

[54] ALLOYS

[75] Inventors: **Greville B. Brook**, Beaconsfield;
Roger F. Iles, Ickenham, both of
England

[73] Assignee: **Fulmer Research Institute Limited**,
Buckinghamshire, England

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[56] **References Cited**

UNITED STATES PATENTS

3,174,851 3/1965 Buchler..... 75/170
3,567,523 3/1971 Jackson et al. 75/122.7 X

3,450,372 6/1969 De Lange et al. 75/170
2,914,433 11/1959 McGeary et al. 75/122.7 X
2,926,113 2/1960 McGeary et al. 75/122.7 X
2,259,459 10/1941 Dean..... 75/134

OTHER PUBLICATIONS

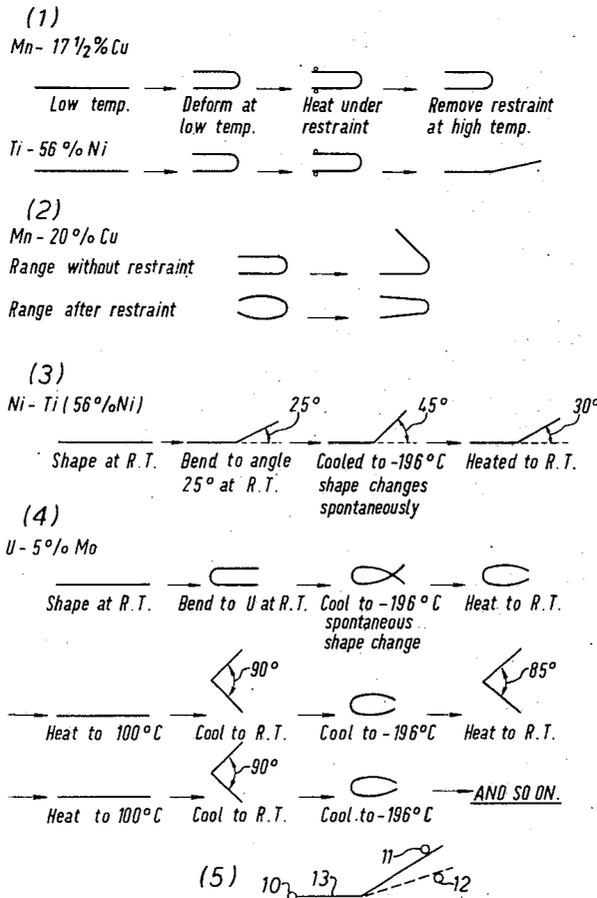
"Metal With a Memory for Shape," Iron Age, Vol. 203 (22), pg. 98, (1969).

