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TRANSFORMATION KINETICS OF
URANIUM-MOLYBDENUM ALLOYS

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October 21, 1954

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TRANSFORMATION KINETICS OF URANIUM-MOLYBDENUM ALLOYS

H. A. Saller, F. A. Rough, and A. A. Bauer

The kinetics and mode of transformation of metastable gamma in the uranium-molybdenum system have been investigated. Electrical-resistance measurements made during isothermal transformation, supported by metallographic and hardness data, indicate the gamma-to-delta transformation to be an ordering reaction which probably proceeds by nucleation and growth of the ordered phase. A "C-curve" type behavior for the transformation is inferred from resistance measurements and metallographic observations of the 30 a/o alloy. An aging effect is attributed to coherency stresses in the matrix prior to precipitation of the ordered phase. The gamma phase of the 21 a/o molybdenum alloy decomposes by a nucleation and growth mechanism to yield a lamellar distribution of the alpha and delta phases. The ordered, intermediate phase, delta, is body-centered tetragonal with $a_0 = 6.84 \text{ \AA}$ and $c_0 = 6.55 \text{ \AA}$. The solubility limits on the high-uranium side of the delta phase are substantiated.

INTRODUCTION

Early investigators^{(1)*} of the uranium-molybdenum system reported that the addition of 20 to 30 a/o molybdenum stabilized gamma uranium down to room temperature. However, it has been shown⁽²⁾ that the gamma phase is metastable, and decomposes to form an intermediate body-centered tetragonal phase on long-time annealing below 580 C. Figure 1, based on more recent investigations^(3,4), shows the delta phase in the uranium-molybdenum system. The limits of this phase lie between 19 and 34 a/o molybdenum at 575 C, the uranium solubility decreasing to about 31 a/o molybdenum at 400 C.

X-ray data for the transformed delta phase are given in Table 1. The X-ray diffraction pattern⁽²⁾ was indexed on a body-centered tetragonal net, giving a body-centered cell of $a_0 = 6.84 \text{ \AA}$ and $c_0 = 6.55 \text{ \AA}$. This was a doubling of the unit cell dimensions reported by Tucker⁽⁵⁾ as $a_0 = 3.42 \text{ \AA}$ and $c_0 = 3.278 \text{ \AA}$, and of Pfeil and Browne⁽⁴⁾ as $a_0 = 3.425 \text{ \AA}$ and $c_0 = 3.282 \text{ \AA}$. It was not clear, on the basis of these results, however, whether doubling was due to a complex cell or superlattice formation during ordering.

*References are given at the end of the report.

FIGURE 1. URANIUM - MOLYBDENUM CONSTITUTION DIAGRAM

TABLE 1. X-RAY DIFFRACTION PATTERN OF DELTA PHASE

Body-Centered Tetragonal, $c_0 = 6.55 \text{ \AA}$, $a_0 = 6.84 \text{ \AA}$, Fe-K		
(hkl)	Relative Intensity(a)	Spacing, d
110	F	4.85
002	VF	3.25
220	MS	2.44
202	S	2.39
130	F	2.17
400	M	1.72
004	MF	1.65
422	S	1.39
224	M	1.35
440	MF	1.21
404	M	1.18
620 }	S	1.08
602 }		
206	MW	1.04
444	M	0.97

(a) S = strong, M = medium, F = faint, W = weak, and V = very.

This investigation was undertaken to determine the nature of the transformation product and the kinetics of the metastable-gamma decomposition. Recently, alloys in this range became of interest because of their corrosion resistance to high-temperature water, and are being considered for possible application in the Pressurized Water Reactor.

EXPERIMENTAL METHOD

As the electrical resistivity of alloys is highly sensitive to structural change, and is readily measured, this property was selected as the one to be followed during isothermal transformation. Metallographic observations and hardness measurements were made to supplement the resistance data obtained.

Alloy and Specimen Preparation

Alloys for this investigation were prepared from selected biscuit uranium.

Alloys were arc melted from five to seven times under a helium atmosphere, finally being cast into a 2-in. wire bar. A zirconium getter button was used to clean the furnace atmosphere prior to melting.

