NAA-SR-6125
METALS, CERAMICS, AND
MATERIALS
17 PAGES

ISOTHERMAL TRANSFORMATION OF U - 14 AND U - 16 WT % Mo ALLOYS AT 550°C; INTERIM REPORT

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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 1 1961

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ABSTRACT

Isothermal transformation kinetics studies of nominal U - 14 and U - 16 wt % Mo alloys were carried out, to determine the limits of gamma-phase stability in these alloys at 550°C. Vacuum induction melted and homogenized samples were gammatized in vacuum at 900°C for 72 hr and ice-water quenched. The gamma phase was retained in each sample. The gammatized samples were then isothermally heat treated in vacuum for specified intervals, ice-water quenched, and examined by x-ray diffraction, metallographic, and microhardness techniques for evidence of transformation.

The retained and metastable gamma phase in U - 14 and U - 16 wt % Mo alloys began to transform to the alpha plus gamma prime and gamma prime phases after 20 and 16 hr, respectively, as indicated by x-ray diffraction and metallography. However, a transition phase, believed to be of alpha phase U-Mo, appeared in the alloys after 0.3 hr in U - 14 Mo and 0.1 hr in U - 16 Mo. A plot was made of the variation in time at 550°C for the beginning of equilibrium transformation and molybdenum content. U - 10 wt % Mo alloys are more gamma stable at 550°C than other alloys in the range of about 5 to 16 wt % Mo. However, U - 16 wt % Mo alloys transform to a stable gamma prime equilibrium phase, a promising structure for high temperature, high burnup reactor service.

I. INTRODUCTION

Gamma-phase stability at 550°C in U - 14 and U - 16 wt % Mo alloys has been investigated by x-ray diffraction, metallographic, and microhardness techniques, to determine the limits of gamma-phase stability at this temperature. Gamma-stable U-Mo alloys are desirable reactor fuels, because of their superior resistance to irradiation damage and their relatively inexpensive fabrication costs. Based on the assumption that increasing molybdenum generally stabilizes the gamma phase, these investigations were inaugurated. Increasing the molybdenum content of U-Mo fuels is done at the expense of a loss in fissile phase density. Any appreciable increase in gamma-phase stability or, in general, increased resistance to irradiation damage, would grossly outweigh the resulting deleterious loss of fissile phase density.

II. EXPERIMENTAL METHOD

Alloys for this study were vacuum induction melted in a 3000 cycle, 100 kw, furnace in batches of approximately 6 kg. Melting was accomplished in yttria (Y_2O_3) lined graphite crucibles. Both melts were bottom poured, through yttria lined spouts and distributors, into yttria lined graphite molds. The melts were poured from approximately 1680°C. The cast melts were free of internal voids, as indicated by gamma radiographs.

Table I shows the nominal and actual chemical analyses of the heats. Both heats suffered carbon contamination. Heat No. 991 and Heat No. 974 contained 1200 and 1600 ppm carbon, respectively.

The heats appeared to be relatively free of oxygen and nitrogen contamination, as indicated metallographically. Quantitative oxygen and nitrogen analyses were not attempted.

The following analytical methods were utilized to carry out chemical analysis of the slugs:

A. MOLYBDENUM

One gram of alloy sample was dissolved in 20 mℓ of 1:1 HNO_3 plus 1 mℓ H_2SO_4. The solution was transferred to a 100 mℓ volumetric flask and 10 mℓ of

TABLE I
CHEMICAL ANALYSIS OF U-Mo ALLOYS

Heat Number	Nominal Composition (wt %)	Analysis (wt %)
991	14 Mo	Top - 13.9 Bottom - 14.1
		Top - 13.8 Bottom - 14.1
974	16 Mo	Top - 15.7 Bottom - 15.9
		Top - 15.9 Bottom - 16.1

silver nitrate solution (20 g/ℓ) were added as an internal standard. After dilution to 100 mℓ with water, an aliquot was placed in an x-ray solution cell and the intensities of the molybdenum K_{β_1} line and the silver K_α line were measured. The ratio of the intensity of the molybdenum to the intensity of the silver was calculated. The percent molybdenum in the sample was determined from a previously determined calibration curve of the percent molybdenum plotted against the ratio of intensities, I_{Mo}/I_{Ag}.

B. CARBON

Carbon was determined by use of a Leco Conductometric Carbon Analyzer. In this procedure, the metal sample was burned in a stream of oxygen. Carbon was converted to carbon dioxide, and this was passed into a barium hydroxide solution. The decrease in conductivity of the barium hydroxide solution was a measure of the carbon present in the sample.