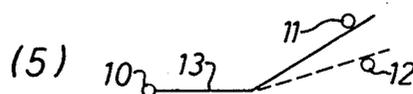
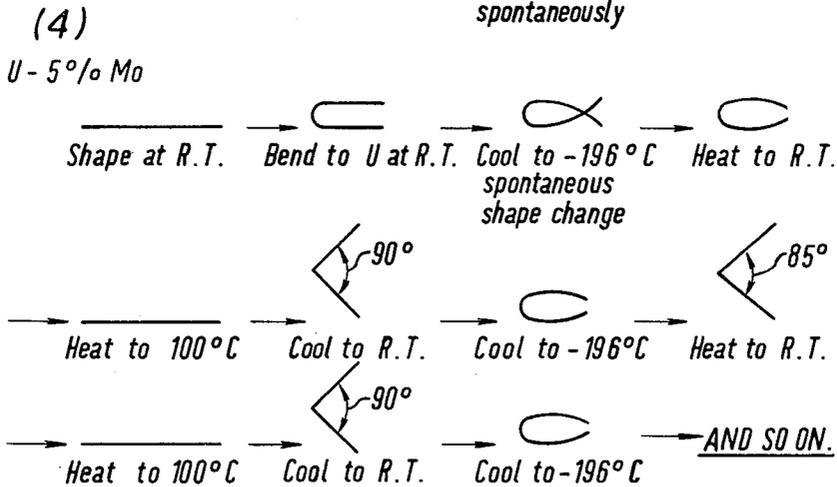
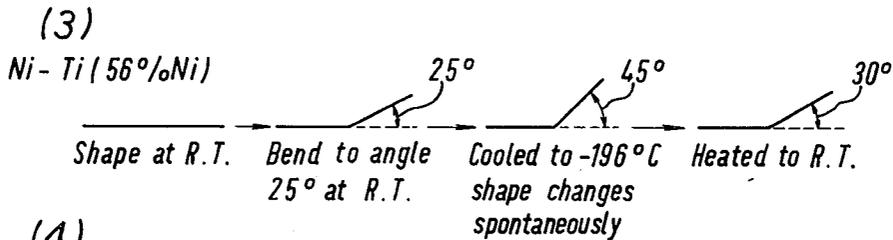
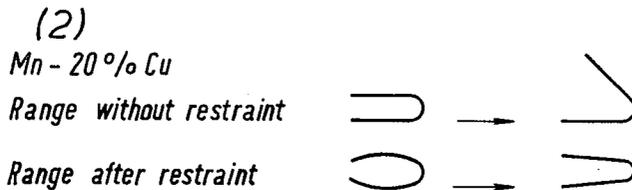
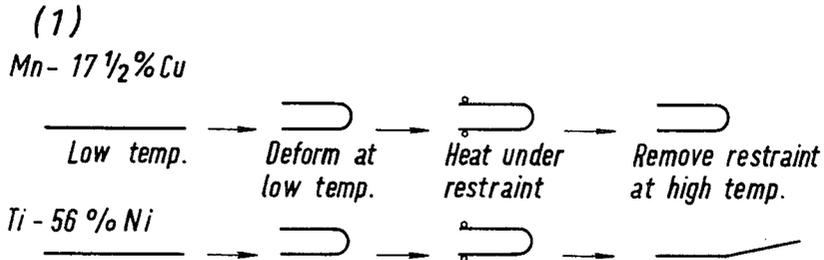
Primary Examiner—Carl D. Quarforth
Assistant Examiner—R. E. Schafer
Attorney, Agent, or Firm—Brady, O'Boyle and Gates

[57] **ABSTRACT**

A method of making a heat-recoverable article from a heat-recoverable alloy, which after suitable treatment changes its shape when appropriate temperature changes are made including the step of applying to the alloy in its high-temperature phase a strain which produces a stress which induces a desired shape for its low-temperature phase. The method may be used with new heat-recoverable alloys which are uranium binary alloys with molybdenum, niobium or rhenium, or manganese-copper binary alloys.

9 Claims, 5 Drawing Figures





INVENTORS

GREVILLE B. BROOK
ROGER F. ILES

BY *Brady, O'Boyle & Galt*
ATTORNEYS

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ALLOYS

This invention is concerned with improvements in or relating to alloys.

It is known that certain alloys are heat-recoverable, that is to say, when a suitably heat-treated article of one shape made from the alloy is caused to deform into another shape at an appropriate temperature and the temperature is subsequently raised sufficiently, the article will at least partly recover its original shape. This change of shape on reheating corresponds to a change of phase in the alloy from a low-temperature phase to a high-temperature phase. The effect of heat-recovery is known to occur with nickel-titanium binary alloys containing 52-56 percent by weight of nickel and with certain gold-cadmium, cadmium silver-gold and indium-thallium alloys.

A characteristic of all heat-recoverable alloys appears to be that, on cooling, they undergo a shear transformation to a banded martensite or retain the high temperature form as quenched, but transform by shear on cold working. The key feature is apparently that, on shaping at a low temperature, a shear transformation occurs which may be of the form described above or may be a change in the type of martensite. It seems that the strain accommodated by this shear transformation is recoverable on heating and it is on this recoverable strain that the heat-recoverable properties depend.

It will be understood that the expressions 'high-temperature' and 'low-temperature' are comparative and that, depending on the alloy, the high-temperature phase may exist for example at room temperature while the low-temperature phase exists at lower temperatures.

