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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.

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 in British Patent 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 a material in its low temperature state, while "austenite" and "austenitic" are used to denote material 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 undeformed 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 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 the transformation to austenite are designated A_s and A_f . Generally, M_s is a lower temperature than A_s , M_f is a lower temperature than A_s , 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, 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, 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 an article by P. V. Titov and L. G. Khandros, *Naukova Dumka*, Kiev, 1970, 199-204, it is disclosed that by means of a rapid heating rate from temperature M_s , it is possible to lower the A_s of a copper-tin alloy to -125°C , and conversely, by employing a slow heating rate, A_s can be raised to $+90^\circ\text{C}$. The authors stated, however, that the copper-tin system appeared to be unique; with a copper-aluminum-nickel alloy, changes in heating rate from 15 to $0.01^\circ\text{C}/\text{sec}$. (those described in this paragraph as rapid and slow) did not affect A_s .

The present invention provides a heat-recoverable article made from a 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. The composition will accordingly have an A_s higher than that 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) austenite is produced at an elevated temperature and quenched "initially formed" denotes such material when initially brought to ambient temperature. Stated another way, this 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 and if the article has been deformed, the temperature at which it will recover, or tend to recover, its original configuration is increased.

The present invention also 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., at less than $1^\circ\text{C}/\text{min}$., heating the alloy from a temperature below its M_s to a temperature in the region to which it is desired to change the A_s . 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., $5^\circ\text{C}/\text{min}$. or greater; preferably $100^\circ\text{C}/\text{min}$. or greater, and the A_s will be found to be determined by and often approximately at the temperature to which it was heated slowly. The present invention also provides an alloy having the properties produced by the above method. This method is referred to hereinafter as "preconditioning", and the resulting alloy as "preconditioned".

For the purpose of illustration, a part that must be serviceable to temperatures as low as -30°C will be considered. For this, an alloy would be selected which has the beginning of transformation on cooling at or below -30°C . For copper-based beta phase alloys, the temperature at which recovery of original shape would begin

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on heating would also be approximately -30°C and the return to the original shape would be completed over the next 40 to 50°C . Thus, by room temperature, the part would have regained its original shape as shown in Fig. 1 of the accompanying drawings. For purposes of comparing recovery characteristics, a more useful graphic presentation is achieved by recording the amount of recovery which occurs during each interval of heating, that is, by plotting the first derivative of the curve in Fig. 1, see Fig. 2. By the present invention, the recovery range can be moved from its usual position at (a) in Fig. 2 to the new position (b).

One alloy that begins to transform on cooling at about -30°C has a composition 66.45 wt. % Cu, 31.55 wt. % Zn, 2.00 wt. % Si. The alloy can be melted and worked into its desired final shape by conventional means. The shaped part is then heated into the all-beta field, i.e., 700°C or higher, but below 950°C . After several minutes at this temperature, the part is quenched into water, then cooled for example by solid carbon dioxide and ethyl alcohol to transform it to the low temperature crystal structure. At the low temperature, the part is deformed to its new shape; good results are obtained with strains of 6–10%. The part is then heated slowly, e.g., 0.25 deg.C/min., in order to delay transformation until the desired recovery temperature is reached, e.g., $+40^{\circ}\text{C}$. The part is cooled back to room temperature. When the part is to be returned to its original shape, it is heated rapidly, e.g., 100°C per minute. Recovery will begin in the vicinity of $+40^{\circ}\text{C}$ and will be complete by about 100°C . On cooling, transformation to the low temperature phase will not occur above -30°C . If the part is cooled again to -79°C and reformed, then rapidly heated, recovery begins at -30°C .

It is believed that there may be a maximum in the temperature increase in A_s that can be achieved by the process of the invention. For example, on raising the temperature of β -brass, there is a tendency for the material to change to an equilibrium mixture of α and β materials. This would prevent any further useful rise in A_s . By the process of the invention, however, the A_s of certain alloys has been raised by 100 deg.C, and it is not believed that this is the maximum achievable.

