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STRESS CORROSION CRACKING IN URANIUM-MOLYBDENUM ALLOYS

J. W. Pridgeon

Y-12 PLANT
Oak Ridge, Tennessee

UNION CARBIDE NUCLEAR COMPANY
DIVISION OF UNION CARBIDE CORPORATION

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- OAK RIDGE GASEOUS DIFFUSION PLANT
- OAK RIDGE Y-12 PLANT
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Division of Union Carbide Corporation

Y-12 PLANT

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STRESS CORROSION CRACKING IN URANIUM-MOLYBDENUM ALLOYS

J. W. Pridgeon

This report is based on a study by the author as partial fulfillment of requirements for the degree of Master of Science in Metallurgical Engineering from the University of Tennessee.

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ABSTRACT

An investigation was conducted to determine the cause of cracking, during tension, on the surface of tensile specimens of uranium-molybdenum alloys. The cracking was observed in alloys that were water quenched from a temperature range in which the body-centered cubic γ phase was stable and, subsequently, stressed in tension. The investigation was carried out on alloys of uranium-molybdenum containing 5 weight per cent molybdenum and 4 weight per cent molybdenum.

It was discovered early in the study that the cracking could be eliminated by testing tensile specimens in a helium atmosphere. Because of this result, tensile tests were performed in vacuum, oxygen, impure nitrogen, and purified nitrogen.

Additional experiments were done to establish the relation of stress state, temperature, strain rate, oxygen pressure, stress magnitude, and grain size to the cracking phenomenon.

Uranium-4 weight per cent molybdenum and uranium-5 weight per cent molybdenum were compared with respect to microstructure and crystal structure, since both alloys cracked during the tensile test.

The origin and propagation of cracks in the microstructure were studied, using motion pictures and metallography.

The results of the various experiments showed that the cracking occurred only in tension and was caused by stress-corrosion cracking due to the presence of oxygen in the atmosphere.

The rate of cracking increased as the temperature was increased above 25° C. Below 10° C cracking was not observed in the uranium-5 weight per cent molybdenum alloy.

Cracking was not associated with just one metastable phase, since it was observed in both the uranium-5 weight per cent molybdenum alloy and the uranium-4 weight per cent molybdenum alloy, which have different crystal structures when rendered metastable by water quenching from the γ phase field.

The path of fracture was transgranular and was not associated with deformation markings in the grains.

ACKNOWLEDGEMENTS

The author would like to thank the management of the Metallurgical Development Department of the Y-12 Plant, Union Carbide Nuclear Company, for permission to conduct the investigation. He would also like to thank the personnel of the department for the aid given to the author throughout the investigation, particularly to W. J. Hobson and R. R. Feron for their work in metallography and motion picture photography. The author would like to express his thanks to H. L. Yakel of the Metallurgy Division of the Oak Ridge National Laboratory for doing the low temperature X-ray diffraction work. Finally, the author would like to express his appreciation to Dr. E. E. Stansbury for his advice, enthusiasm, and encouragement during the investigation.

SUMMARY

An investigation was conducted to determine the cause of cracking, during tension, on the surface of tensile specimens of uranium-molybdenum alloys. The cracking was observed in alloys that were water quenched from a temperature range in which the body-centered cubic γ phase was stable and, subsequently, stressed in tension. The investigation was carried out on alloys of uranium-molybdenum containing 5 weight per cent molybdenum and 4 weight per cent molybdenum.

It was discovered early in the study that the cracking could be eliminated by testing tensile specimens in a helium atmosphere. Because of this result, tensile tests were performed in vacuum, oxygen, impure nitrogen, and purified nitrogen.

Additional experiments were done to establish the relation of stress state, temperature, strain rate, oxygen pressure, stress magnitude, and grain size to the cracking phenomenon.

Uranium-4 weight per cent molybdenum and uranium-5 weight per cent molybdenum were compared with respect to microstructure and crystal structure, since both alloys cracked during the tensile test.