The heats were cast into ten 6-in. long by 3/4-in. diameter slugs. Two slugs from each melt were selected for the kinetics study. These slugs were homogenized in vacuum at 900°C for 72 hr before being cut into hemispherical wafers approximately 3/16 in. thick. The wafers were wrapped in tantalum foil and sealed in quartz capsules that had been twice evacuated and back-filled with argon. Before sealing, the capsules were evacuated to a pressure of 1×10^{-4} mm Hg at 250°C. All materials subjected to elevated temperature exposure were handled in this manner.

After encapsulation, the wafer specimens were gammatized at 900°C for 72 hr and quenched in ice water. Initially, all capsules were cracked in a unique quenching device to insure rapid cooling of the sample. After evaluation of short-time annealed samples (up to 2 hr), the need for rapid cooling to retain the gamma phase was found to be unwarranted. All other samples were quenched in unbroken capsules. This decreased sample cooling rates by about a factor of two. Isothermal treatment of all samples was done in pot furnaces, whose temperatures were controlled and recorded by a power proportioning controller-recorder device. During the entire treatment, the temperature of the furnaces was maintained at 550 ± 5°C. Samples were quenched from the isothermal anneal into ice water and mounted in Bakelite for metallographic study, microhardness measurements, and x-ray diffraction exposure.

Metallographic processing of the samples required special attention, with respect to reliable and consistent reproduction of sample etch. The most reliable combination of polish-etch technique resulted from (1) a finish mechanical polish with Linde B abrasive suspended in a 0.5 vol % solution of HF, (2) vigorous electropolishing in an electrolyte of 50% phosphoric acid, ethylene glycol, and ethyl alcohol, and (3) electroetching in a dilute solution of acetic and nitric acids (see Table II).

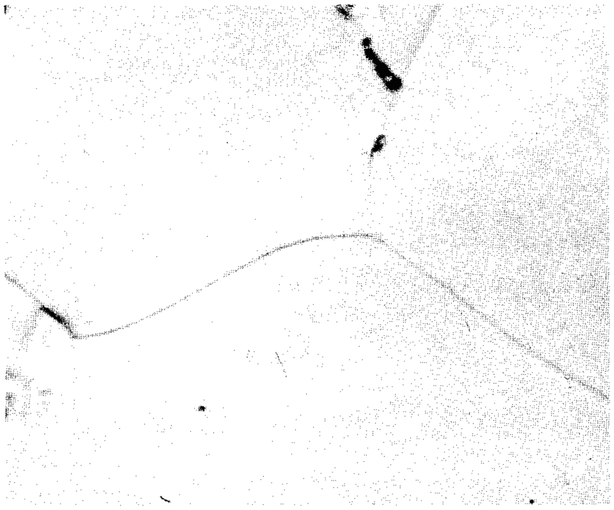
TABLE II

POLISHING AND ETCHING PROCEDURE FOR
U - 14 and U - 16 Mo ALLOYS

Method	Solution	Condition
Fine mechanical polish on silk nap	Linde "B" in 5% HF solution	Light hand pressure for 4 to 5 min
Electropolish	5 parts Phosphoric Acid 5 parts Ethylene Glycol 8 parts Ethyl Alcohol	34 v, 2.1 amp, for 3 sec
Electroetch	1 part Acetic Acid 1 part Nitric Acid (50%) 2 parts Water	9 v, 0.4 amp, for 2 sec
Stain removal	5 parts Phosphoric Acid 5 parts Ethylene Glycol 8 parts Ethyl Alcohol	25 v, 1.9 amp, for 1 sec

Figures 1a through 1f present a photomicrographic survey of the microstructural changes that occur in U - 16 wt % Mo during isothermal transformation at 550°C. The microstructure of U - 14 wt % Mo alloy transformed at 550°C is almost identical to that of U - 16 wt % Mo alloy. The Widmanstättan precipitate in Figures 1b and 1c is metastable, and either redissolves in the matrix or transforms to the gamma prime (γ') phase. Further refinement of metallographic techniques for these samples is under way.