What we have discovered is that the strain to be accommodated at the lower temperature by the shear transformation can be applied at least in part to the high-temperature phase at a temperature above the temperature (the Ms transformation temperature defined hereinafter) at which transformation begins spontaneously and that it is a practical advantage to apply the strain in this way. The essential feature of our invention is therefore that a stress either external or internal, must be present before and during the shear transformation so as to activate, in our belief, martensitic nuclei of the appropriate orientation to give the required shape change.

Difficulties have been experienced hitherto in taking practical advantage of the effect of heat-recovery and it is thus an object of the present invention to render all heat recoverable alloys more readily useful.

The invention provides a method of making a heat-recoverable article from a heat-recoverable alloy, which method includes the step of applying to the alloy in its high-temperature phase a strain which produces a stress which induces a desired shape for its low-temperature phase.

In one manner of performing the invention, said strain is applied by deforming the alloy in its high-temperature phase partly towards the shape required for the low-temperature phase and the temperature is subsequently lowered so that the alloy changes into its low-temperature phase. The change into the low-temperature phase is accompanied by a continued change of shape into the desired shape without the application of an external force. This form of the invention is of great practical value since it provides a means

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of putting an alloy at a comparatively high temperature into a condition in which it will deform spontaneously at lower temperatures to a new shape which is dictated by the initial high temperature deformation. It is therefore unnecessary to effect working of the alloy at low temperatures. In practice, the metastable high temperature phase of the alloy is cooled to between its Md and Ms transformation temperatures. Md is the temperature of the start of the martensitic transformation under stress and Ms is the temperature of the start of the transformation without applied stress. With some alloys the temperature should be as close to the Ms transformation temperature as possible, e.g. within 10° C, to obtain the desired residual internal stress by said partial deformation. In other alloys a greater margin of temperature above Ms is possible. A suitable temperature for a given alloy can readily be found by experiment. The alloy is then deformed a small amount (i.e. less than the final strain it is desired to put into the low temperature phase). Cooling is continued to below the Ms transformation temperature when the alloy will continue to change in shape in the direction indicated by the prior deformation. On reheating this change of shape is wholly or partly reversed and on cooling again the change in shape towards the low temperature shape occurs spontaneously. Continued heating and cooling is accompanied by continued changes in shape.

In another manner of performing the invention, the alloy is deformed into a desired shape in its low-temperature phase and said strain is applied by raising the temperature so that the alloy changes into its high-temperature phase while restraint is applied to the alloy to prevent a change in shape. Thus, according to one aspect of the invention, there is provided a method of making a heat-recoverable article from a heat-recoverable alloy, which method includes the steps of shaping the alloy at an elevated temperature into a first shape, cooling to a lower temperature, deforming the alloy at the lower temperature into a second shape, said temperatures being such that if reheated without restraint to an appropriate temperature the alloy would at least partly resume its first shape, and reheating the alloy to said appropriate temperature while subjecting it to restraint which prevents a change of shape. Depending on the temperatures involved and the intended use of the article, the alloy may be cooled to the lower temperature after reheating, still retaining the second shape. Then if the alloy is reheated without restraint it will change wholly or partly to its first shape but on cooling will revert wholly or partly to its second shape. Continued heating and cooling is accompanied by continued changes in shape.

The provision of restraint when reheating induces a residual internal stress as aforesaid in the alloy at high temperature so that, it is considered, on cooling, the nuclei which are activated on transformation are those which caused the original change in shape on deformation at the low temperature. The same activation is thought to be obtained by partial initial deformation before cooling to the low-temperature phase, when it is considered that sufficient nuclei of the low temperature martensitic phase are activated by the initial deformation on such orientations that on cooling the alloy continues its change of shape.

Reheating under restraint is particularly useful since it enables the upper temperature to which the alloy is heated to be so far above the transformation tempera-

ture that continued reversibility of shape would be lost in the absence of restraint. Nevertheless, the upper temperature must not be sufficient for relaxation of stress to occur by plastic deformation, e.g. creep, or reversibility will be lost.

In all cases, the temperature to which the alloy is heated should be too low for ageing or tempering of the alloy to take place. If precipitation occurs, the alloy assumes its high temperature shape permanently.