The origin and propagation of cracks in the microstructure were studied, using motion pictures and metallography.

The uranium-5 weight per cent molybdenum alloy behaved anelastically in the tension test. This phenomenon was investigated to determine if it could be related to the cause of cracking.

The results of the various experiments led to the following conclusions:

1. The cracking occurred only in tension, and can be considered as stress corrosion cracking, due to the presence of oxygen in the atmosphere.
2. The cracking rate increased as the temperature was increased and could be fitted to the Arrhenius rate equation over the temperature range 25° to 100° C.
3. Below 10° C, cracking in uranium-5 weight per cent molybdenum was not observed.
4. A minimum oxygen pressure between 8×10^{-3} and 130×10^{-3} millimeters of mercury was required to produce cracks on the surface of tensile bars during tensile tests.
5. Elongations greater than 40 per cent (no cracking occurred) were obtained on uranium-5 weight per cent molybdenum when (a) the testing was done in an atmosphere containing a small amount of oxygen, (b) the test temperature was below 10° C, and (c) the crosshead speed of the tensile machine was greater than 10 in/min.
6. The cracking was not associated with only one metastable phase, because a uranium-4 weight per cent molybdenum alloy showed cracking on the surface of tensile specimens, although its crystal structure was different from the structure of uranium-5 weight per cent molybdenum.
7. Uranium-5 weight per cent molybdenum behaved anelastically in the tension test, but the effect could not be related to the cracking mechanism.

8. The stress to cause cracking decreased as the grain size increased.

9. The cracks were always transgranular.

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CHAPTER I

INTRODUCTION

During an investigation of uranium-molybdenum alloys at the Y-12 Plant operated by Union Carbide Nuclear Company for the U. S. Atomic Energy Commission, it was observed that cracking occurred on the surface of tensile specimens during tensile tests. The cracking was found in alloys containing 4.5 to 8 weight per cent molybdenum that were water quenched from the body-centered cubic γ phase, resulting in a metastable condition. Delayed cracking was also observed in welded samples of uranium-7 weight per cent molybdenum following their removal from a helium atmosphere. A uranium-5 weight per cent molybdenum alloy, that was water quenched from the γ phase, was explosively formed into a hemisphere. Hours later, the hemisphere was found severely cracked.

This investigation is a study of the cracking phenomenon in these uranium-molybdenum alloys. A major portion of the investigation was done on uranium-5 weight per cent molybdenum. A lesser amount of work was carried out on uranium-4 weight per cent molybdenum.

It was discovered early in the investigation that the cracking was stress-corrosion cracking caused by oxygen in the atmosphere. The remainder of the investigation was concerned with carrying out a program of research that would establish the variables that affect the cracking and possibly provide a mechanism for the cracking.

The variables that were considered were oxygen pressure, temperature, stress level, strain rate, grain size, and crystal structure. The path of fracture, relative to grain boundaries and deformation markings, was determined.

CHAPTER II

LITERATURE SURVEY

As an initial step in the investigation of cracking in uranium-molybdenum alloys, the literature was surveyed for any evidence of cracking in these alloys. It became evident, as the investigation of the cracking phenomenon progressed, that literature concerning environmental effects on fracture, theory of fracture, and metastable phases in uranium-molybdenum alloys should be studied.

It was observed, near the end of the experimental work, that a uranium-5 weight per cent molybdenum alloy behaved anelastically during the tension test. Therefore, the literature was surveyed for information on this phenomenon and the relation of it to the observed cracking in the alloys.

I PHASE DIAGRAM

Figure 1 is the phase diagram for the uranium-molybdenum alloy system presented by Bostrom and Halteman.[1] It can be used as a guide to the location of the alloys discussed in this investigation.