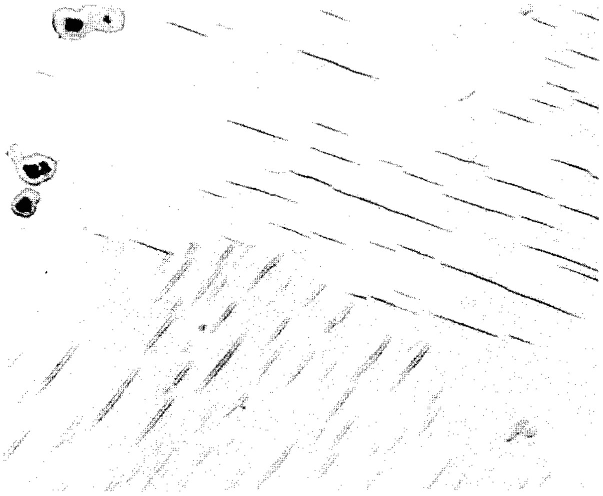
X-ray diffraction studies were accomplished on the massive samples. Powder samples taken from massive samples were unreliable, because of the tendency of the samples to transform back to the gamma (γ) phase, as a result of cold work. Extreme care was exercised with massive samples, since they also tended to revert to γ during rough metallographic polishing, as illustrated by the diffraction patterns in Figure 2. All samples mechanically polished, prior to diffraction studies, were vigorously electropolished to remove any reverted surface material before x-ray diffraction exposure. The gamma prime (γ') phase transformed back to the γ phase, as a result of cold work during polishing. Removal of the cold work surface by electropolishing revealed the γ' phase. The sample used for Figure 2 had been gammatized and isothermally heat treated at 550°C for 500 hr.



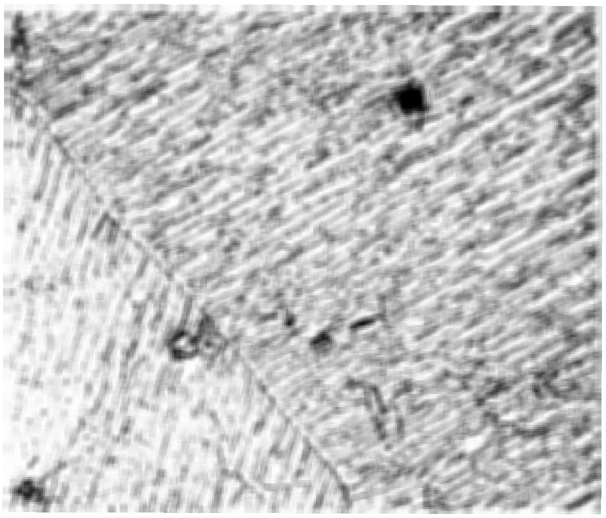
a. Not Heat Treated

650X

b. Isothermally Heat Treated at
550°C for 0.1 hr



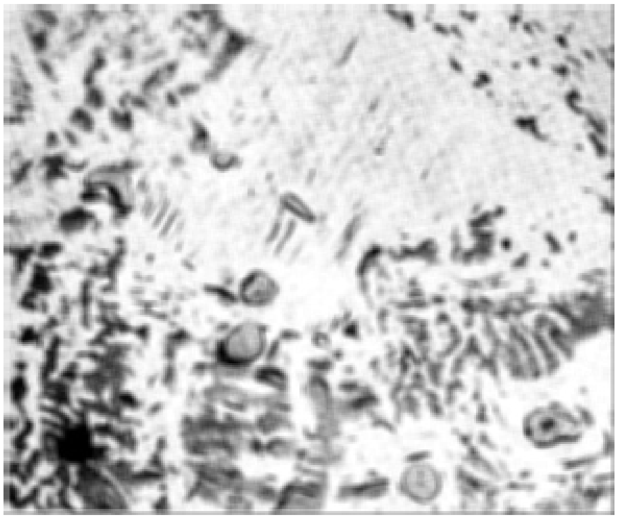
650X



c. Isothermally Heat Treated at
550°C for 6 hr

650X

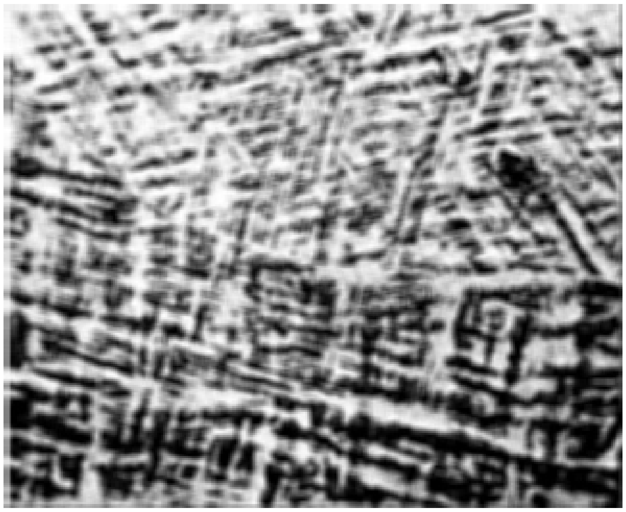
Figure 1. U - 16 Mo, Gammatized at 900°C for 72 hr and Ice-Water Quenched



