NAA-SR-6617
METALS, CERAMICS,
AND MATERIALS
23 PAGES

THE GAMMA TO GAMMA PRIME TRANSFORMATION
IN THE
URANIUM-MOLYBDENUM SYSTEM

By

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A DIVISION OF NORTH AMERICAN AVIATION, INC.
P.O. BOX 309 CANOGA PARK, CALIFORNIA

CONTRACT: AT(11-1)-GEN-8
ISSUED: DEC 30 1961

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ABSTRACT

Electrical resistance measurements and metallography were employed in a study of the kinetics of the gamma to gamma prime transformation in the uranium-molybdenum system at 16 wt% molybdenum.

A non-equilibrium phase, identified by X-ray diffraction as alpha uranium, appeared early in the transformation anneal, reaching a maximum volume fraction at the time the gamma prime emerges. Subsequently, the alpha phase disappears with time.

The gamma matrix transforms to gamma prime faster as the transformation temperature is increased; at 550°C, the gamma prime phase first appears between 48 and 72 hours, while at 500°C it first appeared after a 120 hour anneal.

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I. INTRODUCTION

One of the suggested mechanisms for the agglomeration of small bubbles of fission gas into large bubbles with concomitant swelling is the action of moving grain boundaries or other interfaces in the material. Barnes[1] has demonstrated this effect for the case of helium bubbles in copper and it seems warranted to assume a similar situation exists in irradiated uranium.

When pure uranium is used as a reactor fuel, temperature fluctuations cause it to transform back and forth between the alpha, beta, and gamma forms with associated interphase boundary motion. Also, thermal stresses and stresses due to phase transformations can induce grain boundary migration, especially in the anisotropic alpha and beta phases.

An alloy in which these effects might be minimized is uranium with 16 wt% molybdenum. The sole transformation in this alloy from room temperature to the solidus line is an order-disorder transformation[2,3] which takes place from 565 to 600°C depending on the precise composition (see Figure 1). The width of the ordered phase, gamma prime, on the phase diagram is from 15.5 to 16.3 wt% molybdenum.

In the disordered state, the alloy is a solid solution having a body-centered cubic structure. Upon ordering, the structure becomes tetragonal, with the new unit cell constructed of three of the old unit cells which have become somewhat distorted.[2]

The kinetics of the ordering reaction is the subject of this paper.