Reheating under restraint may also be used to change the positions between which change of shape occurs (but not the amount of change) in alloys which have a low yield stress and deform plastically, such as a binary alloy of manganese containing 20 percent copper and a binary alloy of uranium containing 5 percent molybdenum as hereinafter described.

We have found that the restraint need not always be applied by external mechanical means such as a jig. In some cases, an oxide skin, a metal coating or the like can provide the necessary restraint. We have noted that alloys which, in the as-quenched or rapidly cooled condition, have a strong heat-recovery effect, also have a high internal friction or damping capacity and exhibit an anomalously low pseudo-elastic modulus on loading but a normal modulus typical of the slowly cooled alloy on unloading.

We have found further alloys which possess the above properties and are heat-recoverable. These alloys are uranium-molybdenum binary alloys containing 2 to 7% (preferably 3 to 6.5%, e.g. about 4%) by weight molybdenum, uranium-niobium binary alloys containing 3 to 11% (preferably 4 to 10%, e.g. about 6%) by weight niobium, uranium-rhenium binary alloys containing 2 to 7% (preferably about 4%) by weight rhenium and manganese-copper binary alloys containing 5 to 50% (preferably, for most uses 5 to 30%) by weight copper.

By a binary alloy is meant an alloy consisting essentially of the two metals specified with or without impurities and/or incidental constituents which do not effect the crystal structure or metallurgical properties so as to prevent the heat-recovery effect from existing.

All the above-mentioned uranium and manganese binary alloys can be readily fabricated from cast ingots without difficulty, e.g. by rolling, forging or extrusion as desired.

EXAMPLES

URANIUM BINARY ALLOYS

Uranium binary alloys were treated in the form of strip, 1 mm thick, where the application required that the material bend or flex on recovery, and in the form of rod or tube where the application required that the material change shape longitudinally (rod) or laterally (tube). The material was heated in a protective atmosphere or in a vacuum at a temperature within the γ phase field (e.g. 800° C) for a short time depending on its thickness. It was then cooled rapidly e.g. in water or oil or a jet of cold gas or by radiation if the section was small, so as to prevent precipitation of the α phase or eutectoid. The material was cooled to a temperature below the M_s transformation temperature, at which the transformation to banded martensite occurs. At this temperature, the material was deformed from its original shape e.g. by bending strip, or stretching or compressing the rod or expanding the tube or by deforming

it as desired. On reheating above a critical temperature, the original shape was at least partly restored.

In uranium-molybdenum binary alloys, at least 2%Mo by weight was needed. However, in an alloy with as little as 2%Mo, the amount of strain which could be applied at ambient temperature was very small and the temperature to which the alloy must be reheated to reverse the shape change was approximately 500° C at which rapid precipitation of α phase occurs. An alloy containing 3%Mo could be deformed at ambient temperature and started to recover its original shape at 350° C and completed the recovery at 450° - 500° C. However, exposure to 500° C for more than 10-30 minutes cumulatively caused α phase and eutectoid to form after which the heat-recoverable property was lost.

Alloys with more than 3% and less than 5%Mo are most useful in practice. An alloy containing 4%Mo could be deformed at ambient temperature and started to recover its shape on heating to 200° C. For example, a straight 1 mm thick strip of this alloy was bent through an angle of 100° at ambient temperature. On heating for 3 minutes at 250° C, the strip partially straightened to 30° and on cooling to ambient temperature, the movement was reversed to 70°. In this example, it was noticed that restraint was applied by a thick oxide skin formed by heating at 800° C in inadequate vacuum.

An alloy containing 4.5%Mo was also examined. A strip was bent at ambient temperature and started to straighten at 80° C. On heating to 250° C, almost complete recovery of the original shape was obtained and little reversal took place on cooling to R.T. For example, a straight strip bent through 120° at ambient temperature recovered to 30° after 3 minutes at 100° C. On cooling ambient temperature, reversal to 45° occurred. If the recovery temperature was raised to 250° C, more complete recovery was obtained and the amount of reversal was less e.g. a straight strip bent through 90° at ambient temperature recovered to 5° at 250° C and reversed to 10° on cooling to ambient temperature.

