TEMPERATURE-INDUCED SHAPE MEMORY IN POLYCRYSTALLINE URANIUM-BASE NIOBIUM ALLOYS: CHARACTERIZATION

Ross J. Jackson
Wilbur L. Johns

THIS DOCUMENT CONFIRMED AS UNCLASSIFIED
DIVISION OF CLASSIFICATION
BY J. Kahn
DATE 1/25/71

THE DOW CHEMICAL COMPANY
ROCKY FLATS DIVISION
P. O. BOX 888
GOLDEN, COLORADO 80401

U.S. ATOMIC ENERGY COMMISSION
CONTRACT AT(29-1)-1106

DISTRIBUTION OF THIS DOCUMENT IS UNLIMITED
DISCLAIMER

This report was prepared as an account of work sponsored by an agency of the United States Government. Neither the United States Government nor any agency thereof, nor any of their employees, makes any warranty, express or implied, or assumes any legal liability or responsibility for the accuracy, completeness, or usefulness of any information, apparatus, product, or process disclosed, or represents that its use would not infringe privately owned rights. Reference herein to any specific commercial product, process, or service by trade name, trademark, manufacturer, or otherwise does not necessarily constitute or imply its endorsement, recommendation, or favoring by the United States Government or any agency thereof. The views and opinions of authors expressed herein do not necessarily state or reflect those of the United States Government or any agency thereof.
DISCLAIMER

Portions of this document may be illegible in electronic image products. Images are produced from the best available original document.
This report was prepared as an account of Government sponsored work. Neither the United States, nor the Commission, nor any person acting on behalf of the Commission:

A. Makes any warranty or representation, expressed or implied, with respect to the accuracy, completeness, or usefulness of the information contained in this report, or that the use of any information, apparatus, method, or process disclosed in this report may not infringe privately owned rights; or

B. Assumes any liabilities with respect to the use of, or for damages resulting from the use of any information, apparatus, method, or process disclosed in this report.

As used in the above, "person acting on behalf of the Commission" includes any employee or contractor of the Commission, or employee of such contractor, to the extent that such employee or contractor of the Commission, or employee of such contractor prepares, disseminates, or provides access to, any information pursuant to his employment or contract with the Commission, or his employment with such contractor.
TEMPERATURE-INDUCED SHAPE MEMORY IN POLYCRYSTALLINE URANIUM-BASE NIOBIUM ALLOYS: CHARACTERIZATION

Ross J. Jackson
Wilbur L. Johns

LEGAL NOTICE
This report was prepared as an account of work sponsored by the United States Government. Neither the United States nor the United States Atomic Energy Commission, nor any of their employees, nor any of their contractors, subcontractors, or their employees, makes any warranty, express or implied, or assumes any legal liability or responsibility for the accuracy, completeness or usefulness of any information, apparatus, product or process disclosed, or represents that its use would not infringe privately owned rights.

THE DOW CHEMICAL COMPANY
ROCKY FLATS DIVISION
P. O. BOX 888
GOLDEN, COLORADO 80401


DISTRIBUTION OF THIS DOCUMENT IS UNLIMITED.
CONTENTS

Abstract .................................................. 1
Summary .................................................. 1
Introduction ............................................. 1
Shape Memory after Bending-Induced Strains .......... 2
  Bending Deformations and Subsequent Dilatometric Analysis 2
  Reversible and Irreversible Shape Changes .......... 3
  Athermal and Isothermal Behavior .................. 4
  Additional Observations ............................ 5
Shape Memory after Uniaxially Induced Tensile
  and Compressive Strains; and Rolling Strains .... 6
References ............................................... 7
ACKNOWLEDGMENT

An acknowledgment is extended to Mr. J. F. Boland for first observing the phenomenon characterized in this report. Mr. D. H. Hansen is acknowledged for designing one of the dilatometers and for assisting in some experimental aspects of the study. Thanks are also extended to Mr. S. Beitscher for several stimulating discussions.
TEMPERATURE-INDUCED SHAPE MEMORY IN POLYCRYSTALLINE URANIUM-BASE NIOBIUM ALLOYS: CHARACTERIZATION

Ross J. Jackson and Wilbur L. Johns

Abstract: Certain polycrystalline uranium-base niobium alloys undergo unusual shape changes on heating or cooling. The shape changes are athermal and under certain conditions completely reversible. This behavior is referred to as temperature-induced shape memory. The shape changes occur in the composition range of 6- to 21-atomic % Nb and in the temperature range of −200°C to +400°C. For the alloy to exhibit shape memory it must first be cooled rapidly from the gamma region and then subjected to a plastic deformation below 425°C. This report characterizes the effects of composition, temperature, time at temperature, and types of strain, on the shape memory.