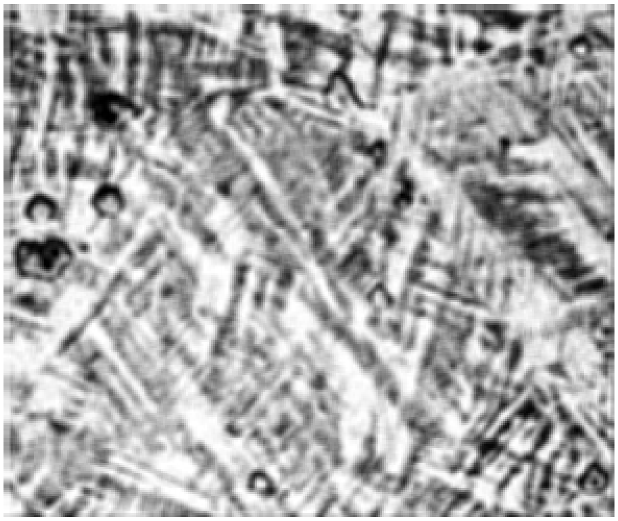
d. Isothermally Heat Treated at 550°C for 16 hr

650X

e. Isothermally Heat Treated at 550°C for 264 hr



650X



f. Isothermally Heat Treated at 550°C for 1029 hr

650X

Figure 1. (Continued)

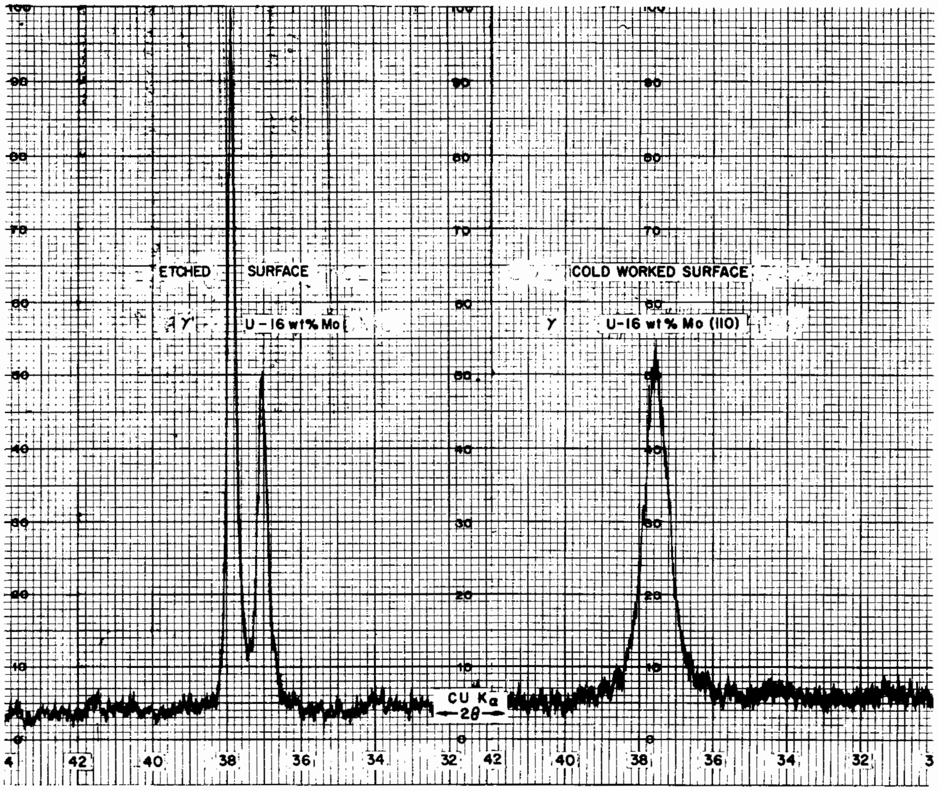


Figure 2. X-ray Diffraction Patterns of Mechanically Polished U - 16 Mo [(right) Before and (left) After Electropolishing]