The wire bars were hot rolled, from a helium-atmosphere furnace at 980 C, to 1/4-in. rod. The rods were pickled to remove oxide and a sample was taken for chemical analysis. All samples were analyzed for molybdenum and carbon content. Carbon contents ranged from 0.01 to 0.03 w/o carbon. Initially three compositions were selected for study: 21 a/o (9.8 w/o), 26.4 a/o (12.6 w/o), and 30 a/o (14.8 w/o) molybdenum. Later work was confined to the 30 a/o alloy when it was found that this composition was more closely centered in the delta region.

All alloys were homogenized 5 hr at 1060 C. Resistance specimens, 2-1/4 in. long, of dumbbell shape, with the central 1-3/4-in. length 0.050 in. in diameter, were machined from the 1/4-in. rod. All specimens, as well as additional samples for later heat treatment, were then annealed 4-1/2 hr at 800 C and water quenched. These heat treatments were carried out in a vacuum furnace under a pressure of 5×10^{-5} mm mercury or less. Any surface film, formed during quenching, was removed by an electrolytic pickle.

Isothermal-Transformation Technique

The resistance specimens were isothermally transformed by inserting them in a Vycor U-tube which was placed in a lead bath held at the desired temperature of transformation. A stirrer in the lead bath, directly below the U-tube, served to eliminate gradients in the bath and also permitted closer temperature control of the bath. The U-tube was kept under a dynamic vacuum of about 10^{-5} mm of mercury. The specimens remained bright and shiny even after 500 hr at temperature.

Resistance measurements were made by the potentiometric method. Tantalum current leads and voltage probes were spot welded to the ends of the resistance specimens. A low-discharge battery was used as the current source, and voltage readings to five and six significant figures on the standard resistance and resistance specimen, respectively, were made by means of an L and N Type K-2 potentiometer.

Readings were taken at temperature every 3 hr, except at the start of transformation, when readings were taken at shorter intervals. Alternate resistance readings were taken, in which the flow of current through the specimen was reversed, to eliminate the effect of spurious potentials arising as a result of any temperature gradient across the specimen. A thermocouple, spot welded to the specimen, was used to measure the specimen temperature. It was found that less than 5 min was required for the specimen to come to the bath temperature.

Upon completion of a run, additional samples were prepared for metallographic examination, along with the transformed specimen. These were transformed at the temperature of interest for times selected on the basis of the resistance changes observed. They were examined metallographically and hardness measurements were made.

Metallographic Preparation

Specimens for metallographic examination were ground wet through 600-grit paper and given a final polish on Forstmann cloth covered with diamond abrasive.

The 21 a/o molybdenum alloy was etched electrolytically at 20 v with a mixture (by volume) of 1 part chromic acid base solution to 18 parts acetic acid. The base solution consisted of 118 g of chromic oxide dissolved in 100 cm³ water.

For all other alloys, the most satisfactory etchant was found to be one consisting of equal parts, by volume, of hydrogen peroxide and ammonium hydroxide. It was applied by swabbing.

The specimens were examined both under bright field and polarized light. Polarized-light techniques were found to be the most satisfactory for observation of the 26.4 and 30 a/o alloys. The etchant described above was used in all cases to remove worked metal from the surface prior to examination.

RESULTS AND DISCUSSION

Alloys containing 21, 26.4 and 30 a/o molybdenum were isothermally transformed at 500 C and electrical resistance and metallographic data obtained for their transformation. When metallographic examination of the transformed structures showed the 30 a/o alloy to be the only one that was single phase, all further effort was concentrated on this composition.

Additional data, during transformation at 540, 440, and 400 C were obtained for this alloy. No attempt was made to obtain data at still lower temperatures when the transformation at 400 C was found to be exceedingly sluggish.

Uranium-21 a/o Molybdenum Alloy

Electrical resistance and Vickers hardness, versus the logarithm of the time, are plotted in Figure 2 for the 21 a/o molybdenum alloy. The resistance curve shows an induction period, a transformation period, and finally a stage of no further change once transformation is complete. The hardness changes follow the resistance changes quite closely, a slight softening, once transformation is complete, probably resulting from coalescence of the precipitated particles.