II EVIDENCE OF CRACKING

Hills, et al,[2] observed cracking in a uranium-15 atomic per cent molybdenum alloy that was quenched from the γ phase and stressed at room temperature. They observed a stress-induced phase change in the alloy that cracked. There

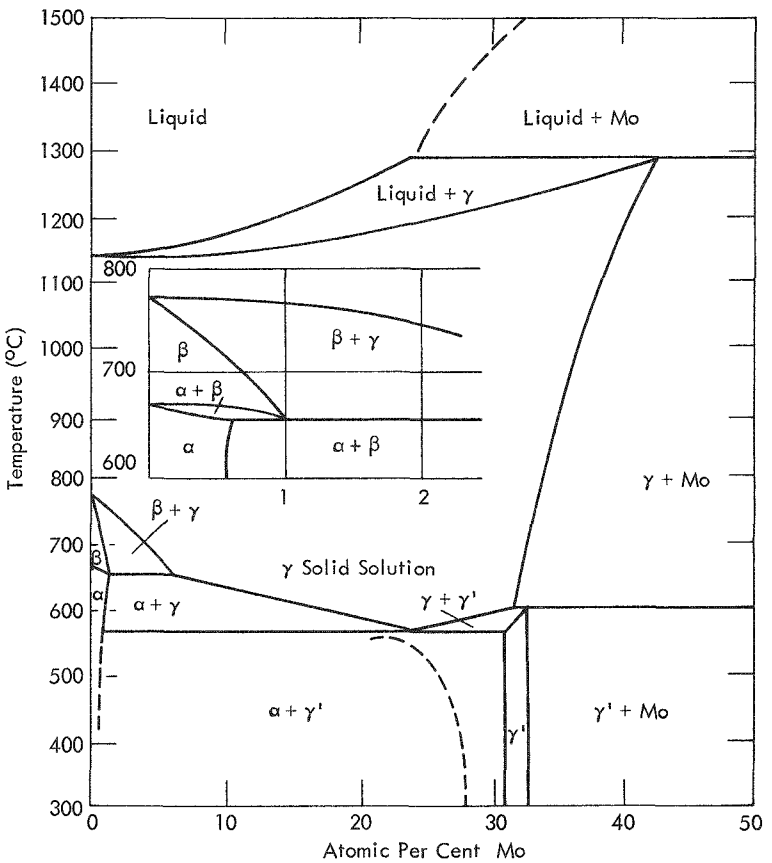


FIGURE 1

THE URANIUM-MOLYBDENUM PHASE DIAGRAM

was no further evidence in the literature of cracking in uranium-molybdenum alloys.

III METASTABLE PHASES

Metastable phases formed in uranium alloys are designated α-phase alloys or γ-phase alloys. Alloys in the α phase are based on the stable orthorhombic α phase found in uranium, while γ-phase alloys are based on the stable body-centered cubic γ phase. The three metastable phases found in uranium-molybdenum alloys are designated as α', α'', and γ_o. Hills, et al,[2] designated γ_o as γ_1. Tangri[3] reported the crystal structure of α' as orthorhombic, α'' as monoclinic, and γ_o as base-centered tetragonal. Hills, et al,[2] reported γ_o as body-centered tetragonal. Tangri[3] discovered γ_o was ordered, and to arrive at the base-centered tetragonal unit cell the a and b axes of the body-centered tetragonal unit cell must be doubled. He deduced that the location of the uranium atoms in the γ_o structure are at (000), (1/2 1/2 0), (1/4 1/4 1/2), (3/4 1/4 1/2), and (3/4 3/4 1/2); the molybdenum atoms are located statistically at (1/2 0 0) and (0 1/2 0). Tangri found that body-centered cubic γ phase when metastable at room temperature was ordered. He designated this as γ_s. The unit cell can be formed by doubling the a, b, and c axes of the γ structure.