SUMMARY

An unusual internally induced, athermal, and reversible strain behavior has been observed in certain uranium-niobium alloys. This effect occurs in the composition range of 6-to 21-atomic % Nb, and reaches a maximum near the U-15 atomic % Nb composition. The phenomenon occurs over a temperature range of at least −200°C to +400°C. The dimensional change per temperature increment varies as a function of temperature, composition, and cooling rate from the gamma region.

Two conditions necessary for subsequent temperature-induced shape change are: (a) the sample must be cooled rapidly from the gamma region, and (b) the as-quenched shape must be subjected to a plastic deformation below approximately 425°C.

Any type of induced plastic strain (e.g., bending, cupping, uniaxial tension, uniaxial compression, and rolling) can give rise to subsequent temperature-induced motion.

The motion on heating above the forming temperature is always in the direction of the as-quenched shape. The motion on cooling below the forming temperature is always in the direction opposite to the as-quenched shape. On the reverse part of the thermal cycle, the motion is always in the direction opposite to that of the forward part of the cycle.

In cycling to subzero temperatures the shape change is dimensionally reversible. On cycling above the forming temperature there is a nonreversible component and a reversible component of shape change. Following the first cycle, the nonreversible component is minimal except at the higher cycling temperatures.

The shape changes, to a first approximation, are athermal in character. However, at the higher cycling temperatures, the shape change shows an isothermal character. Not only does a shape change occur with time, but the magnitude of the shape change on continued cycling is decreased. This effect becomes more easily measured as the temperature and time increase. Holding at 400°C for 15 minutes will completely erase any memory and subsequent shape-change behavior.

The memory for the quenched-in shape is remarkable in that cyclic and unusual bending patterns will not destroy the memory for that shape as long as deformations are not too severe.

A macro-residual stress sufficient to cause the observed shape change does not exist in the bend specimens that exhibit temperature-induced strain.

INTRODUCTION

During formability studies on uranium-base niobium alloys, an unusual temperature-induced shape memory was observed. The U-15 atomic % Nb alloys, water quenched from the single phase gamma region (e.g., 850°C) and then plastically bent, reverted towards their as-quenched shape on subsequent heating. When the deformed sample was heated and cooled through one temperature cycle, the shape change behavior was partially reversible. Sequence photographs illustrating the temperature-induced shape memory are shown in Figure 1.

The temperature-induced shape memory has not been previously reported for uranium alloys. Somewhat similar, temperature-induced, macroscopic shape changes following deformation have been observed in at least three other binary systems: the In-Ti\(^1,2\), Au-Cd\(^3,4\), and Ti-Ni\(^5,6\), systems. The temperature-induced shape changes occurring in the three systems have been attributed to a single martensitic phase transformation occurring over a relatively small temperature interval. In general, these systems do not show the shape change behavior over the wide range of temperature and compositions that the uranium
prior grain size (20-40 microns) and somewhat random orientation was obtained by repeated heating into the \( \gamma \) region (850°C) and cross-rolling. The rolling temperature varied from 850°C to 550°C. Samples of various dimensions were machined from the cross-rolled sheet. The machine samples were solution treated 4 hours at 850°C in vacuum and water quenched. Water quenching a sample of this size yields a cooling rate of approximately 1000°C/sec. The prior \( \gamma \) grain size of this material was approximately 100 microns and the grains were equiaxed. The grains were randomly oriented. Prior to deformation, the samples were electropolished in a cold electrolyte to remove the surface film developed on quenching.

**SHAPE MEMORY AFTER BENDING-INDUCED STRAINS**

**Bending Deformations and Subsequent Dilatometric Analysis:**

Flat, as-quenched specimens of dimensions 2.00-by 0.375-by 0.61-inch were plastically deformed by bending a fixed distance at 0°C on a three-point bending jig. The bending jig consisted of a base plate to which were welded two 0.5-inch rounds whose centers were separated by 1.375 inches. A third 0.5-inch round was welded to a platen and served as the punch. The U-11 atomic % Nb, U-15 atomic % Nb, U-19 atomic % Nb alloys, and a type 304 stainless steel were bent until the center section of the sample encountered the base of the fixture. For the U-9 atomic % Nb alloy, a 1/8-inch shim was placed on the base of the fixture. This shim was necessary because this composition fractured on bending through the larger bend angle.