This S-type transformation curve is typical of transformation occurring by a nucleation and growth mechanism. If the resistance change is assumed proportional to transformation, and is then plotted on a probability scale versus log time, a straight line results as shown in Figure 3. White⁽⁶⁾ obtained a similar decomposition curve for the nucleation and growth of alpha in beta uranium-chromium alloys during isothermal transformation.

If 1 per cent of the resistance change is taken as the beginning of transformation, and 99 per cent as the end of transformation, it is found that the transformation begins in 27 hr and ends at about 170 hr. If comparison of these times is made with the times required to obtain the microstructures shown in Figure 4, it is seen that good agreement exists between the two. The transformed structure consists of lamellar alpha-uranium and delta phases, which are nucleated at the gamma grain boundaries and grow inward to consume the gamma grain. After 80 hr at temperature, the initially equiaxed metastable gamma grains show somewhat less than 50 per cent decomposition (Figure 4b) whereas after 170 hr the alloy is apparently fully transformed (Figure 4c).

There is excellent agreement between resistance, hardness, and metallographic data obtained for this alloy. This agreement tends to validate the experimental techniques used to follow the transformation.

Uranium-26.4 and -30 a/o Molybdenum Alloys

In the 26.4 a/o alloy, transformed at 500 C, the resistance increased for the first 55 hr and then decreased (Figure 5). The resistance showed an initial 1.34 per cent increase followed by a 0.6 per cent decrease.

FIGURE 2. RESISTANCE AND HARDNESS CURVES OF A 21 α/o MOLYBDENUM SAMPLE DURING ANNEALING AT 500°C

A-12567

FIGURE 3. TRANSFORMATION CURVE BASED ON RESISTANCE MEASUREMENTS OF A 21 at% MOLYBDENUM SAMPLE DURING ANNEALING AT 500 C

A-12568

100X

N6876

(a) Bright Field. Annealed 4-1/2 Hr 800 C, Water Quenched

100X

N7715

(b) Bright Field. Annealed 4-1/2 Hr 800 C, Water Quenched. Transformed 80 Hr 500 C

100X

N15393

(c) Bright Field. Annealed 4-1/2 Hr 800 C, Water Quenched. Transformed 170 Hr 500 C

500X

N6877

(d) Bright Field. Annealed 4-1/2 Hr 800 C, Water Quenched. Transformed 360 Hr 500 C

FIGURE 4. MICROSTRUCTURES OF 21 a/o MOLYBDENUM ALLOY

FIGURE 5. RESISTANCE CURVE OF A 26.4 at% MOLYBDENUM SAMPLE DURING ANNEALING AT 500 C

A-12569

In the 30 a/o alloy, the initial increase occurred for 33, 28, and 43 hr at 540, 500, and 440 C, respectively. This is shown in Figures 6, 7, and 8. Transformation of an additional specimen at 400 C was discontinued after 500 hr, during which time the resistance increased continuously. The initial increase at 540 and 500 C (Figures 6 and 7) was 3.6 per cent followed by decreases of 0.3 and 0.5 per cent during the following 255 and 352 hr, respectively. At 440 C (Figure 8), the resistance increased by 3.9 per cent during the first 43 hr and then decreased by 2.5 per cent from the peak value during the ensuing 461 hr at temperature.

The resistance changes are perhaps more significant when comparison before and after annealing is made of measurements taken at room temperature. When the resistance of the 26.4 a/o alloy was compared at room temperature before and after transformation, the resistance had decreased by 5.93 per cent. In the 30 a/o alloy, the resistance of the specimens annealed at 540 and 440 C was found to have decreased by 5.35 and 7.8 per cent, respectively. For this alloy, these decreases in resistance at room temperature compare with over-all increases in resistance of 3.3 and 1.8 per cent when measurements were taken at the temperature of transformation.

This resistance decrease is characteristic of an ordering-type reaction. The over-all increases in resistance, when measurements are made at the temperature of transformation, contrasted with the sizeable decreases, as measured at room temperature, appear to be reasonable. Apparently, the temperature coefficient of resistivity of the ordered state is much larger than that of the disordered state.

The large unit cell reported⁽²⁾ for the delta phase, as obtained by X-ray diffraction, results from superlattice formation during ordering. The ordered cell is body-centered tetragonal with $a_0 = 6.84$ Å and $c_0 = 6.55$ Å.