Tangri and Williams[4] determined the composition limits within which the metastable phases were produced when the cooling rate from the γ field was constant. Using a cooling rate of 1000° C/sec, α' was formed in alloys containing

2.95 to 6.20 atomic per cent molybdenum, α" was produced in alloys containing 7.20 to 11.18 atomic per cent molybdenum, γ_o was observed in alloys containing 11.39 to 12.73 atomic per cent molybdenum, while γ_s was observed in alloys of 13.26 to 19.74 atomic per cent molybdenum.

The metastable phases are formed by a shearing movement of the atoms; i.e., a martensitic transformation. Tangri and Williams[4] describe the shearing process as follows: "Increasing additions of molybdenum progressively stiffen the uranium lattice, thus making it more and more resistant to shear, the effect of increased cooling rate is to favour the shear process. This presumably arises from increased hydrostatic pressures caused by faster cooling rates and also from increased transformation stresses due to faster rates of transformation once shear has started."

In order to rationalize the observations, they developed a qualitative factor defined as a stress/stiffening ratio, which is the ratio of quenching stresses to lattice stiffening. They state there is an optimum stress/stiffening ratio to form any given martensitic phase. Tangri and Williams propose that the martensitic phases are produced by a shearing of atoms on the {112} planes of the body-centered cubic structure in a <111> direction. An increase in molybdenum content stiffens the lattice and limits the amount of shear, whereas the effect of slower cooling rates is to limit the amount of shear that takes place. Tangri's and Williams' explanation accounts for the observations made by Hills, et al.[5] The latter observed in an end-quenched specimen of uranium-10 atomic per cent molybdenum that the quenched

tip was α", while the slow-cooled end was γ_o. The same effect was observed in a 7.5 atomic per cent molybdenum alloy. The quenched tip was α', while the slow-cooled end was α". The maximum amount of shearing occurs in the formation of the α' phase, resulting in an orthorhombic structure. A smaller amount of shearing gives the monoclinic structure, while an even lesser amount of shearing on two $\{112\}$ planes of the γ phase results in γ_o.

IV ENVIRONMENTAL EFFECTS

It has been known for a long time that enrivonment can affect the properties of materials. Roberts-Austen[6] observed in 1886 that hard-drawn 13 carat gold cracked when immersed in ferric chloride. Coblentz[6] first recorded that rock salt crystals can be deformed in liquids that dissolve sodium chloride. This is now known as the Joffe effect. Liquid metal embrittlement was first studied in 1914.[6] Heyn[6] studied the mercury embrittlement of beta brass containing 2 per cent aluminum.

Rehbinder[6] observed a change in flow stress and work-hardening behaviour of metals tested in fatty acids and alcohols. The phenomenon is now called the Rehbinder effect.

Westwood[6] divided the environmental effects into three classes: (1) solid environments, (2) liquid environments, and (3) gaseous environments. He divided the gaseous environments into five classes. The uranium-molybdenum alloys do not fall under any class mentioned, but are better described in a class under liquid

environments stated as "those in which the crystal is only sparingly soluble such that dissolution tends to follow a preferred path."

V THEORIES OF STRESS-CORROSION CRACKING

The electrochemical theory of stress-corrosion cracking was first expressed by Dix.[7] He thought the alloy must contain continuous paths where susceptibility to selective corrosion would occur. The susceptibility was present when the internal structure was microscopically heterogeneous and the phase forming the continuous path was anodic in the specific corrosive medium to the area composing the major part of the structure. According to Dix, the effect of stress was to open up fissures which destroy any protective films. The exposed fresh anodic material then reacted with the corrosive medium. He thought the responsible precipitates or heterogeneities in composition along crack-sensitive paths existed in the alloy from heat treatment, aging, or cooling from the melt. According to Uhlig,[7] strain-induced anodic areas can be generated by plastic flow and need not be present initially.

Harwood[8] explains that stress-corrosion cracking occurs in the following steps:

1. Localized electrochemical corrosion occurs along narrow paths producing trench-like fissures.
2. The fissure grows deeper and sharper, resulting in increasing stress concentration at its tip.