Applicability of the invention is to some extent dependent on the composition of the alloy. Whereas some response to control of the recovery temperature range was found in the alloys described in the Fulmer applications and patents a much more restricted range responded significantly better. The composition range of good response in the Cu-Zn-Si system includes alloys in which the transformation is as low as about -80°C . The change in recovery range on heating has been found to be less mobile (only 10 to 40°C) in Cu-Zn-Al than in Cu-Zn-Si alloys, but significant response is found over wider composition limits than in Cu-Zn-Si. Most of the applications suggested above require the start of transformation on cooling to be below room temperature. As will be shown later, this restriction does not apply to all application. Certain alloy compositions in which transformation on cooling begins at or above room temperature have been found to respond well to the process of this invention. Alloys with good response and with the beginning of transformation on cooling in the vicinity of $+100^{\circ}\text{C}$ have been found in the Cu-Zn-Al and Cu-Zn-Si systems.

The amount of recovery which occurs in the elevated recovery range is decreased if the alloy is held at the temperature at which slow heating is stopped for an extended time before commencing rapid heating or cooling to a lower storage temperature.

In the complete specification of our co-pending application No. 27937/76 (Serial No. 1,490,182), divided from the present application, it is pointed out that while 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 that certain compositions may fail to make the transformation completely from martensite to austenite on heating; this characteristics which is undesirable, is herein denoted as a "tendency to lose reversibility".

In that specification, there is described and claimed 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.

The divided application 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.

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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 that 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 martensitic 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 inhibit loss of the reversible austenite-martensite transformation when the materials are stored at e.g., room temperature. The present invention, therefore, also provides materials which, in addition to having a raised A_s , are storage stable at 23°C. The higher the aging treatment temperature, the shorter the treatment time needs to be.

It is believed that, for a given alloy, there is a range of heating rates, up to a maximum, which qualify as "slow", and a range of rates, from a minimum, which qualify as "fast". Between this maximum and minimum, there is a critical range wherein the A_s temperature will vary between its normal value and a very high temperature.

It is not possible to define numerical ranges for "fast" and "slow" which will be appropriate for all alloys, because this depends on a number of factors. One is that physico-chemical processes are temperature-dependent, and such processes take place very much more slowly at, say, -40°C than at +40°C. For an alloy having M_s at -40°C, it is generally true that both "slow" and "fast" heating rates will be slower than an "otherwise similar" material having M_s at +40°C. Further, as an otherwise similar material will necessarily have slightly different proportions of the component elements, these elements and proportions will in any case affect the limits of "fast" and "slow".

Further, required heating rates are dependent on alloy content and aging time. For example, in an alloy of copper-zinc-silicon with, say, a 1% silicon content or which has been subjected to a short aging time, the critical values of both "slow" and "fast" heating rates are higher than in material with a lower silicon content or longer aging time. It is a matter of routine experiment to determine preferred and critical rates for a given alloy. Suffice it to say, however, that for a given alloy, there will be an upper limit for "slow" heating and a lower limit for "fast" heating, and these limits may be readily ascertained for the given alloy by simple routine experiment.

Preferably, the alloy is an intermetallic compound. Among suitable alloys there may be mentioned β phase alloys, for example those in the copper-zinc and copper-aluminium system, in which zinc and aluminium may replace each other and may be replaced usually in relatively small proportions, by silicon, tin or manganese, or mixtures thereof which alloys may, it is believed, 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; 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% or even 4½% aluminium, these being weight percentages. The processes of the invention are applicable to alloys having, for example, M_s temperatures lower or higher than ambient, and to alloys, for example those based on gold or silver, other than copper-based.

Further alloys are those disclosed in the above-mentioned Fulmer Research Institute's patents and applications.

In the thermal preconditioning method of the invention, the material may be deformed either before the initial slow heating, or after the slow heating and subsequent cooling, the deformation taking place in each case below M_s , advantageously below M_f and preferably just below M_f .