III. RESULTS

The retained γ phase in gamma quenched U - 14 and U - 16 wt % Mo alloys begins to transform to equilibrium structure after isothermal heat treatment at 550°C for 20 and 16 hr, respectively. However, a metastable transition phase, believed to be of alpha (α) U-Mo, begins to form after 0.3 hr in U - 14 Mo and 0.1 hr in U - 16 Mo. To date, the firm identity of the transition phase has not been established. This transition phase disappears from the alloys after about 100 hr and 60 hr, for U - 14 and U - 16 wt % Mo, respectively. The appearance of the γ' phase was detected in each sample by x-ray diffraction and metallographic techniques, after about the same isothermal exposure. This excellent agreement of techniques suggests further refinement of metallographic detection is paramount, since the x-ray diffraction technique is sensitive only to constituents present in excess of about 10 vol %. No indication of the transition phase was detected by x-ray diffraction. The sensitivities of various methods of monitoring phase transformations in this system have been discussed by Van Thyne and McPherson.[1]

Figures 1a through 1f show the initiation and progress of transformation of gammatized U - 16 wt % Mo alloy to equilibrium structure at 550°C. The nucleation and growth of the transition phase is shown in the early stages of transformation and as the equilibrium phase, γ' (as a function of time at temperature), appears. Whether the transition phase is redissolved into the γ phase matrix or whether it transforms directly to equilibrium γ' cannot be deduced from available data.

U - 14 wt % Mo alloys transform to an equilibrium structure of $\alpha + \gamma'$, and U - 16 wt % Mo alloys transform to an equilibrium structure of γ' (see Figure 3). The α phase is an orthorhombic solid solution of molybdenum in α uranium. The γ phase is a body-centered cubic solid solution of molybdenum in γ uranium. The γ' phase is an ordered state of the γ phase, and is of tetragonal structure with a c/a ratio of 2.871.[2]

None of the photomicrographs (Figures 1a through 1f) are of equilibrium structure, but reflect metastable conditions of transformation. According to accepted nomenclature[3] for phases in the U-Mo alloy system, γ' best describes the equilibrium transformation product shown in Figure 1f. The progress of transformation at temperature for U - 16 wt % Mo alloy can best be seen in Figure 4, a composite photograph of x-ray diffraction patterns of U - 16 Mo. The