Metallographic examination of the 26.4 and 30 a/o alloys did not reveal any evidence of transformation within the grains to accompany the initial sharp increase in resistance. After 55 hr at 500 C, corresponding to the time at which the resistance was a maximum in the 26.4 a/o alloy, small amounts of lamellar alpha and delta precipitated at the grain boundaries (Figure 9b) but there was no evidence of transformation within the gamma grains. After 170 hr, a platelike transformation along crystallographic planes was seen to be taking place (Figure 9c). Similarly, in the 30 a/o alloy, 45 hr at 440 C (Figure 10b) resulted in precipitation of alpha plus delta at the grain boundaries, but no transformation within the grains was observed. After 180 hr (Figure 10c), the same platelike transformation product appeared. The resistance increase in the 30 a/o alloy, transformed at 400 C, was also accompanied by the appearance of small islands of alpha and delta at the gamma grain boundaries, but again with no evidence of transformation within the grains.

FIGURE 6. RESISTANCE AND HARDNESS CURVES OF A 30 a/o MOLYBDENUM SAMPLE DURING ANNEALING AT 540C

A-12570

FIGURE 7. RESISTANCE AND HARDNESS CURVES OF A 30 a/o MOLYBDENUM SAMPLE DURING ANNEALING AT 500C

A-12571

FIGURE 8. RESISTANCE CURVE OF A 30 α/o MOLYBDENUM SAMPLE DURING TRANSFORMATION AT 440C

A-12572

100X

N17166

(a) Bright Field. Annealed 4-1/2 Hr 800 C, Water Quenched

100X

N8668

(b) Bright Field. Annealed 4-1/2 Hr 800 C, Water Quenched. Transformed 55 Hr 500 C

100X

N8670

(c) Polarized Light. Annealed 4-1/2 Hr 800 C, Water Quenched. Transformed 170 Hr 500 C

FIGURE 9. MICROSTRUCTURES OF 26.4 a/o MOLYBDENUM ALLOY

100X

N7060

(a) Bright Field. Annealed 4-1/2 Hr 800 C,
Water Quenched

100X

N8788

(b) Bright Field. Annealed 4-1/2 Hr 800 C,
Water Quenched. Transformed 45 Hr 440 C

100X

N15392

(c) Polarized Light. Annealed 4-1/2 Hr 800 C,
Water Quenched. Transformed 180 Hr 440 C

100X

N7118

(d) Bright Field. Annealed 4-1/2 Hr 800 C,
Water Quenched. Transformed 4 Hr 500 C

100X

N8435

(e) Bright Field. Annealed 4-1/2 Hr 800 C,
Water Quenched. Transformed 80 Hr 500 C

100X

N7718

(f) Polarized Light. Annealed 4-1/2 Hr 800 C,
Water Quenched. Transformed 80 Hr 500 C

FIGURE 10. MICROSTRUCTURES OF 30 a/o MOLYBDENUM ALLOY

100X

N8438

(g) Bright Field. Annealed 4-1/2 Hr 800 C,
Water Quenched. Transformed 380 Hr 500 C

100X

N7109

(h) Polarized Light. Annealed 4-1/2 Hr 800 C,
Water Quenched. Transformed 380 Hr 500 C

100X

N17165

(i) Bright Field. Annealed 4-1/2 Hr 800 C,
Water Quenched. Transformed 40 Hr 540 C

100X

N15391

(j) Polarized Light. Annealed 4-1/2 Hr 800 C,
Water Quenched. Transformed 288 Hr 500 C

FIGURE 10. (Continued)

The presence of the alpha phase in these three specimens is in agreement with the constitutional diagram shown in Figure 1, in which decreasing solubility of uranium in the delta phase with decreasing temperature is indicated.

The 30 a/o alloys transformed at 500 and 540 C showed no evidence of transformation during the initial resistance increase. Neither 4 hr at 500 C (Figure 10d) nor 40 hr at 540 C (Figure 10i) produced any great change in the gamma-quenched structure, although after 80 hr at 500 C (Figures 10e and f) the platelike structure appeared. Under bright-field illumination the effect is difficult to show, but polarized light indicates extensive transformation has begun. After 380 hr at 500 C (Figures 10g and h), both bright-field and polarized-light techniques sharply delineate the transformed plates.