The bend angle after springback was 105°, 95°, 120°, and 88° for U-11 atomic % Nb, U-15 atomic % Nb, U-19 atomic % Nb and 304 stainless steel, respectively. These samples, after bending but prior to springback, had a bend angle of 76°. The difference of the two values is a measure of the springback in the samples.

After deformation, the bend specimen was placed in a simple quenching dilatometer and the amount of temperature-induced motion was measured as a function of temperature and time. The quenching dilatometer consisted of a Sheffield 0-1000 microns, machinist-dial gauge, with an extended push rod of 304 stainless steel. The sample holder was of thin-gauge stainless steel, and was integral with the dial gauge. A small guide mark was drilled at the apex of the bend specimen to accept the pointed push rod.

The heating and cooling of the sample was conducted in an isothermal manner. That is, the dilatometer and sample were placed in one bath at temperature \( T_1 \) and held until motion ceased (generally less than 2 minutes). The portable dilatometer including sample was then transferred (less than 5 seconds) to a bath at \( T_2 \) and...
held until the sample ceased moving (again generally less than 2 minutes). This procedure was usually carried through six complete cycles. A silicone oil was used as the heating medium from 0°C to 290°C. Above 290°C a vertical muffle furnace with an argon atmosphere was used. Liquid N₂ was used for the −196°C bath. A dry ice, trichlorethylene slurry was used for the −70°C bath.

The dilatometer yielded the change in bend height (Δh) on thermal cycling. The bend height after bending and spring-back is h₀ and h−h₀ is Δh. The ordinate used in plotting the data is Δh/h₀. The abscissa is the thermal cycle. The value Δh/h₀ was used since it is easily measured and is not measurably influenced by the normal uniform thermal expansion of the material.

Reversible and Irreversible Shape Changes:

The temperature-induced shape memory was briefly described in the introduction. Figures 2, 3a, 3b, and 3c characterize the temperature-induced shape change following a bending strain for the U-15 atomic % Nb, U-9 atomic % Nb, U-11 atomic % Nb, and U-19 atomic % Nb alloys, respectively. A separate sample was used for each curve. A type 304 stainless steel was given the same treatment as the uranium-niobium alloys. On thermal cycling between 0°C and 350°C the stainless steel showed no measurable temperature-induced vertical movement.

Figure 2. Temperature-Induced Shape Change of the U-15 Atomic % Nb Alloy Following a Bending Deformation. Separate samples were cycled six times between the indicated temperatures.

Figure 3. Temperature-Induced Shape Change of Three Uranium-Niobium Alloys: (a) U-9 Atomic % Nb, (b) U-11 Atomic % Nb, and (c) U-19 Atomic % Nb. Separate samples were cycled six times between the indicated temperatures.
Prior to the dilatometric studies represented in Figures 2 and 3, the sample underwent two necessary operations: (a) the sample was quenched from the gamma region, (e.g., 850°C); and (b) the sample was plastically strained at a temperature below approximately 425°C (in this case, 0°C).

Seven salient features are portrayed by the dilatometric results in Figures 2 and 3.

1. The internally induced strain occurs over a temperature range of at least 600°C (i.e., -200°C to +400°C).
2. The internally induced strain occurs over a composition range of at least 9- to 19-atomic % Nb. (Subsequent studies showed that the temperature-induced strain occurs for compositions in the range of 6- to 21 atomic % Nb.)
3. On cooling below the forming temperature, the sample changes shape in an athermal manner such that the bend height is increased. On reheating to the forming temperature, the sample returns to the initial bend height, \(h_0\). Therefore, the shape change is dimensionally reversible on thermal cycling below the forming temperature.
4. On heating above the forming temperature, the sample changes shape in an athermal manner such that the bend height is decreased (as-quenched shape). On returning to the forming temperature, the bend height increased (as-formed shape); but the sample does not attain the initial bend height value. Thus, on the first thermal cycle above the forming temperature, there are reversible and irreversible components of shape change.
5. On continued temperature cycling above the forming temperature the sample changes shape in a near-reversible manner as long as the upper temperature in feature 4 (above) is not exceeded. Also, the upper temperature must be less than approximately 275°C for the change to be near-reversible.
6. At the higher cycling temperatures (e.g., 375°C), there is an irreversible component on each thermal cycle, such that the reversible component diminishes to zero on continued thermal cycling.
7. The molybdenum content has a strong effect on the magnitude of shape change. For the data presented, the magnitude of shape change is largest for the U-15 atomic % Nb alloy and smallest for U-9 atomic % Nb alloy. Likewise, the dimensional change per temperature increment varies with composition. Examples of this are: (a) for the U-11 atomic % Nb alloy, the reversible and irreversible components increase in a linear manner with temperature; (b) for the U-15 atomic % Nb alloy, the dimensional change per temperature increment reaches a large-valued maximum in the vicinity of 110°C; and (c) for the U-19 atomic % Nb alloy, the dimensional change reaches a maximum below 150°C and is nonexistent above this temperature.