3. A crack may now propagate through the metal, causing immediate failure, or it may stop after propagating a finite distance.
4. Mechanical extension of the crevice exposes clean metallic surfaces, and the corrosive agent is drawn up into the crack.
5. The corrosion rate is accelerated due to exposure of unfilmed surfaces.
6. Step 1 repeats.

Nielson[6] proposes stress-corrosion cracking occurs when the corrosion product occupies a larger volume than the volume of metal destroyed. The applied stress and the stress from the wedging action of the corrosion product may be large enough to propagate a crack.

Coleman, et al[9] have utilized the Stroh[10] -Petch[11] theory of fracture for stress-corrosion cracking, which leads to a relationship between grain size and fracture stress in brittle fracture. The equation Stroh and Petch developed is

$$\sigma_f = \sigma_o + Kd^{-1/2},$$

where:

σ_f is the fracture stress,

d the average grain diameter,

σ_o a constant,

and

$$K = (6\pi G\gamma)^{1/2} / (1 - \nu)^{1/2},$$

where:

G is the shear modulus,

ν is Poisson's ratio,

and

γ is the energy associated with the formation of new surface in fracture.

If the equation holds, a plot of σ_f versus $d^{-1/2}$ would result in a straight line of slope K and intercept σ_o. The surface energy can be calculated from the plot if G and ν are known. Coleman, et al, propose that the reduction in surface energy by adsorption of the species that cause cracking is the mechanism for stress-corrosion cracking, liquid metal embrittlement, and hydrogen embrittlement. The theory does not account for the absence of stress-corrosion cracking in pure metals.

Robertson and Tetelman[6] have developed a theory for stress-corrosion cracking called the "unified structural mechanism." They consider that there are only two necessary and sufficient conditions for the occurrence of the stress-corrosion cracking: (1) the existence of a structural path along which the intensity of chemical reactivity is high relative to the surrounding matrix, and (2) a mechanism for the concentration of stress across the path of chemical reactivity. They propose that the connecting link between composition, strain, and reactivity is the stacking fault energy of the material. Robertson and Tetelman suggest a mechanism for the stress-corrosion cracking of Cu_3Au immersed in a $FeCl_3$ solution. The structural

sites where corrosion first occurs on the surface are aggregates of dislocations held up by Lomer-Cottrell barriers. The strength of the barrier is revealed by the number of dislocations that can pile up behind the barrier. The number of dislocations that pile up behind the barriers is a function of the stacking fault energy, which depends on the composition of the alloy. The strain energy of the piled-up group of dislocations at the Lomer-Cottrell barrier and the stacking fault energies of the individual dislocations are responsible for the preferred chemical reactivity directed along the barrier.

In Cu_3Au crystals this was observed to be a <110> direction. Robertson and Tetelman[6] propose that as the reaction proceeds, one of the components of the alloy is removed from the lattice by chemical dissolution at the surface, and the reacting component then diffuses to the surface leaving vacancies in the barrier. The vacancies that remain condense to form a cavity, or a disordered structure, through which dislocations cannot move freely to destroy the barrier by recombination or crossslip processes. Figure 2 illustrates the Robertson-Tetelman mechanism for Cu_3Au.

VI ANELASTIC BEHAVIOUR

Lazan[12] defined anelasticity as an important type of dynamic hysteresis, where the existence of permanent set (after a long time) is not recognized when the load is removed. Nonelastic behaviour, as defined by Zener[13], implies a permanent set after the load is removed. The term anelastic was, therefore, used to