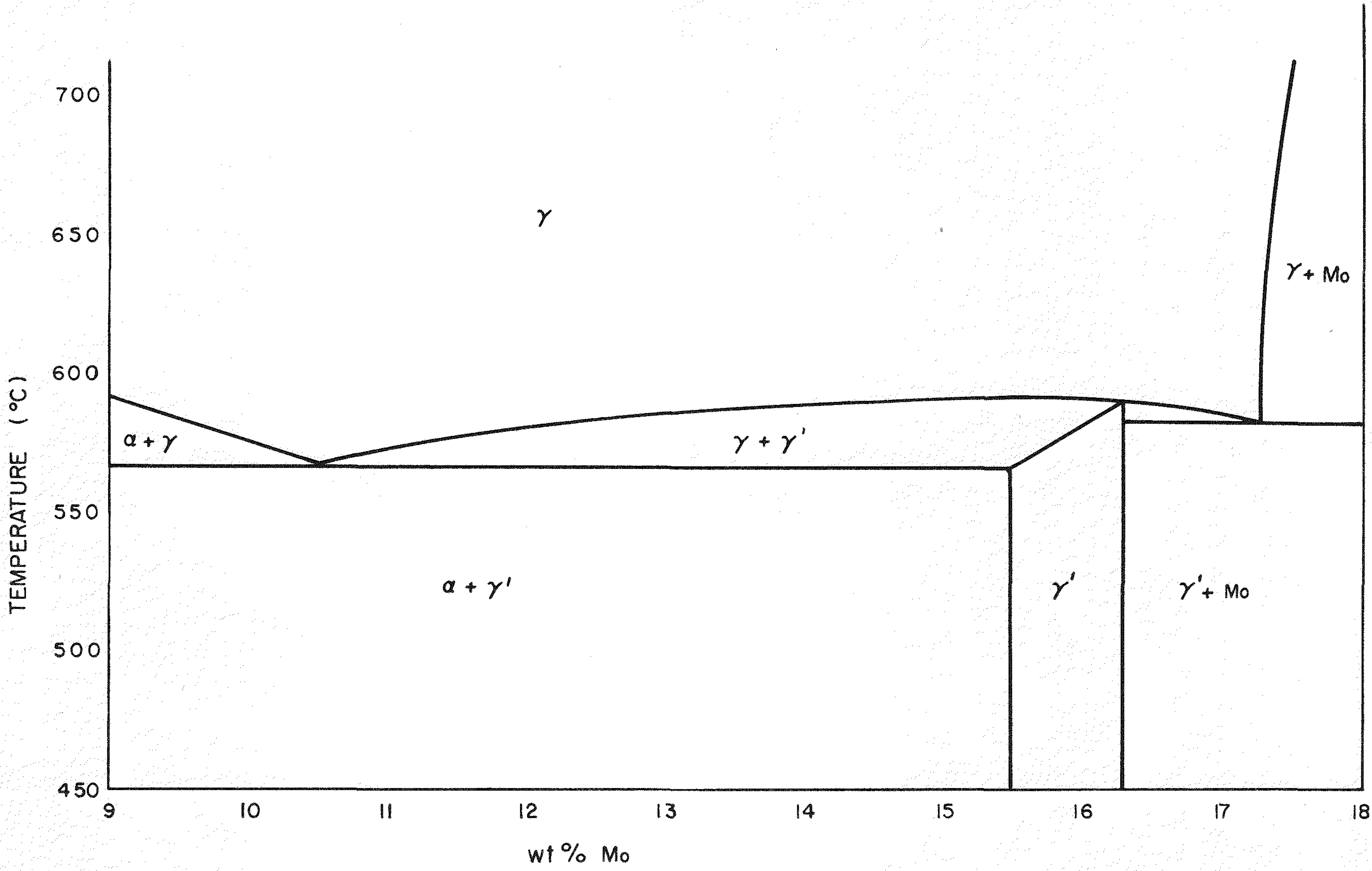

Figure 1. A Portion of the Uranium-Molybdenum Phase Diagram (after Dwight[3])

II. EXPERIMENTAL

A. PREPARATION OF ALLOYS

Alloys for this study were prepared by vacuum induction melting in thoria crucibles (from normal reactor grade uranium and 99.5 wt% molybdenum pellets). Two ingots were prepared, and sections of the top and bottom of each ingot were chemically analyzed for uranium and molybdenum content. The results of the analyses appear in Table I. Both ingots proved to be quite homogeneous.

TABLE I

COMPOSITION OF ALLOYS

Alloy	Weight Percent	
	Mo	U
16M	16.1	82.9
16M3	16.3	82.8

B. ELECTRICAL RESISTANCE MEASUREMENTS

To monitor the progress of the transformation from gamma to gamma prime, electrical resistance measurements were made on samples during transformation at temperature. These were cut from ingot 16M3 having a square cross-section 2 by 2 mm and a length of 25 mm. Four electrical lead wires (two for current and two for voltage probes) were spot welded to the sample, a pair at each end. It was found that platinum would not form a good spot weld to the alloy whereas tantalum did. Therefore, platinum wires were joined to a small length of tantalum wire by spot welding for the purpose of spot welding to the sample.

The sample with lead wires attached was sealed in a quartz capsule evacuated to 5×10^{-6} mm of mercury. The wires came out of the capsule through a graded glass seal.

Each encapsulated sample was treated at 1050°C for 24 hours and transferred directly to another furnace at a desired transformation temperature. The resistance of the sample was obtained by measuring (with a Leeds and Northrup model K3 potentiometer) the voltage drop across a standard resistor in series with the sample and the voltage drop across the sample.

C. METALLOGRAPHY

Samples of 16M were wrapped in tantalum foil, sealed in evacuated quartz capsules, and annealed at 1110°C prior to being transferred directly to the transformation temperature. They were subsequently examined metallographically after various times at temperature to determine the progress of the transformation. Electron photomicrographs were taken of selected samples. Details concerning specimen preparation for photomicrographs shown in this report appear in Appendices I and II.

III. RESULTS

Figure 2 shows the results of the electrical resistance measurements for three transformation temperatures. The ordinate, $\Delta\Omega/\Omega_o \times 100$, represents the percent change in resistance from Ω_o, which is the value of the resistance after one hour at the transformation temperature. A natural log scale is used for the abscissa to compress the time scale.

The salient features of the three curves are an initial early rise in resistance followed by a level period prior to a small decrease.

In Figure 3, the portions of the curves to 30 hours shown in Figure 2 are replotted on a linear time scale for easier comparison of the resistance changes during the first stage of transformation.

Figures 4 through 10 show the microstructure of 16M samples treated at 550°C for increasing times. Surprisingly, one sees a phase appearing after 1 hour (Figure 4) which bears no resemblance to gamma prime. This phase continues to grow until it reaches a maximum after circa 48 hours (Figure 7). After 72 hours at 550°C, the gamma prime phase is clearly visible under polarized light in its usual form while the transient phase is present in considerably reduced amount. Figure 10 shows that after 120 hours this phase has almost disappeared.