Variables which must be borne in mind when operating the method of the invention are as follows:

Preferably, where it is desired or necessary to quench the material, it is quenched from a temperature within the range 700 or 880°C or in some cases, as high as 950°C. The alloy should be in the β or substantially in the β -phase at the temperature from which it is quenched. A relatively rapid cooling rate from the high temperature is preferred, since too slow a rate allows precipitation of α -phase material, in certain alloys, for example, copper-zinc and copper-aluminium alloys. Quenching to below M_s may adversely affect the heat-recoverable properties, whereas in some cases quenching to much above the M_s may not give sufficiently rapid quench to prevent α -phase precipitation in the copper alloys mentioned above. The preferred quench temperature is one that does not adversely affect heat-recoverable behaviour and about 20°C is convenient in practice especially for alloys with M_s below 0°C.

The heating rate from the low temperature martensite is important. Qualitatively a "slow" heating rate is one which is sufficiently slow to substantially prevent martensite reversal to austenite at and above the normal A_s temperature. For example, rates of 0.01 to 1.0 degrees centigrade/minute are believed to be suitable for copper-zinc alloys containing aluminium and/or silicon. A "fast" heating rate is one that allows a normal A_s temperature when heating directly from the martensite, or one that enables martensite reversion to austenite at a chosen higher A_s temperature when it is used after "slow" heating.

Whereas the process can be used to control the recovery temperature range of unstrained samples, the application of strain interacts with the composition in determining optimum conditions for control of the recovery range. For example, as the strain is increased, lower concentrations of silicon give optimum response in the Cu-Zn-Si system.

Stress, also, must be taken into consideration since the cooling transformation range moves to higher temperatures with higher stress. Similarly the temperature needed for complete recovery on heating is higher if the part recovers under stress or becomes stressed as a consequence of recovering.

The effect of the slow heating treatment of the present invention may be to create a new A_s , termed herein as A_{ss} , at which substantially all of the heat recovery begins to occur upon the application of heating for recovery purposes. Alternatively, the effect of the slow heating treatment of the present invention may be to create a new A_{ss} while retaining some manifestation of the normal A_s . While the applicants are not to be bound to any particular theory of operation of their invention, it is believed that the retention of some manifestation of the normal A_s may result from inherent dominance of the rate of heat recovery at the slow heating rate over the expansion of the hysteresis loop at normal A_s or, alternatively, may be created intentionally by performing the initial portion of the slow heat treatment of the present invention at a rate rapid enough to cause some heat recovery at normal A_s .

It is to be understood from the foregoing that A_{ss} will be determined by that temperature at which slow heating is terminated. Slow heating may be terminated either by cooling or by initiating rapid heating which, if performed for a sufficient length of time, will result in complete transformation of all of the transformable martensite present at the time rapid heating is initiated. Thus, it is contemplated by and within the scope of the present invention to create a new A_{ss} at which useful recovery of an article made from a metallic composition so treated can be initiated.

The configuration in either recoverable or recovered state of articles prepared according to the present invention will depend upon the end use to which the articles are to be put. For example, cylindrical articles may be prepared such that they contract radially inwardly or expand radially outwardly or the configuration may change from twisted to non-twisted or vice versa, or the article may undergo a change in length, or the transition may be from an I to an L shape, etc.

Thus, stated simply, the present invention includes a process for controlling the

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recovery temperature of heat recoverable metallic articles such that the article can be provided with a pre-set recovery range which may be varied over substantial limits simply by terminating slow heating at a selected point.

The products of the present invention will be martensitic over a broader temperature range than products having the same composition but not subjected to treatment according to the present invention. Since martensitic compositions have excellent damping properties, are capable of undergoing deformation without fatigue, deform easily, and have a low Young's modulus, the present invention makes available metallic compositions having these properties which were not previously available.

As described in copending application No. 1,490,182) divided from the present application, there may be provided a method in inhibiting 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.

When metallic articles are subjected to the process of the present inventions and to the process for inhibiting loss of reversibility according to the invention and hence are storage stable, e.g., at 23°C; 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; the present invention also provides articles having an elongation to failure of at least 5% of which the composition has a raised A_s , and which are storage stable.