It should be noted that the transformed metallographic structures are consistent with an ordering reaction. Essentially the same platelike structures have been observed during ordering of a cobalt-platinum alloy, Co-Pt. (7)

Hardness measurements were made on the 30 a/o specimens which were transformed at the two temperatures, 540 and 500 C, to show pure gamma-to-delta transformations, with no initial precipitation. The hardness curves for these specimens are shown with their resistance curves, in Figures 6 and 7. The hardness curves, for both temperatures of transformation, follow the resistance curves quite closely, the hardness increasing slightly and then decreasing with time.

Both the hardness and resistance increases are assumed to be caused by strain developed in the alloy as coherent nuclei of the ordered tetragonal phase form in the gamma matrix. This induction period, which may correspond to a period of short range order, is ended when the nuclei become of sufficient size to lose coherency with the parent matrix. The hardness and resistance decrease thereafter, as the ordered plates grow at the expense of the disordered parent matrix. This period is accompanied by observable precipitation of the ordered plates.

Further evidence of a stressed condition during the initial period of transformation was observed in a series of 30 a/o specimens transformed at 500 C for 2, 4, 80, and 170 hr and water quenched. The specimens annealed for 2, 4, and 80 hr showed intergranular cracks near the edges upon metallographic examination, whereas the specimen transformed for 170 hr, as well as a sample in the initial gamma-quenched condition, showed no evidence of such cracks. Evidently, superposition of quenching stresses upon those in the material as a result of the induction period are sufficient to cause cracking.

If the resistance curves of the 30 a/o alloy (Figures 6, 7, and 8) are compared, the peak resistances are found to occur after 33, 28, and 43 hr at 540, 500, and 440 C, respectively. At 440 C, the resistance increased continuously for 500 hr, at which time the transformation was discontinued. This period appeared to coincide with the stage of increasing resistance at the other temperatures.

These variations suggest a C-curve behavior for the alloy, the nose of the curve lying close to 500 C. Upon the basis of the metallographic observations, the C-curve represents the end of an induction period and the start of transformation.

In general, the transformation of the 30 a/o molybdenum alloy at 540, 500, and 440 C may be regarded as essentially complete. However, the end of transformation, which may be expected to show a C-curve behavior also, apparently was not reached, since the resistance continued to decrease even after long periods at temperature. Another possible explanation is that the resistance decrease is the result of coalescence of ordered plates.

The C-curve behavior for the alloy is a consequence of the tendency to order, which increases with decreased temperature, and the rate of diffusion, which decreases with decreased temperature. The nose of the C-curve occurs at the temperature at which these two controlling factors are balanced for optimum transformation.

SUMMARY AND CONCLUSIONS

Transformation of the 21 a/o molybdenum alloy occurs by a nucleation and growth mechanism. The alpha and delta phases are nucleated at the gamma grain boundaries and grow inward to consume the gamma grains. The decomposition products have a lamellar distribution. Resistance and hardness measurements during transformation show an induction period, a period of transformation, and finally a stage where no further change occurs.

The 26.4 and 30 a/o molybdenum alloys transform by an ordering reaction which probably occurs by a nucleation and growth mechanism. Sufficient data are available to indicate that the transformation in the 30 a/o alloy has a C-curve-type behavior. During transformation of the alloys, the electrical resistance and hardness first increase and then decrease with time, the peaks in resistance and hardness almost coinciding. Transformation is not observed metallographically until after the resistance and hardness peaks are passed.

The increased hardness and resistance during aging are attributed to strain developed in the matrix as a result of the formation of coherent

nuclei. Precipitation, and loss of coherency, are accompanied by a decrease in resistance and hardness. The induction period, preceding transformation, and attendant C-curve behavior originate in the temperature dependence of the tendency of the alloy to order and of the rate of diffusion.

The transformation of gamma to delta is sluggish at all temperatures, and the rate decreases rapidly below 440 C. The optimum temperature of transformation, or nose of the C-curve, lies close to 500 C.

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