Samples of 16M were also treated at 500°C in the same manner. The transient phase was present and disappeared after 500 hours. The gamma prime was first detected after 120 hours at 500°C.

Because of its high optical activity under polarized light, we suspected that this non-equilibrium phase was alpha uranium. X-ray diffraction patterns taken on bulk samples treated at 550 and 500°C showed relatively large amounts of this phase. The (002), (021), and (020) reflections of alpha uranium were detected in both types of samples identifying the metastable phase. A high degree of preferred orientation prevented the observation of all the above reflections in each sample.

In Figures 11 and 12, one sees the alpha phase, previously shown in Figures 6 and 7, at high magnification, the distance between markers being one micron. These photographs were taken with the electron microscope from surface replicas described in the appendix.

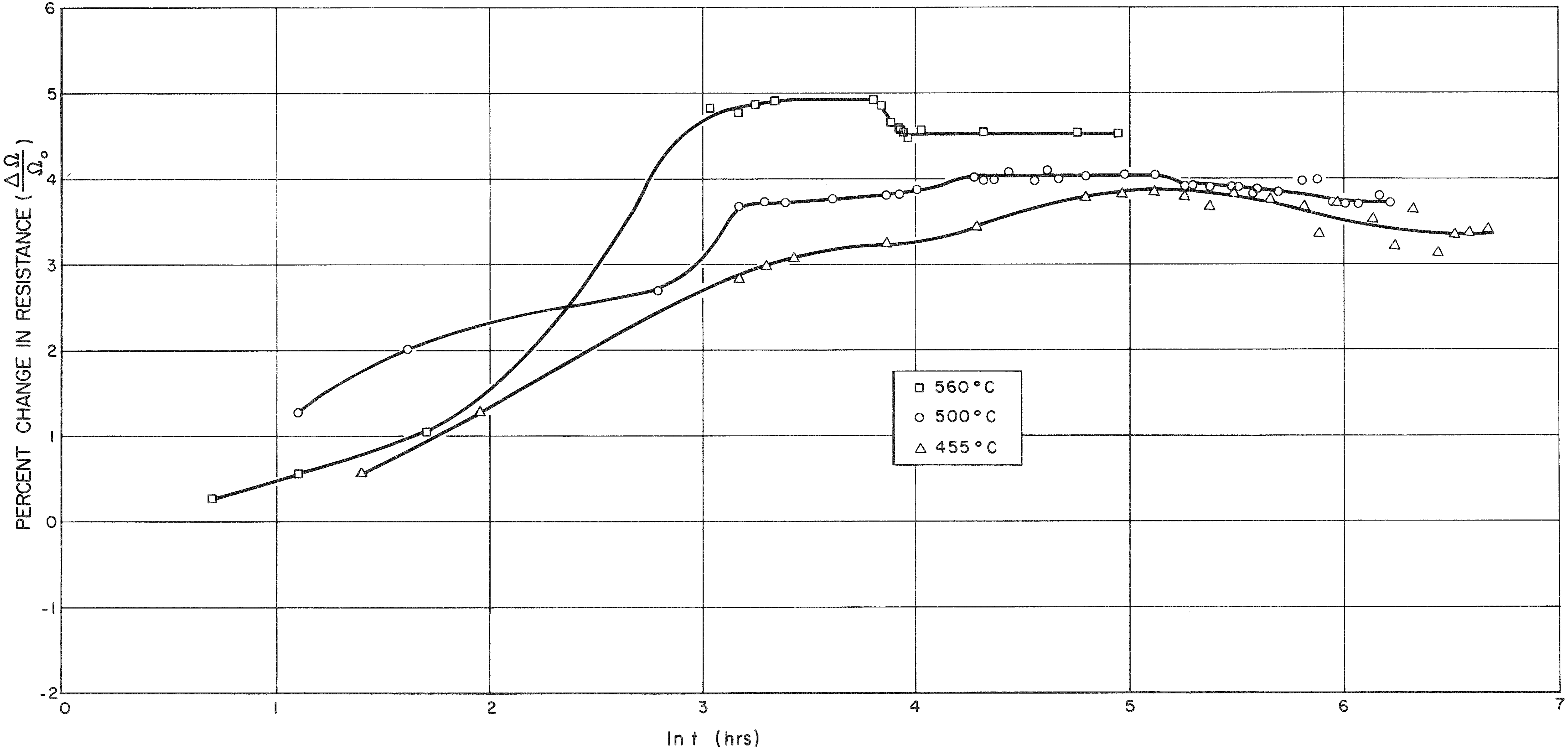

Figure 2. Percent Change in Electrical Resistance of Samples of Alloy 16M3 Treated 24 Hours at 1050°C then Brought to the Above Indicated Temperatures.