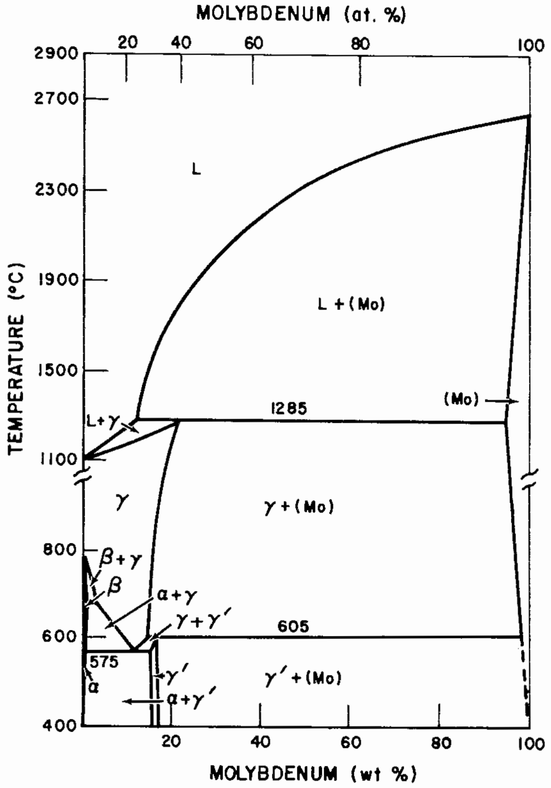
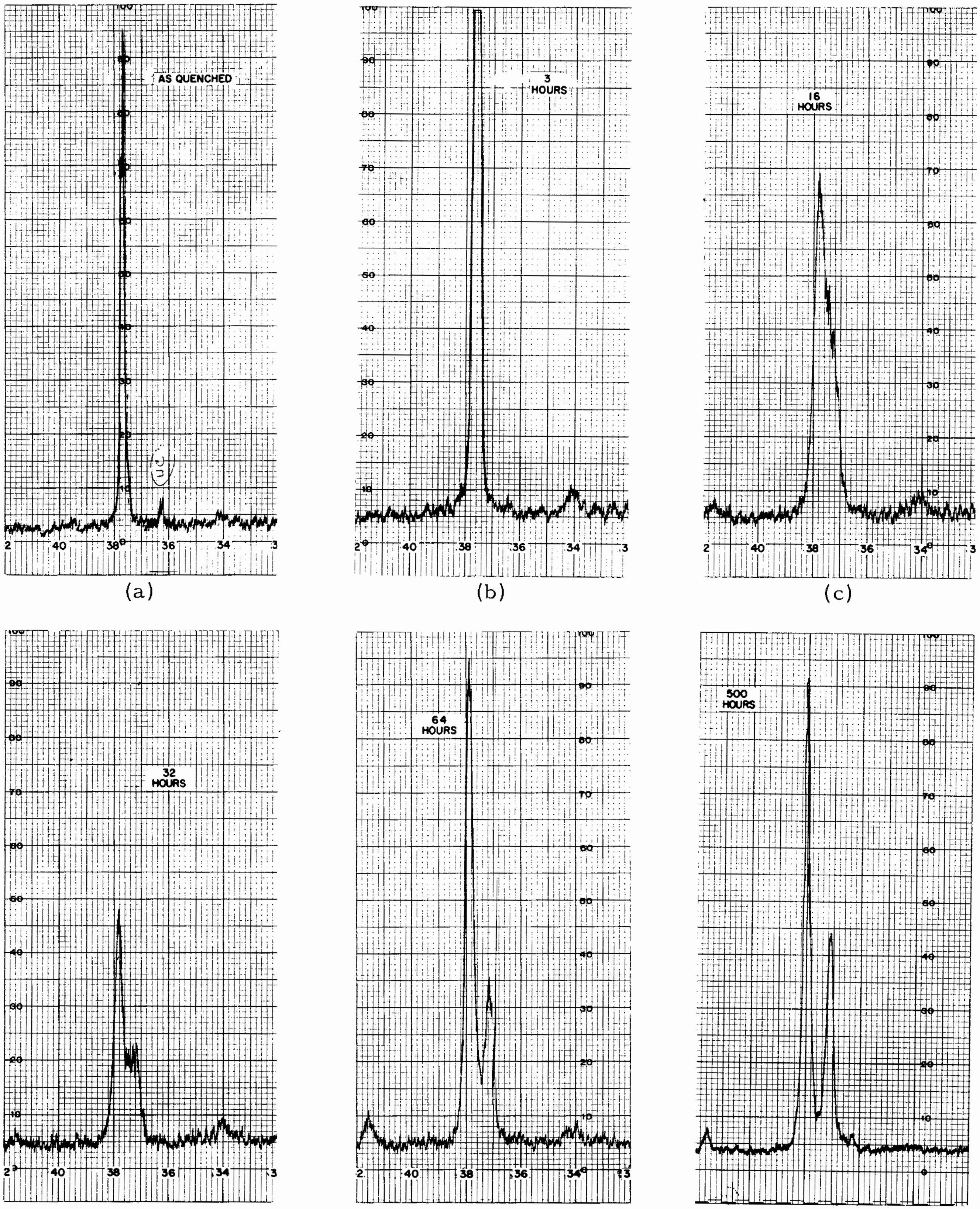


Figure 3. Uranium-Molybdenum Equilibrium Diagram (After Saller, Rough, and Bennett)

patterns shown in Figure 4 were made from massive samples. Therefore, the peak intensities are of little quantitative value. The appearance (16 hr) and separation (32, 64, and 500 hr) of new peaks indicate the beginning and progress of transformation at 550°C. Transformation occurs over an extended time interval, and probably has not reached equilibrium, even after 500 hr. Equilibrium, as determined by x-ray diffraction, would be indicated by the interplanar (d) spacing of the products. In the case of U - 16 wt % Mo after 500 hr at 550°C, the d spacings of the γ' peaks (see Figure 2) are 2.429 Å for the (110) and 2.335 Å for the (103). The equilibrium d values for these spacings are 2.415 Å and 2.366 Å, as reported by Lehmann,[4] and 2.425 Å and 2.372 Å, as reported by Halteman.[5] This deviation is attributed to the metastable condition of the γ' phase. However, impurity phases could have contributed to this shift.