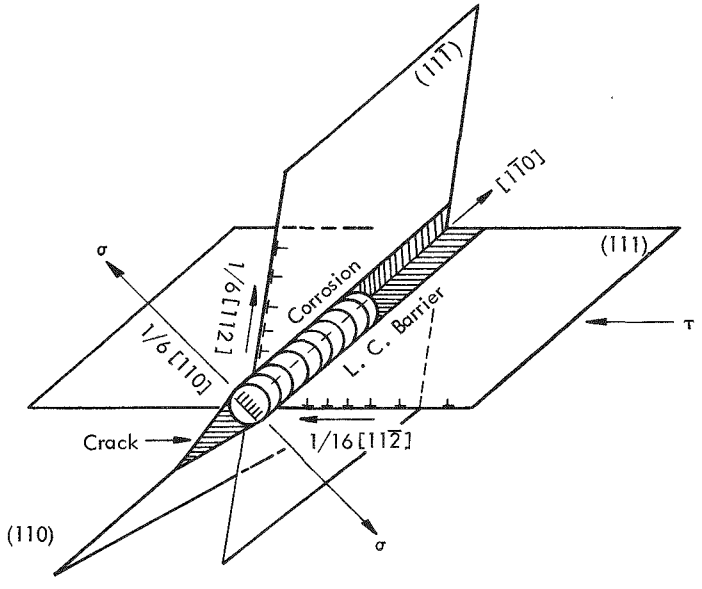


FIGURE 2

ILLUSTRATION OF THE ROBERTSON-TETELMAN MECHANISM FOR STRESS-CORROSION CRACKING AT A LOMER-COTTRELL BARRIER IN Cu_3Au

describe the stress-strain hysteresis in the uranium-5 weight per cent molybdenum alloy.

A survey of the literature failed to provide any evidence of anelastic behaviour in uranium-molybdenum alloys, but a thorough discussion of anelasticity in metals and alloys has been presented by Zener.[13]

CHAPTER III

EXPERIMENTAL PROCEDURE

I ALLOY PREPARATION

Alloys of uranium-5 weight per cent molybdenum and uranium-4 weight per cent molybdenum were prepared by vacuum induction melting high-purity uranium with -200 mesh molybdenum powder[(a)] in graphite crucibles flame sprayed with zirconium oxide. The melts were held at 1400° C for 20 minutes and bottom poured into 7-inch x 4-inch x 1 1/2-inch molds that were coated with zirconite mold wash. A furnace pressure of less than 10^{-2} millimeters of mercury was generally obtained during melting and casting. Each of the resulting billets weighed between 13 and 15 kilograms. Table I gives the chemical and spectrographic analyses of the molybdenum and uranium used in the castings, along with a typical analysis of the uranium-5 weight per cent molybdenum alloy after casting, rolling, and heat treatment.

Generally, the data for a particular experiment was obtained from one billet because of the variables that might arise from casting, fabrication, composition, and heat-treatment differences in more than one billet.

(a) The molybdenum powder was purchased from the Wah Chang Corporation, 63 Herbhill Road, Glen Cove, New York.

TABLE I

CHEMICAL AND SPECTROGRAPHIC ANALYSIS OF URANIUM, MOLYBDENUM, AND URANIUM-5 WEIGHT PER CENT MOLYBDENUM

Element	Uranium (ppm)(2)	Molybdenum (ppm)	Uranium-5 Weight(1) Per Cent Molybdenum (ppm)
Carbon	45	137	63
Calcium	75	-	10
Aluminum	15	100	3
Iron	75	200	90
Magnesium	5	-	2
Nickel	25	100	15
Silicon	17	400	90
Manganese	35	50	10

(1) The molybdenum contents of the uranium-5 weight per cent molybdenum alloys were between 5.1 and 5.3 per cent on the alloys that were analyzed.

(2) Parts per million.

Fabrication of the billets into suitable sizes was done by hot rolling. The billets were initially soaked in a lithium carbonate-potassium carbonate salt bath at 800° C for 1 1/2 hours before rolling, and they were reheated in the bath when the temperature reached approximately 650° C during rolling. A total reduction in thickness of 67 per cent was obtained on all billets, with equal amounts of hot work in the longitudinal and transverse directions.