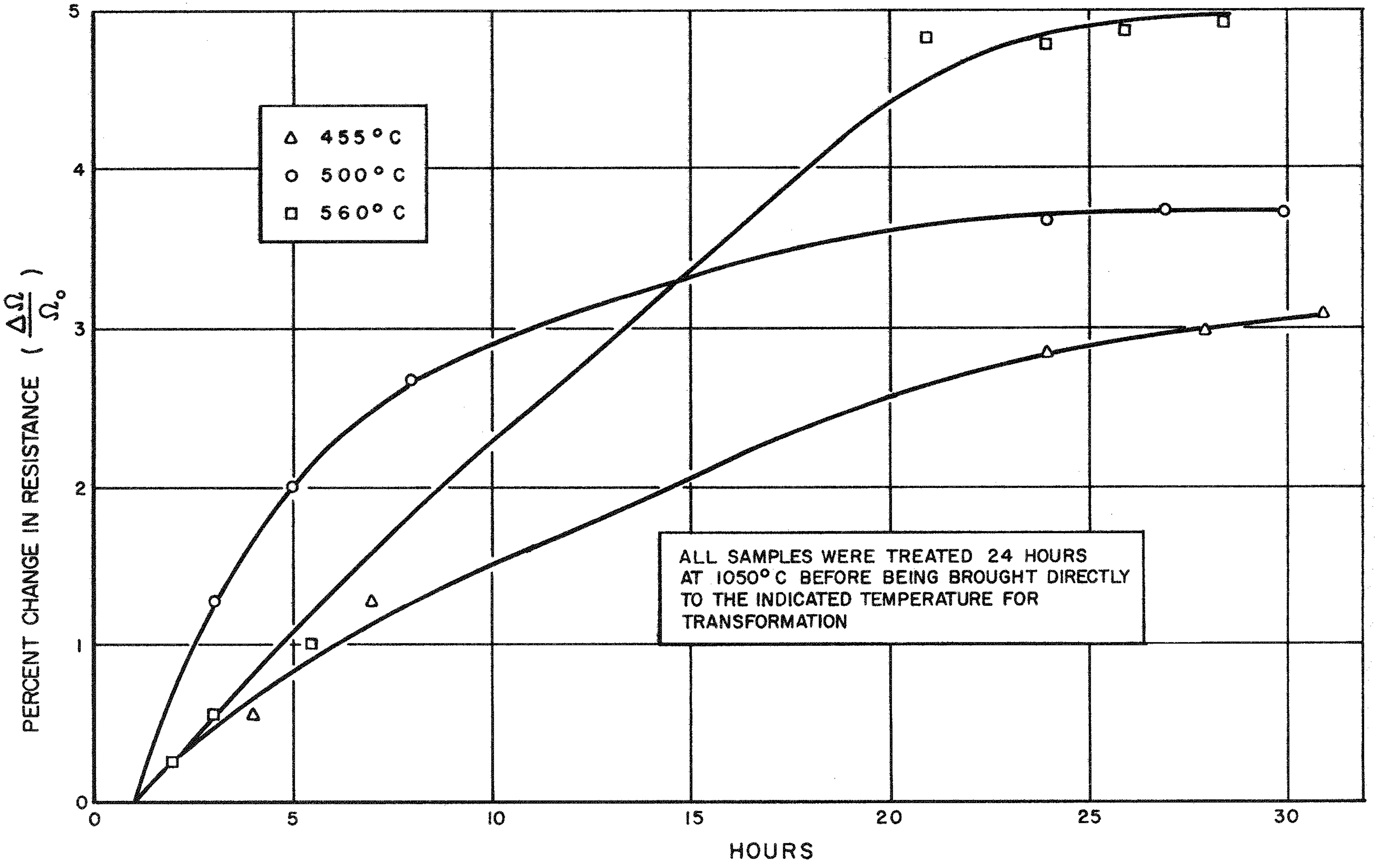

Figure 3. Fractional Change in Resistance During the Early Stages of Transformation.