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 preconditioning 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 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.,

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

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. 3a is a small part of the copper-zinc silicon system, for unaged samples,

Fig. 3b is a small part of the same system, for aged samples,

Fig. 4. is a graph indicating the effect of different "slow" heating rates on the same system, for both aged and unaged samples,

Fig. 5 indicates the effect on the "Figure of Merit" of varying degrees of strain, for two samples of the system,

Figs. 6a and 6b correspond to Figs. 3a and 3b but for the copper-zinc-aluminum system, while

Fig. 6c illustrates the "Figure of Merit" for aged samples "slowly" heated to 100°C.

Referring now to Figs. 3a and 3b, the figure-of-merit is plotted versus composition in Figures 3a and 3b 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 3 in the range 1.8 to 2.7 Si, 66.2 to 67.5 Cu, balance Zn. Comparison of Fig. 3a with 3b shows that aging 10 minutes at 100°C broadens the optimum from the same general central point. The arbitrary selection of 40°C at 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 4. 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 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 5. While twelve percent strain appears to be beyond optimum for 66.5 wt. % Cu, 30.8 wt. % Zn, 1.96 wt. % Si, it gives better response in the 64.2 wt. % Cu, 34.8 wt. % Zn, 1.0 Si than 0 or 6% strain.

A topographical presentation of the figure-of-merit results for the CuZnAl system appears in Figure 6. Again, the constant figure-of-merit zones lie parallel to the iso-transformation contours. A more distinct optimum region was defined by the unaged samples, Figure 6a than for the aged, Fig. 6b.

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 6c; the new optimum lies parallel to that in Fig. 6b, 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.

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.

It will be appreciated that the aging periods and conditions selected for Figs. 3b and 6b 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. 3b and line 20 in Fig. 6b are novel, and are especially suited for

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the process of the invention, and the present invention accordingly provides aged alloys, preferably aged as described above, as novel alloys. The unaged alloys, bounded by the lines designated 60 and 80 in Fig. 3a and lines 20, 40 and 60 in 6a are also novel, and accordingly the present invention provides such alloys as novel compositions.

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

An alloy containing 64.5% copper, 34.5% zinc and 1% silicon, by weight was used in this Example. Its basic A_s 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_s . Recovery was 4%, about 0.8% taking place below, and 3.2% above, 75°C.

EXAMPLES 3 to 6

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 2, 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_s , °C	Recovery on Fast Heat to 75°C	Total Recovery on Fast Heat %
30 3	7.40	0.95	5 min.	85	0	5.30
4	6.80	1.20	90 min.	86	0	4.40
5	7.65	1.60	16 hrs.	85	0	4.30
6	7.30	1.60	168 hrs.	86	0	3.60

From Examples 2 to 6 it can be seen that the alloys may be deformed either before or after slow heating.

EXAMPLE 7

Three samples of an alloy having M_s of -40°C (63.7% copper, 35.3% zinc, 1% silicon) were quenched from 850°C into water at +20°C and transferred to alcohol at -70°C; all samples were martensitic at this stage. Two samples then had a deformation of 5% introduced. One deformed and the undeformed sample were heated at 10 degrees C per hour (slow heating), the other deformed sample was heated at 10 degrees C per minute (fast heating). In the undeformed sample heated slowly transformation took place between -46°C and -32°C. In the deformed sample heated slowly, no transformation took place until +30°C. At this stage, it was heated rapidly; 3.7% of the deformation was immediately recovered; all 5% was recovered by 80°C. In the deformed sample heated rapidly from -70°C, recovery started at about -46°C and all deformation was recovered by -10°C. Thus, deformation and heating rate both affect A_s .

EXAMPLE 8

A copper-zinc alloy containing 1% silicon and having a basic M_s of 0°C, A_s of -10°C, A_f of +12°C, was used.