The rolled plates were usually heat treated at 800° - 850° C for two hours in an argon atmosphere and water quenched to room temperature. Temperature control was maintained by a Leeds and Northrup Micromax Controller which was calibrated using a Leeds and Northrup Potentiometer. Tensile specimens, to be used in various experiments on the cracking phenomenon, were machined from the heat-treated plates. The tensile specimens were machined to a diameter of 0.252 inch, with a gage length of 1 inch, unless it is specified otherwise in the experimental procedure.

II TESTING OF ALLOYS UNDER DIFFERENT ENVIRONMENTS

Tensile tests were performed on a uranium-5 weight per cent molybdenum alloy using various gaseous environments. The atmospheres were provided by sealing plastic bags around the tensile grips and introducing the desired gas through a hypodermic needle inserted through the wall of the bag. The gas exited through any leaks in the bag. Specimens were tested in helium, oxygen, and nitrogen.

A chamber for testing tensile specimens at any pressure between 1×10^{-3} millimeters of mercury and atmospheric pressure was built. Figure 3 is a photograph of the chamber positioned on the testing machine.

Tensile specimens of uranium-5 weight per cent molybdenum were tested in an oxygen atmosphere at partial pressures between 8×10^{-3} millimeters of mercury and atmospheric pressure. Tests were also performed in an atmosphere of nitrogen, which was passed over copper chips at 550° C and then through a cooling coil before entering the test chamber.

Two samples of uranium-5 weight per cent molybdenum were compressed 20 per cent and 50 per cent in air.

III DETERMINATION OF THE EFFECT OF STRESS MAGNITUDE ON TIME TO FRACTURE

Tensile specimens were loaded to stresses between 40,000 and 76,000 psi on a 120,000-pound Tinius-Olsen electromatic testing machine. The machine was stopped at the desired stress level, and the time to fracture was measured. Measurement of the time was done by connecting a limit switch in series between a power source and a Leeds and Northrup direct-inking recorder. The limit switch was placed under the bottom rod that connected the tensile grip to the testing machine. When the specimen failed, the connecting rod would drop down, engaging the limit switch and stopping the recorder. The time to fracture was calculated by measuring the travel distance on the recorder chart and dividing it by the travel speed of the chart.