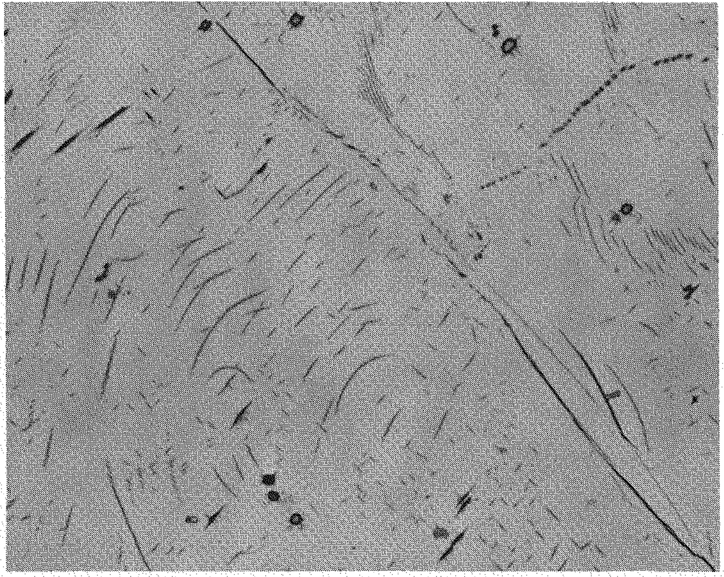

Figure 4. Alloy 16M annealed one day at 1110°C, then one hour at 550°C, and air cooled. (500X)

Figure 5. Alloy 16M annealed one day at 1110°C, then twenty-four hours at 550°C, and air cooled. (500X)

Figure 6. Alloy 16M annealed six days at 1110°C, then thirty-one hours at 550°C, and air cooled. (500X)

Figure 7. Alloy 16M annealed six days at 1110°C, then forty-eight hours at 550°C, and air cooled. (500X)

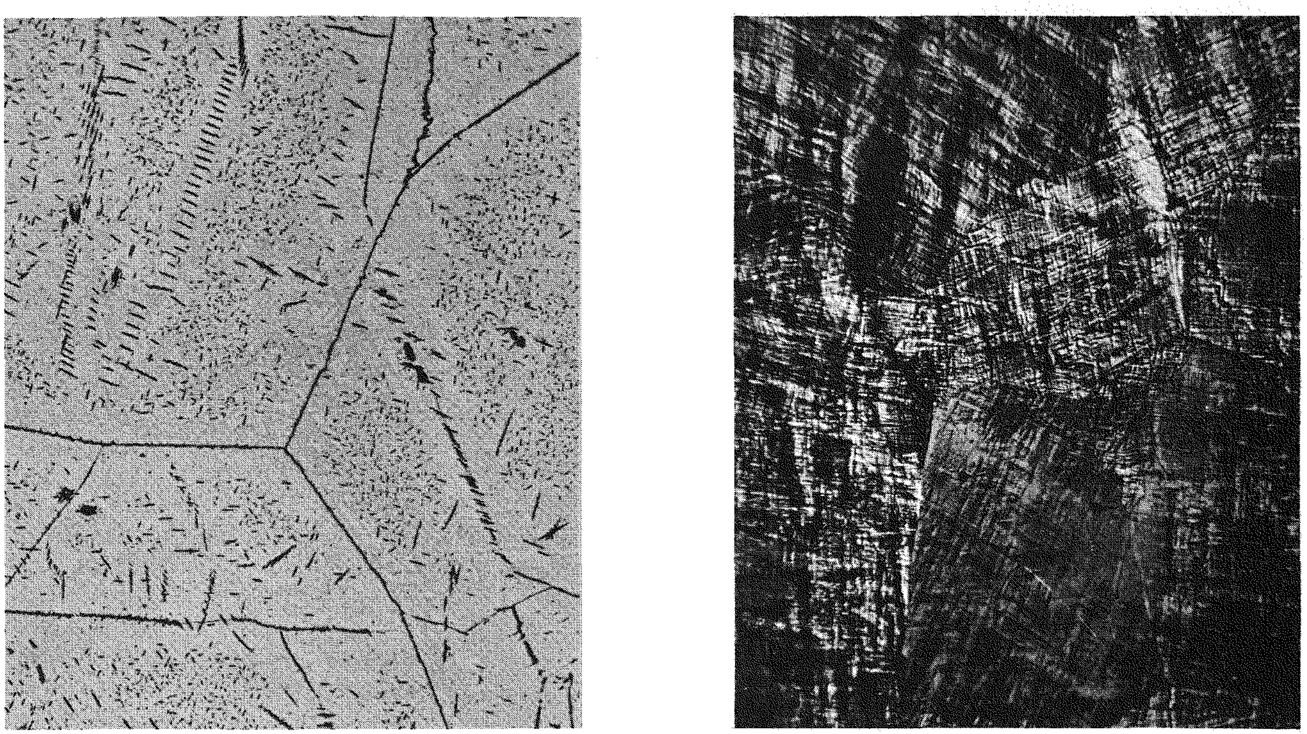

Figure 8. Alloy 16M annealed four days at 1110°C, then seventy-two hours at 550°C, and air cooled. Photographed in bright field to reveal alpha phase and in polarized light to reveal gamma prime phase. ((500X BF and 100X PL)

