holding the article in a deformed configuration under constraint at a temperature above M_s for a time sufficient to cause at least a portion of the deformation to be retained when the constraint is removed.
2. A method as claimed in claim 1, wherein the article is held under constraint, at a temperature below M_d.
3. A method as claimed in claim 1 or claim 2, wherein the article is initially deformed while in the austenitic state.
4. A method as claimed in claim 1 or claim 2, wherein the article is initially deformed at a temperature below the holding temperature and its temperature is then raised to the holding temperature while it is still under constraint.
5. A method as claimed in claim 4, wherein the article is initially deformed at about M_s.
6. A method as claimed in claim 4, wherein the article is initially deformed at a temperature within the M_s-M_f range.
7. A method as claimed in claim 4, wherein the article is initially deformed at a temperature below the M_s-M_f range.
8. A method as claimed in any one of claims 1 to 7, wherein after completion of the

Table IV

Aging Time	Pre Con Holding Temp (°C)	Pre Con Holding Time	Strain per cent	A106s Temp 1st	C 2nd	Recovery above 2nd A_s per cent strain	Total Recovery percent strain
3 hrs at 100°C	40	10 mins	7.15	—40	—6	5.65	6.50
		1 hr	7.70	—33	—2	5.75	6.60
		5 hrs	6.10	—28	23	4.35	5.35
		16 hrs	7.35	—29	20	5.70	6.65
3 hrs at 50°C	80	10 min	7.80	—33	43	4.85	6.10
		1 hr	6.75	—32	53	3.40	5.10
		5 hr	8.25	—26	102	1.90	3.30

The overall effect of the higher aging temperature is to reduce the raised A_s temperature and increase heat recoverable strains.

The increase in preconditioning temperature from 40°C to 80°C has a much greater effect than the aging temperature on the raised A_s temperature. As shown in Table IV increasing the holding time at 80°C from 10 minutes to 5 hours raises the preconditioned (2nd) A_s from 43°C (i.e. less than the holding temperature). Heat recovery is correspondingly reduced as the 2nd A_s temperature increases.

Example 8

An alloy containing 62.2 wt % copper, 37.3 wt % zinc and 0.5 wt. % aluminum having an M_s of −33°C and an alloy containing 67.5 wt. % copper, 29.5 wt. % zinc and 3.0 wt. % aluminum having an M_s of −30°C were studied. These alloys were treated in the manner as described for the other copper-zinc-aluminum alloys in Examples 6 and 7. Results of mechanical preconditioning after aging in the beta-phase for three hours at 50°C and holding under constraint for different times at 40°C, are shown in Table 5. Under the same experimental conditions the heat recoverable strains between the 2nd A_s temperature and A_f are greater in the 3% aluminum alloy than in the alloy with 0.5% aluminum.

Table V

Alloy	Aging Time	Pre Cond. holding time (40°C)	Strain per cent	A_s Temp 1st	C 2nd	Recovery above 2nd A_s per cent strain	Total Recovery percent strain
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		1 hr	8.35	—39	34	3.80	4.80
		5 hr	7.90	—44	12	4.90	5.95
		16 hr	8.15	—47	29	4.25	5.30
67.5% Cu	3 hrs at 50°C	10 mins	6.65	—27	8	5.75	6.40
		1 hr	7.25	—40	24	5.35	6.60
		5 hr	7.15	—33	11	6.05	6.60
		16 hr	7.60	—21	26	5.15	6.60

WHAT WE CLAIM IS:

1. A method for treating an article made from a memory metal composition which is capable of undergoing a reversible transformation between austenitic and martensitic states, the method comprising holding the article in a deformed configuration under constraint at a temperature above M_s for a time sufficient to cause at least a portion of the deformation to be retained when the constraint is removed.
2. A method as claimed in claim 1, wherein the article is held under constraint, at a temperature below M_d.
3. A method as claimed in claim 1 or claim 2, wherein the article is initially deformed while in the austenitic state.
4. A method as claimed in claim 1 or claim 2, wherein the article is initially deformed at a temperature below the holding temperature and its temperature is then raised to the holding temperature while it is still under constraint.
5. A method as claimed in claim 4, wherein the article is initially deformed at about M_s.
6. A method as claimed in claim 4, wherein the article is initially deformed at a temperature within the M_s-M_f range.
7. A method as claimed in claim 4, wherein the article is initially deformed at a temperature below the M_s-M_f range.
8. A method as claimed in any one of claims 1 to 7, wherein after completion of the

treatment, the constraint is removed and wherein the temperature of the article is lowered below M_s prior to removal of the constraint.

9. A method as claimed in claim 8, wherein the temperature is lowered to within the M_s-M_f range prior to removal of constraint.

10. A method as claimed in claim 8, wherein the article is cooled to below the M_s-M_f range prior to removal of the constraint.

11. A method as claimed in any one of the preceding claims in which the article is initially deformed while in the martensitic state, and wherein it is slowly heated to the holding temperature.

12. A method as claimed in any one of claims 1 to 11, wherein, prior to its deformation, the article is held at a temperature above M_s while in the austenitic state for a time sufficient to reduce the loss of reversibility between the martensitic and austenitic states and to improve its amenability to treatment by the method.

13. A method as claimed in any one of claims 1 to 12, wherein the metal is an alloy that forms an electron compound.

14. A method as claimed in claim 12, wherein the alloy is a body centered cubic type analogous to beta-brass having a ratio of about 3 valence electrons to 2 atoms.

15. A method as claimed in any one of claims 1 to 12, wherein the metal is a beta-phase alloy comprising copper and zinc or copper and aluminum.

16. A method as claimed in claim 15, wherein the metal is a beta-phase alloy comprising by weight 60-85% copper, up to 40% zinc and/or up to 14% aluminium; 0-5% silicon, and/or 0-15% manganese.

17. A method as claimed in claim 15 or claim 16, wherein the alloy comprises copper, zinc and silicon.

18. A method as claimed in claim 15 or claim 16, wherein the alloy comprises copper, zinc and aluminium.

19. A method as claimed in claim 15 or claim 16, wherein the alloy comprises copper, zinc, aluminium and manganese.

20. A method as claimed in claim 15 or claim 16, wherein the alloy comprises copper aluminium and manganese.

21. A method as claimed in claim 15 or claim 16, wherein the alloy is as specified in any one of the Examples herein.

22. A method as claimed in claim 1, conducted substantially as described in any one of the Examples herein.

23. An article which has been treated by a method as claimed in any one of claims 1 to 22.

24. An article as claimed in claim 23, which is heat-recoverable.

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