It will be seen that the amount of reversal on cooling decreases as the reheating temperature is raised.

An alloy with 5%Mo started to recover on heating to 50° C and almost complete recovery occurred at 250° C e.g. a straight strip was bent to a specific angle at room temperature (R.T.) and then heated to a temperature T° and then cooled to room temperature and the following table shows the amount of recovery.

Temp. to which strip heated, T°	Angle of deformation at R.T.	Angle after recovery at T°	Angle after cooling to R.T.
60°C	80°	20°	30°
100°C	85°	10°	20°
150°C	90°	15°	30°
200°C	95°	10°	15°
250°C	90°	5°	10°

A straight strip of alloy with 5%Mo was cooled to -196° C and deformed to U-shape. On heating to ambient temperature, the U opened to a right angle. Further heating to 100° C caused the strip to flatten completely. Cooling to -196° C caused the strip to revert to the right angle position. On cycling from -196° C to +100° C, the specimen changed shape from L (right angle) at -196° C to ____ (flat) at 100° C, i.e.:-

U-shape
 $\overline{-196^{\circ}\text{C}} \rightarrow -196^{\circ}\text{C} \rightarrow \text{R.T.} \rightarrow \overline{100^{\circ}\text{C}}$
 by deforming
 $-196^{\circ}\text{C} \rightarrow \overline{100^{\circ}\text{C}} \rightarrow -196^{\circ}\text{C}$ and so on

An alloy with 6%Mo did not transform to the martensitic structure until cooled below room temperature. When a strip deformed to a U-shape at ambient temperature was heated to 100° C, only a slight change in shape occurred. The U-shaped piece was cooled to a temperature approximately -80° C and was deformed by straightening completely. On reheating to ambient temperature, the strip recovered to a U shape again. As the molybdenum content was increased to 7%, the temperature at which deformation must be carried out was lowered. 7% Mo represented the practical upper limit when deforming at temperatures down to -196° C.

Uranium-niobium binary alloys behaved in a similar way to U-Mo alloys. 3% Nb was needed to obtain the same effect as 2%Mo but such an alloy was of little practical use as the amount of recoverable deformation was small and the temperature of recovery so high that α and eutectoid formation occurred and no further recovery was possible. With 4%Nb, recovery was possible at 350° C and with 5% Nb, recovery occurred at 250° - 300° C, after deformation at ambient temperature. 7%Nb alloy recovered at about 100° C and is comparable to a 5%Mo alloy. Alloys with 8 to 10%Nb could be deformed at -80 to -196° C and recover on heating to ambient temperature.

U-Re binary alloys containing 2 to 7% rhenium behave in like manner.

Experiments were also carried out with a ¼ inch diam rod of uranium-molybdenum binary alloy containing 5%Mo. The specimen was cooled to -196° C at which temperature it was compressed 3.8%. On reheating to ambient temperature, the specimen expanded 3.2% over and above the normal thermal expansion. Another rod specimen was cooled to -196° C and was then compressed 4%. It was then reheated to room temperature but under restraint so that the expansion on recovery was prevented. A stress of 73,900 lbf/in² was developed. This demonstrates another use of this invention in developing a force capable of doing work.

MANGANESE — COPPER BINARY ALLOYS

These alloys were treated and tested similarly to the uranium alloys.

An alloy containing 5% to approximately 15% copper showed heat-recovery effects if the low temperature at which deformation took place was about 150° C for 5%Cu to about 100° C for 10%Cu and 50° C for 15%Cu. These alloys then recovered their shape partially on heating to 250° C. The shape change was continuous over this temperature range.

17.5% copper alloy recovered after deformation at room temperature when it was heated to 150° C. The amount of recovery was not 100% but the change was reversible e.g. when a 1mm thick strip of this alloy was deformed into a U-shape with the tips of the legs of the U separated by 2.7mm at 25° C heating to 150° C expanded the separation of the tips to 4.5mm. On cooling to 25° C, the tips closed to 3.7mm. Reheating to 150° C expanded the tips again to 4.5mm and cooling to 25° C reversed this to 3.65mm.