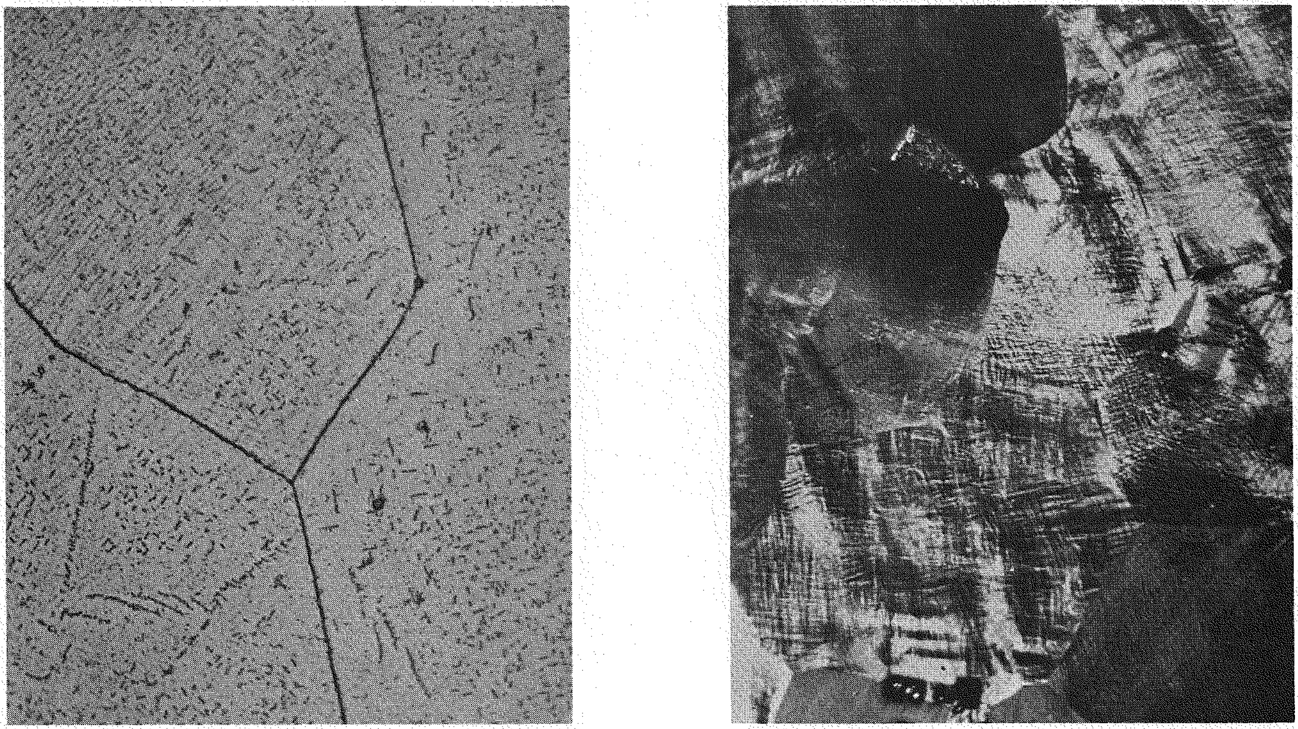

Figure 9. Alloy 16M annealed four days at 1110°C, then ninety-six hours at 550°C, and air cooled. Photographed in bright field to reveal alpha phase and in polarized light to reveal gamma prime phase. (500X BF and 100X PL)