Isothermal transformation at 550°C did not appreciably affect the hardness of the alloys, as indicated in Figure 5, although both alloys suffered decreases in hardness. The hardness of the 16 wt % Mo alloy decreased more than the 14% alloy. If hardness alone is a quantitative indicator of tensile and creep strength in this system, alloys approaching 16 wt % Mo may perform as well as γ-phase alloy fuels in high temperature reactor service. A program, designed to determine the creep and tensile strengths of complete γ'-phase U - 16 wt % Mo alloy, is under way at Atomics International.

The equilibrium product of isothermally transformed γ-phase U - 16 wt % Mo alloy completely excludes the α phase. Alpha phase U-Mo is generally considered to be a prime source of weakness, with respect to the irradiation damage resistance, of transformed U-Mo alloy. Gammatized and isothermally transformed U - 14 wt % Mo alloy contains only a small amount of the α phase. The



(a) (b) (c)

(d) (e) (f)

Figure 4. X-ray Diffraction Patterns of Gammatized and Isothermally Heat Treated (550°C) U - 16 Mo

lack of the α phase in transformed U - 16 wt % Mo alloy is expected to inherently increase the irradiation damage resistance of this alloy, since data to date reflect that the mechanical and physical properties of γ and γ' U-Mo alloy are quite similar. If this assumption is true, U - 16 wt % Mo alloy would offer a fuel whose resistance to irradiation damage is about the same, throughout the entire range of reactor operating temperatures, theoretically limited only to loss of strength near its melting point. If the γ and γ' phases are mechanically and physically similar, the irradiation damage resistance of U - 16 wt % Mo fuel should not be sensitive to structure change during reactor service, as is characteristic of lower Mo-containing, two-phase alloys.

If, however, the transition product proves to be α-phase U-Mo, a serious challenge to the superior properties of U - 16 Mo as a reactor fuel exists. A program, designed to identify the transition phase and the exact conditions under which it forms, is under way at Atomics International.

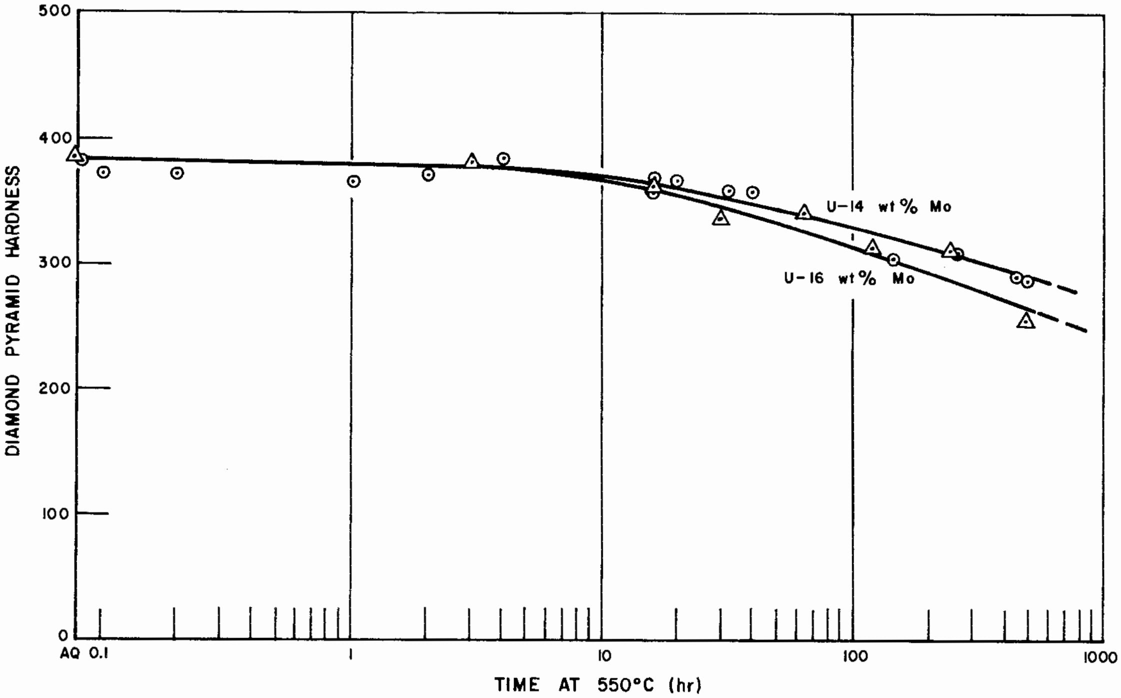


Figure 5. Hardness of Isothermally Transformed U - 14 and U - 16 wt % Mo

Data obtained at other sites,[6] and at Atomics International, on the transformation kinetics of U-Mo alloys at 550°C are plotted in Figure 6. The curve indicates that, after homogenization at 900°C, U - 10 wt % Mo alloys, because they