**Athermal and Isothermal Behavior:**

Thermocouples were embedded near the bend radius in all the samples. Plots of bend height changes, \(\Delta h\), versus sample temperature, showed, to a first approximation, that sample motion ceased when the bath temperature was reached. Thus, to a first approximation, the temperature-induced motion is a function of temperature and not time at temperature (i.e., it is athermal in character).

Time at temperature, however, does have an effect on the shape change behavior. Figure 4 shows the temperature-induced strain of the U-15 atomic % Nb alloy subjected to isothermal holds at 150°C and 250°C. The isothermal holds were midway of the first cycle. The remaining cycles followed the normal procedure. Thus, upon isothermal holding a shape change occurs that reduces...
the magnitude of the reversible dimensional change. Further, the loss in reversibility increases as the holding temperature increases.

The isothermal effect is also illustrated in Figure 2. The sample cycled from 0°C to 375°C showed a decreasing shape change with each cycle. By the sixth cycle the shape change was practically nonexistent. Figure 2 shows a similar behavior in the 0°C to 350°C and 0°C to 400°C cycle. On heating to higher temperatures (i.e., above 290°C), it took about 5 minutes for the sample to reach thermal equilibrium. This was a considerably longer time than for the oil bath used below 290°C and should be considered in comparing the curves.

Figure 5. Temperature-Induced Shape Change of the U-15 Atomic % Nb Alloy. Only one sample was used. The subzero cycles were completed first and then successively higher cycling temperatures were achieved on the one sample.

The isothermal effect, or at least a cycling effect, can also be seen at the lower temperatures. On cycling from 0°C to 250°C there is a small but easily measured decrease in dimensional change with each cycle. This effect is partially the result of a slight warming of the low-temperature bath and cooling of the high-temperature bath on rapid cycling. However, a correction for this effect would account for, at most, only one-third of the irreversibility.

The effect that lower temperature cycling has on cycling at a higher temperature is shown in Figure 5. This figure shows the temperature-induced strain of the U-15 atomic % Nb alloy on cycling the same specimen in the following sequence: (a) 0°C to -196°C, (b) 0°C to 90°C, (c) 0°C to 165°C, (d) 0°C to 215°C, (e) 0°C to 250°C, (f) 0°C to 350°C, and (g) 0°C to 400°C. There were six cycles at each temperature interval except the last one. When these data are compared with those of Figure 2, it is seen that the lower temperature cycles do appear to have an effect on cycling to a higher temperature. Prior low-temperature cycling appears to cause an increase in the reversible portion of the shape change observed during subsequent high-temperature cycling.

Additional Observations:

Additional observations concerning temperature-induced shape changes associated with a bending deformation are:

1. The effect of quenching rate on magnitude of shape change was investigated. A U-15 atomic % Nb alloy was air quenched from 850°C, and then plasticly bent in the normal manner. Subsequent dilatometric analysis between 0°C and 150°C showed a behavior similar to the water-quenched sample. However, the magnitude of the change was only about one-half that of the water quenched sample. Thus, the cooling rate from the gamma region has a distinct effect on the magnitude of shape change on subsequent thermal cycling.

2. Plastic deformation of the quenched shape is necessary for subsequent motion on thermal cycling. Non-deformed quenched samples did not show any motion on thermal cycling in the range -200°C to 400°C. The effect of bending prior to quenching was also examined. A U-15 atomic % Nb alloy was bent at room temperature in the normal manner. This sample was mounted in a jig to maintain this shape, heated to 850°C, and subsequently water quenched. The sample was then subjected to dilatometric analysis on thermal cycling in the normal manner. No motion of the sample was observed. Thus, plastic deformation of the quenched shape is required for the motion observed during subsequent thermal cycling.

3. Non-uniform plastic deformations give rise to residual stresses, and these can cause shape changes with changes in time and temperature. Thus, it was desirable to see if a significant macroresidual stress pattern existed in the bend specimens that exhibited temperature-induced strain. A previously water-quenched U-15 atomic % Nb specimen...
was bent in the normal manner. Material was continually removed from the extension side of the bend by electropolishing until only the contraction side remained. During electropolishing, the specimen was free to move and no change in curvature occurred. Thus, it is concluded that the temperature-induced motion is not due to a macro-residual stress.