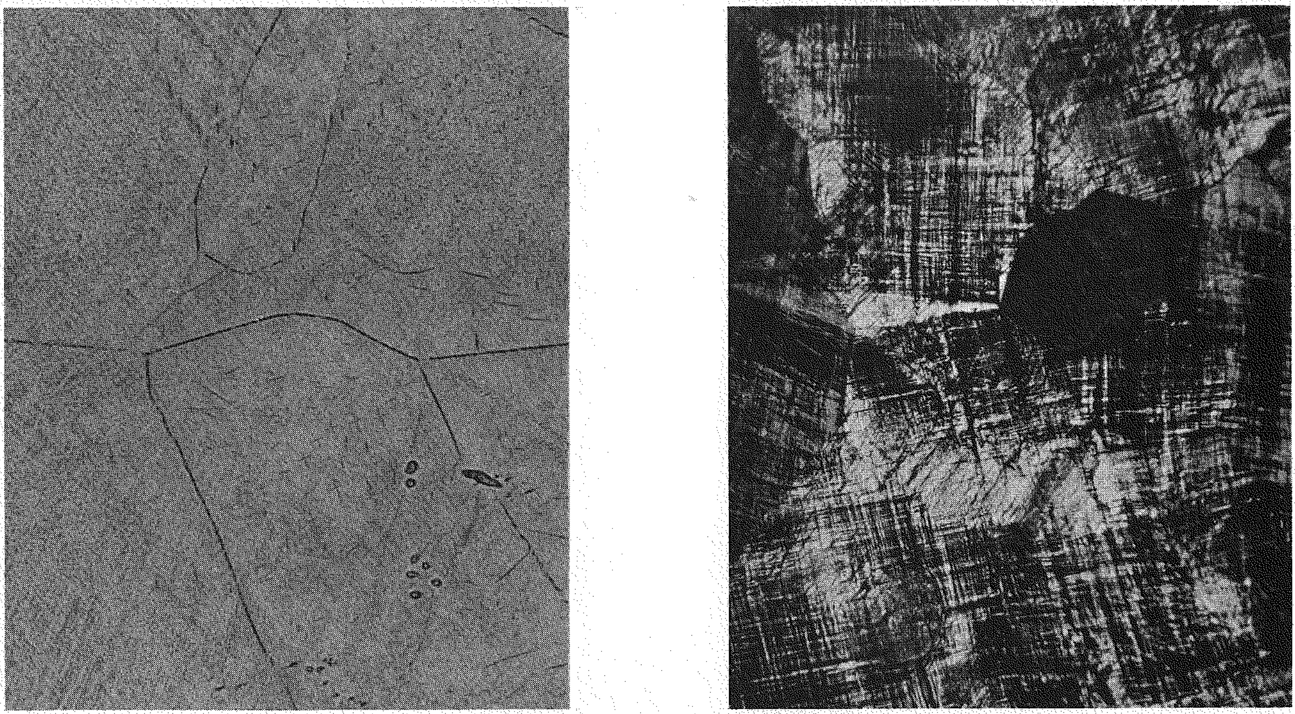

Figure 10. Alloy 16M annealed six days at 1110°C, then one-hundred-twenty hours at 550°C, and air cooled. Photographed in bright field to reveal alpha phase and in polarized light to reveal gamma prime phase. (500X BF and 100X PL)

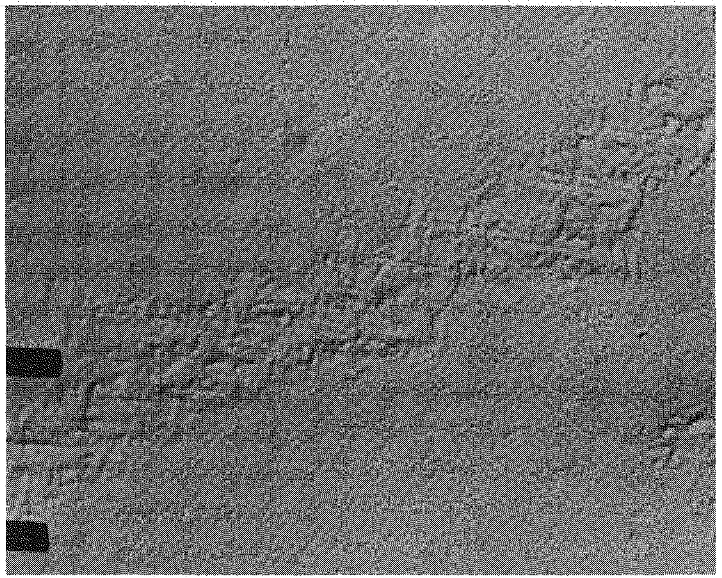

Figure 11. Alloy 16M annealed six days at 1110°C, then thirty-one hours at 550°C, and air cooled.