A sample was quenched from 850°C into water at 20°C and then transferred to alcohol at -40°C and deformed 4%. The sample was then heated slowly to +40°C, no recovery taking place. The sample was then recooled to -40°C and rapidly reheated to +40°C. No recovery of deformation took place on rapid reheating. To effect recovery, the sample was heated above +40°C.

Subsequent to recovery, the sample was again cooled to -40°C, deformed and heated rapidly. Recovery was complete by 20°C, behaviour consistent with the original A_s of 12°C.

EXAMPLE 9

Sixteen samples of (80.8 wt. % Cu, 10.5 wt. % Al, 8.7 wt. % Mn) were betatized 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 as follows:

Sample	Betatization Temp.	Time	Post-quench Treatment	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%	

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.

Averaged Effects:			
Percent Strain Recovered above 100°C			
Un-aged	1.00	Fast heated	0.15
Aged	0.36	Preconditioned	1.21

In the descriptions above, emphasis has been placed on shape memory and simple recovery. Other modifications made possible by this invention include such techniques as fast heating to give partial recovery, followed by slow heating to set an elevated recovery range, followed by cooling to the low-temperature structure range, then re-deforming. This gives a product which, upon rapid heating, recovers in two steps, one at the usual range for the beginning of recovery on rapid heating, the other starting at the elevated recovery range. This technique can be multiply applied with a succession of slow heating steps to give a multiplicity of recovery ranges. Likewise, the resistivity can be made to vary in a stepped fashion on heating.

The invention can be used as a technique for extending the range of the low-temperature structure to higher temperatures. This can give alloys with high fatigue resistance to strains of about 10%, good damping properties, unusual colour, or any other characteristic which accompanies the low-temperature structure.

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WHAT WE CLAIM IS:—

1. A heat-recoverable article made from a metallic composition which exhibits an expanded M_s/A_s hysteresis loop, its A_s being higher than the A_s of a material of the same composition as initially formed into the austenitic state.
- 5 2. An article comprising a metallic composition which exhibits an expanded M_s/A_s hysteresis loop, its A_s being higher than the A_s of a material of the same composition as initially formed into the austenitic state the article having an elongation to failure of at least 5%.
- 10 3. The article of claim 2 which article is storage stable at 23°C.
4. The article of claim 2 wherein the metallic composition has a M_s below room temperature.
5. The article of claim 2 wherein the metallic composition has the property of reverting to its normal hysteresis loop when heated to a temperature above the raised A_s temperature of the expanded hysteresis loop.
- 15 6. An article as claimed in claim 1, formed from a copper-zinc alloy or a copper-aluminium alloy having an expanded hysteresis loop.
7. The article as claimed in claim 6 wherein the alloy contains a third metal selected from aluminium, manganese, silicon, and tin.
- 20 8. The article as claimed in claim 6 wherein the alloy contains a third metal selected from manganese, silicon, tin and zinc.
9. A composition within the contour lines on any of Figs. 3a, 3b, 6a, 6b or 6c which has an expanded hysteresis loop, its A_s being higher than the A_s of a material of the same composition as initially formed into the austenitic state.
- 25 10. An alloy composition substantially as described in any one of Examples 2 to 9 herein and having an expanded hysteresis loop.
11. A method comprising treating an article to raise the A_s of the metallic composition comprising slowly heating the article to a temperature above the normal A_s to impart an elevated A_s , hereinafter referred to as A_{ss} , terminating the slow heating and cooling of a temperature below A_{ss} , wherein the article is deformed while its composition is in the martensitic state to impart heat recoverability.
- 30 12. A method as claimed in claim 11, wherein the slow heating is terminated by cooling.
13. A method as claimed in claim 11, wherein the slow heating is terminated by rapid heating.
- 35 14. The method as claimed in claim 11, wherein the composition is deformed before slow heating.
15. A method as claimed in claim 11, wherein the composition is transformed to the martensitic state after cooling to a temperature below A_{ss} and the article is then deformed.
- 40 16. An alloy composition substantially as described in Example 1 herein and having an expanded hysteresis loop, by virtue of its having an A_s higher than a material of the same composition as initially formed into the austenitic state.

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