4. The memory for the as-quenched shape exhibited on heating is remarkable in that cyclic and unusual bending patterns will not fool the material as long as deformations are not too severe. Experiments confirming this statement are: (a) samples cyclically bent many times always showed a temperature-induced motion upon heating in the direction of the as-quenched shape; (b) samples bent into complex shapes always showed temperature-induced motion towards the as-quenched shape; and (c) as-quenched flat plates that were subsequently cupped and then sectioned, would, upon heating, return toward the as-quenched shape.

SHAPE MEMORY AFTER UNIAXIALLY INDUCED TENSILE AND COMPRESSION STRAINS; AND ROLLING STRAINS

The question arises as to whether or not the temperature-induced shape change is peculiar to a bending-induced strain. Would any type of plastic deformation give rise to shape changes on a subsequent heating and cooling? Three other means of inducing the plastic deformation were investigated, these were: (a) uniaxially applied tension, (b) uniaxially applied compression, and (c) cold rolling.

The quenching dilatometer used in these studies consisted of a perforated, fused-quartz outer-tube in which the sample set vertically. A vertical, fused-quartz push-rod rested on the sample. Connected to the push rod and the portable stand was a 0.1-inch strain-gauge extensometer. The strain-gauge output was amplified and recorded using an Instron Model TTDL testing unit. The homemade, portable, quenching dilatometer coupled with the Instron strain-gauge extensometer system proved to be a stable and sensitive unit.

Figure 6 shows the temperature-induced shape-change behavior of a uniaxially compressed sample and a uniaxially stretched sample. The compression sample was a right cylinder 0.50-inch long by 0.40-inch diameter. This sample was water quenched from 850°C, and subjected to three subzero cycles (23°C ↔ -196°C) and three elevated temperature cycles (23°C ↔ 200°C) using the quenching dilatometer. This same sample was then water quenched from 850°C, uniaxially compressed (resulting in a permanent 22% decrease in length), and thermally cycled in the same manner as above using the quenching dilatometer. The dilatometric changes of the nondeformed state were subtracted from those of the plastically deformed state, and this difference is plotted in Figure 6.

The extension sample was a water-quenched flat bar 2.00-in by 0.375-in by 0.061-inch. The extension sample in the nondeformed state was dilatometrically analyzed in the same manner as the compression sample. This sample was then water quenched from 850°C, and given a 15% uniform plastic elongation over a one-inch gauge length at a strain rate of 0.02 in./in./minute. The extended gauge length section was removed and
dilatometrically analyzed in the same manner as the nondeformed state. The percent dilatometric changes of the nondeformed state was subtracted from those of the plastically deformed state and the difference is plotted in Figure 6.

Figure 6 shows the compression sample to expand on heating and contract on cooling, whereas the extension sample behaves in an opposite manner; that is, it contracts on heating and expands on cooling. This is, of course, the same behavior that occurs in the tension and compression regions of a bend specimen. Thus, one can conclude that either uniaxially induced tensile or compressive plastic strains give rise to the temperature-induced, shape-change behavior.

In a similar experiment, two tensile test bars of the U-15 atomic % Nb alloy were prepared, then held 2 hours at 850°C and water quenched. The bars were given a 14% and 11% uniform plastic elongation, respectively, over a one-inch gauge length at a strain rate of 0.02 in./in./minute. The gauge length section was then removed and measured. The sample given a 14% uniform elongation was heated 10 minutes at 350°C and was then rapidly cooled to 23°C. Remeasurement showed that 11% of the longitudinal extension and lateral contraction that occurred under uniaxial tension had been permanently recovered on heating to 350°C.

The sample that was given an 11% uniform elongation was heated to 400°C and held for 10 minutes and was then rapidly cooled to 23°C. Remeasurement showed that 16% of the initial longitudinal plastic extension had been permanently recovered during the subsequent thermal treatment. Thus, both samples given uniform elongations exhibited irreversible shape changes on thermal cycling in the same manner as the previously discussed bend specimens.

To test the effect of a cold deformation induced by rolling, a previously water-quenched 2.00 in long, U-15 atomic % Nb specimen was extended in length to 2.50 inches by cold rolling in one pass. Dilatometric analysis showed that on heating to 200°C, the specimen decreased 20 mils in length (4% of the extension induced by rolling) and recovered 8 mils on cooling to the rolling temperature (23°C). The 8-mil longitudinal-length change was dimensionally reversible on continued thermal cycling between 23°C and 200°C. Thus, the three means of plastic deformation discussed in this section, all give rise to a shape change behavior similar to that observed after a bending deformation.

REFERENCES