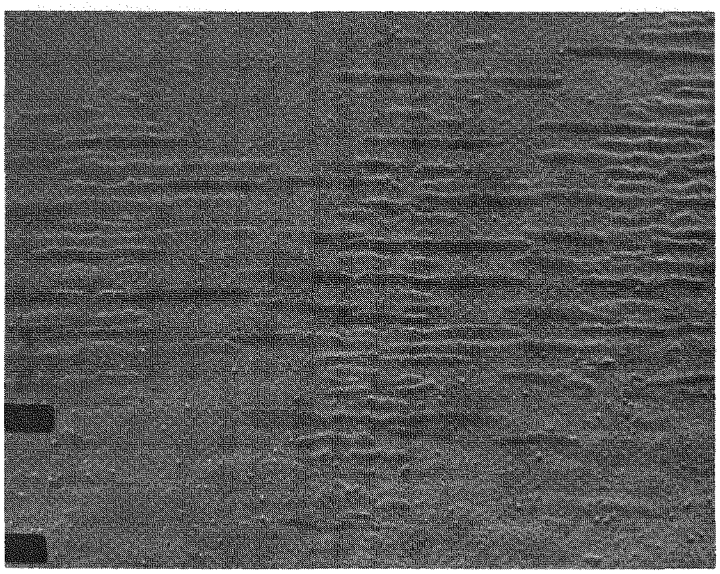

Figure 12. Alloy 16M annealed six days at 1110°C, then forty-eight hours at 550°C, and air cooled.

The form of the alpha precipitate in Figure 11 is one of intersecting platelets probably following an internal boundary such as one delineating a sub-grain, while the alpha phase shown in Figure 12 consists of parallel plates. Both forms were found in each sample.

IV. DISCUSSION

As seen in Figure 2, the early rise in resistance of the samples can be attributed to the precipitation of alpha uranium. Later in time, the molybdenum-rich matrix transforms to the gamma prime structure and continues to order until the equilibrium degree of long-range order for that temperature is reached. During this time, the alpha phase is disappearing, causing the resistance of the samples to fall, but only a small amount. Apparently, the ordered structure has a higher resistivity than the disordered state.

The curves in Figure 3 reveal that the fastest rate of alpha phase precipitation occurs at 500°C, while the maximum amount of this phase present during the transformation increases with temperature. For times shown in Figure 3, no gamma prime phase is present in any of the samples; the sole process affecting the resistance of the samples is alpha phase precipitation.

The presence of substantial amounts of alpha phase is undesirable for two reasons. First, the alpha phase has inherently poor resistance to radiation damage, and second, moving interphase boundaries between alpha and gamma or gamma prime phases is precisely the phenomenon that we are trying to avoid. However, the effect of irradiation is to homogenize an alloy so that even during severe temperature fluctuation this material might remain completely in the gamma phase.

REFERENCES

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2. E. K. Halteman, "The Crystal Structure of U_2Mo," Acta Cryst. 10, 166 (1957)
3. A. E. Dwight, "The Uranium-Molybdenum Equilibrium Diagram Below 900°C," J. Nuclear Materials 2 No. 1, 81 (1960)

APPENDIX I

SAMPLE PREPARATION FOR OPTICAL METALLOGRAPHY

For direct visual observation and photomicrography, samples of alloy 16M were first ground on silicon carbide abrasive papers of grits 240, 400, and 600. Three-micron diamond paste on a billiard cloth was used for coarse polishing, and 1/4 micron diamond paste on a microcloth was used for fine polishing. The samples were then electropolished in a solution of 4 parts glacial acetic acid and one part chromic acid (50% CrO_3 in H_2O). The current density used for electropolishing in this solution was 7-10 amp/cm^2; the current was applied to the sample in one second intervals for a total of 10 seconds. (If the current is sustained for longer than one second, the electrolyte will heat up and the rate of attack will increase beyond the desired level.)

Since the gamma prime phase is tetragonal, its presence can be detected by viewing the sample in polarized light. To increase the contrast between gamma prime plates, the sample was electro-etched in a 10% oxalic acid solution. A current density of 0.2 amp/cm^2 was applied for one second. This very slight etching was sufficient to provide a marked increase in contrast for polarized light viewing.

To reveal the alpha uranium phase, the sample was electro-etched in the 10% oxalic acid solution, using a current density of 0.2 amp/cm^2 applied for five seconds. This was sufficient to reveal the alpha phase by both delineating the interface between the alpha and gamma phases and by lightly staining the alpha phase. Longer etching times stain the alpha phase darker.

APPENDIX II

SAMPLE PREPARATION FOR ELECTRON METALLOGRAPHY

The degree of electropolishing and electro-etching is very critical on sample surfaces to be observed in the electron microscope. The etching technique described for optical observation of the samples produces distorted structures when observed in the electron microscope. Therefore, a solution of 8 parts ethyl alcohol, 5 parts ethylene glycol, and 5 parts phosphoric acid was used as the electrolyte for electropolishing these samples. The current density used was 5 amp/cm^2 and the current was applied in one second intervals for a total of five seconds. The sample was also etched in this solution at a current density of 0.3 amp/cm^2 for approximately two seconds.

A Faxfilm replica was then made of the sample surface. This replica was shadowed with chromium and a carbon layer was then evaporated onto the chromium. The Faxfilm was subsequently dissolved away, leaving the final chromium-shadowed carbon replica.