17.5% Cu alloy demonstrated recovery more effectively when it was deformed at -196° C. A U loop with a separation between the tips of the legs of 3.95mm expanded to a separation of 5.5mm on heating to 25° C, 6.8mm at 100° C and virtually straightened at 150° C. On cooling the separation reduced to 6.4mm at 100° C, 6.2mm at 25° C and 5.95mm at -196° C. It expanded to 6.25mm again at 25° C.

25%Cu alloy was deformed at room temperature and heated to higher temperatures but no recovery occurred. This was as expected because at room temperature the 25%Cu alloy deforms by plastic deformation and not by shear transformation. It was necessary to cool this alloy and deform at -196° C. On deforming at -196° C and heating this alloy, it behaved like the 17.5%Cu alloy except that most deformation was recovered between -196° C and room temperature and less between room temperature and 100° C. Cooling down again caused reversal of the change of shape, and changes of shape continued with repeated heating and cooling.

Like all of the other manganese-copper alloys, the 25% Cu alloy changed in shape over a considerable range of temperature and not sharply over a narrow range.

With 30 to 50% Cu alloys it is necessary to cool and deform the alloy well below -196° C. This makes the alloys useful for special cryogenic applications.

The lack of complete recovery in the Mn-Cu alloys can be explained by the fact that their yield stress is relatively low and the reversal of the transformation is taken up by plastic strain in the high temperature phase as it forms. This was demonstrated by deforming a strip of Mn-Cu binary alloy containing 17.5%Cu at low temperature into U-shape and heating under restraint. When the restraint was removed at high temperature, no change in shape occurred. When a strip of material of high yield stress (in the test a nickel-titanium binary alloy containing 56% nickel was used) was treated in the same way, the U-shaped strip sprang open when the restraint was removed at high temperature. The accompanying drawing shows these changes at (1).

APPLICATION OF STRAIN TO INDUCE INTERNAL STRESS

An example of an effect of reheating under restraint has been given above in connection with a manganese-copper binary alloy containing 17.5%Cu and a nickel-titanium binary alloy containing 56%Ni.

Tests made on manganese-copper binary alloys containing 20% Cu and uranium-molybdenum binary alloys containing 5% Mo showed that reheating under restraint changed the position over which the change of shape occurred but not the angular range. This effect in a strip of manganese-copper binary alloy containing 20% Cu is illustrated in the accompanying drawing at (2).

Further tests were made on strips of various alloys by cooling the metastable high temperature form of the alloy to just above its Ms transformation temperature (between the Ms and Md temperatures but nearer to the Ms temperature), deforming the specimen a small amount (i.e. less than the final deformation needed in the low temperature form), continuing cooling to below the Ms transformation temperature, during which the specimen continued to change in shape in the direction indicated by the prior deformation. On

reheating this change in shape is wholly or partly reversed and on cooling again the change in shape occurs spontaneously.

A test on a strip of nickel-titanium binary alloy containing 56%Ni heated to 850° C and quenched to room temperature in the flat condition is illustrated in the accompanying drawing at (3).

The strip was bent through an angle of 25° at room temperature. On cooling to -196° C the angle changed spontaneously to an angle of 45°. On heating again to room temperature the angle changed to 30°. On heating and cooling between room temperature and -196° C, the angle of the strip changed from 30° to 45° reversibly.

A test on a strip of uranium-molybdenum binary alloy containing 5% Mo, heated to 800° C and quenched to room temperature in the flat condition is illustrated at (4) in the accompanying drawing.

The strip was bent to U-shape at room temperature. It was cooled to -196° C when its shape changed spontaneously, the legs of the U moving towards each other and crossing. Heating to room temperature nearly restored the U-shape so that a C-shape was formed. Continued heating to 100° C caused the strip to become flat again. Subsequent cooling to room temperature caused the strip to assume a right angle shape and further cooling to -196° C caused it to become C-shaped again. Reheating to room temperature resulted in an angle of 85° between the legs of the strip and further heating to 100° C caused the strip to flatten. Cooling to room temperature resulted in a right angle shape and further cooling to -196° C resulted in a C-shape. On continued heating and cooling, the shape changes continued in the same way. It will be seen that hysteresis occurs so that at room temperature the shape is slightly different when heating and cooling. The original shape at -196° C is not recovered completely, but it is considered that cooling below -196° C would cause complete recovery of the original shape because there is hysteresis at -196° C as well as at room temperature.