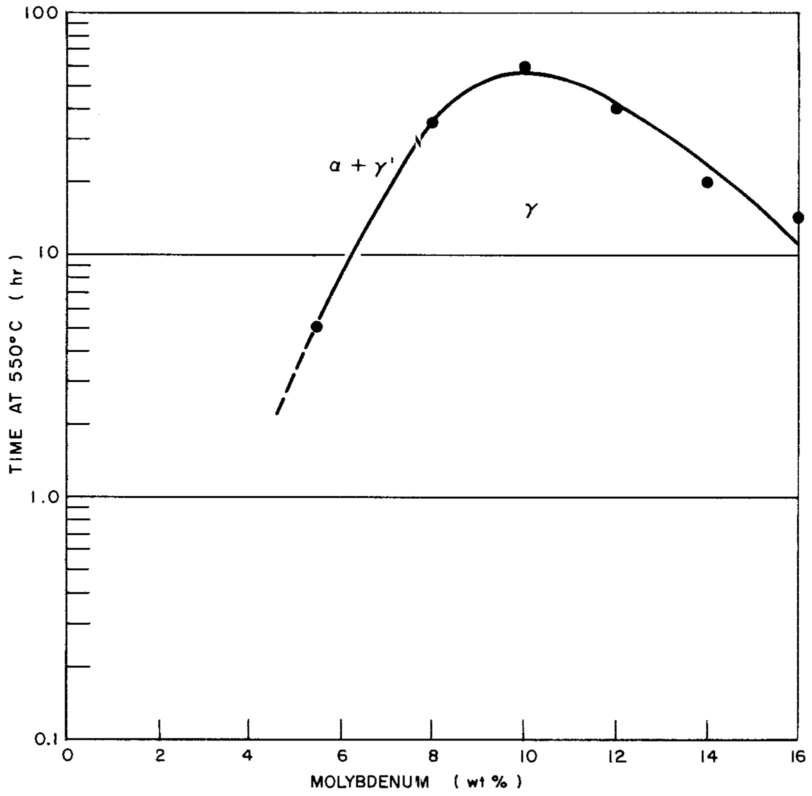


Figure 6. Variation of Time at Temperature to Commence Transformation for Various Molybdenum Contents (as determined by x-ray diffraction techniques)

transform more slowly, are more gamma-stable at 550° C than any other alloys between about 5 and 16 wt % Mo. Information on the mechanics of transformation in this alloy system is sparse. However, these data suggest that near-eutectoid alloys are more sluggish in transforming than hypo- and hypereutectoid alloys, and that hypoeutectoid alloys transform faster than hypereutectoid alloys.

IV. CONCLUSIONS

When gammatized at 900° C and isothermally heat treated at 550° C, the metastable γ-phase in U - 14 and U - 16 wt % Mo alloys begins to transform to equilibrium structure after 20 and 16 hr, respectively, at this temperature. However, a transition phase, believed to be α U-Mo, precipitates in U - 14 and U - 16 wt % Mo alloys after 0.3 hr and 0.1 hr at 550° C, respectively. U - 10 wt % Mo alloys, because they transform more slowly, are more gamma-stable than any other alloy between about 5 and 16 wt % Mo at 550° C. However, as the molybdenum content increases, from 10 to 16 wt %, the equilibrium transformation product contains progressively less of the highly anisotropic α phase.

REFERENCES

1. R. J. Van Thyne and D. J. McPherson, "Transformation Kinetics of Uranium-Molybdenum Alloys," ASM Transactions (1957) p 576

2. E. K. Halteman, "The Crystal Structure of U_2Mo," WAPD-T-208 (September, 1955)

3. J. Lehmann and R. F. Hills, J. Nuc. Mat. 2, No. 3 (1960) pp 261-268

4. J. Lehmann, 'Etude Des Processus Des Transformations Dans Les Alliages Uranium-Molybdene De Teneur 0.5 A 4% En Poids De Molybdene," Centre D'Etudes Nucleaires De Saclay, (1959)

5. E. K. Halteman, "The Crystal Structure of U_2Mo," WAPD-T-208 (September, 1955)

6. R. J. Van Thyne and D. J. McPherson, "Transformation Kinetics of Uranium-Molybdenum Alloys," ASM Transactions (1957) p 576