A test on a strip of manganese-copper binary alloy containing 17.5%Cu showed that when partly deformed into a U-shape at room temperature and then cooled to -196° C, the legs of the U moved towards each other to close the U. A 20%Cu alloy gave the same results but even more movement was obtained.

Articles made by the methods and from the heat-recoverable alloys described herein are useful for many purposes where a change of shape is necessary. For example, they may be used as tubes in couplings, which tubes change shape to grip two elements to be connected together, as temperature-responsive elements in switching devices, and as formers or dies on which a plastics or metal sheet is shaped whereafter the former or die is caused to shrink away, allowing the removal of the shaped sheet and the former or die is then caused to revert to its original shape for the next operation. The accompanying drawing at (5) shows a temperature-responsive switch having three contacts 10, 11 and 12. A bent strip 13 made by a method and of an alloy as hereinbefore described makes an electrical connection between the contacts 10 and 11 at one temperature and between the contacts 10 and 12 at a different temperature.

We claim:

1. A method of making a heat-recoverable article from a heat-recoverable alloy, which article is repeat-

edly changeable in shape from a first shape towards a second shape by lowering its temperature and from the second shape towards the first shape by raising its temperature, said changes in shape corresponding to changes in phase in the alloy from a high-temperature phase to a low-temperature phase and from the low-temperature phase to the high-temperature phase respectively, which method comprises the steps of deforming the alloy in its low-temperature phase so as to change its shape from the first shape to the second shape, applying restraint to the alloy in the second shape so formed, raising the temperature so that the alloy changes into its high-temperature phase while said restraint prevents a change in shape, and subsequently repeatedly altering the temperature to cause said changes in shape without applying any further deformation to the alloy.

2. A method according to claim 1 in which after raising the temperature while applying said restraint the alloy is cooled so that it changes into its low-temperature phase, still retaining said second shape.

3. A method according to claim 1 in which the alloy is selected from the group consisting of binary alloys of uranium containing 2 to 7% by weight molybdenum, 3 to 11% by weight niobium and 2 to 7% by weight rhenium.

4. A method according to claim 1 in which the alloy is a manganese-copper binary alloy containing 5 to 50% by weight copper.

5. A method according to claim 1 in which the alloy is a nickel-titanium binary alloy containing 52 to 56% by weight nickel.

6. A method of making a heat-recoverable article from a heat-recoverable binary alloy selected from the group consisting of uranium-molybdenum containing 2 to 7% by weight molybdenum, uranium-rhenium containing 2 to 7% by weight rhenium, manganese-copper containing 5 to 50% by weight copper and nickel-titanium containing 52 to 56% by weight nickel, which method includes the steps of deforming the alloy in its high-temperature phase partly towards the shape required for the low-temperature phase, thereby applying to the alloy in its high-temperature phase a strain which produces a stress which induces a desired shape for its low-temperature phase, and subsequently lowering the temperature so that the alloy changes into its low-temperature phase and assumes the required shape.

7. A method of making a heat-recoverable article from a heat-recoverable binary alloy selected from the group consisting of uranium-molybdenum containing 2 to 7% by weight molybdenum, uranium-rhenium containing 2 to 7% by weight rhenium and manganese-copper containing 5 to 50% by weight copper, which method includes the steps of shaping the alloy at an elevated temperature into a first shape, cooling to a lower temperature, and causing the alloy to deform at the lower temperature into a second shape, said temperature being such that if reheated to an appropriate temperature the alloy would at least partly regain its first shape.

8. A method according to claim 7, in which the alloy is a binary alloy of uranium containing 3 to 6.5% by weight molybdenum.

9. A method according to claim 7 in which the alloy contains 5 to 30% by weight copper.

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