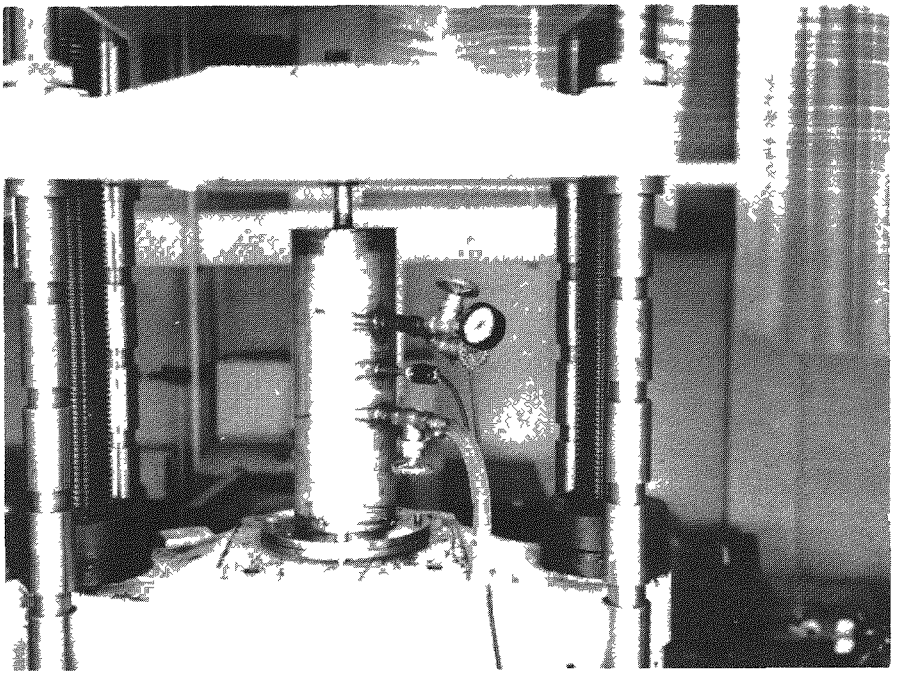


FIGURE 3

VACUUM CHAMBER FOR TENSILE TESTS
IN VARIOUS ENVIRONMENTS

IV TESTING OF TENSILE SPECIMENS AT AT VARIOUS DEFORMATION SPEEDS

Tensile tests were carried out on a uranium-5 weight per cent molybdenum alloy at various speeds of deformation. The tests were done on a Tinius-Olsen electromatic machine, using crosshead speeds between 0.025 in/min and 20 in/min. The ultimate tensile strength, elongation, and reduction in area were obtained on all specimens. Each of the broken samples was examined for cracking.

V TENSILE TESTS AT VARIOUS TEMPERATURES

Mechanical properties of a uranium-5 weight per cent molybdenum alloy were determined at temperatures between 0° and 150° C. The mechanical properties of a uranium-4 weight per cent molybdenum alloy were determined at temperatures between 5° and 25° C. An Amico high temperature-subzero cabinet was used to obtain the desired temperatures. The temperature was measured with a mercury thermometer and could be controlled within 1° C of the desired temperature.

The effect of temperature on time to fracture was determined on a uranium-5 weight per cent molybdenum alloy. Each tensile specimen was loaded, in tension, to a stress of 55,000 psi, and the machine was stopped to hold the stress on the sample. As the samples cracked, the load level dropped, due to the elongation of the uncracked portion of the sample. The total time, after loading, until fracture

occurred was measured at various temperatures, using the limit-switch time-measuring device described previously.

VI PREPARATION OF SAMPLES FOR METALLOGRAPHIC EXAMINATION

Samples for metallographic examination were mounted in Araldite epoxy resin. The usual polishing procedures were followed, with the final steps performed on a syntron vibratory polisher using a gamal polishing cloth to which "Linde B," an aluminum oxide abrasive, was added. Samples were then electropolished in a solution of 60 cc phosphoric acid, 15 cc ethylene glycol, and 15 ethyl alcohol, using a voltage of 20 volts. The microstructure was examined under polarized light.

VII PREPARATION OF SAMPLES TO REVEAL DEFORMATION MARKINGS AND FOR USE IN MOTION PICTURES

Two types of samples were used in producing deformation markings on the surface of the uranium-5 weight per cent molybdenum alloy. A standard metallographic sample that had been through the polishing procedure was compressed in a vise, and the surface was examined metallographically for deformation markings. The second type of sample used for revealing deformation markings was a flat tensile specimen with a gage dimension of 1 inch x 0.250 inch x 0.250 inch. The flat tensile specimens were given the same polishing procedure as the metallographic specimens, except the electropolish was eliminated. After the specimens were

tested to failure in tension, the polished surfaces were examined metallographically for cracking and deformation markings.

In an effort to determine the origin of the cracks, motion pictures were taken of the surface of flat tensile specimens during tensile tests. The specimens were given the same polishing procedure as the ones used in revealing surface deformation markings. A Cime-Kodak Special II 16-millimeter camera was mounted on a horizontal microscope which, in turn, was mounted to the 120,000-pound Tinius-Olsen testing machine. The pictures were taken at a speed of 8 frames per second, using a magnification of 100X. Figure 4 is a photograph showing the camera and microscope mounted on the testing machine.

VIII X-RAY DIFFRACTION EXAMINATION

X-ray diffraction spectrometer traces were obtained on uranium-5 weight per cent molybdenum in the water-quenched, cold-worked condition to determine if a phase change occurred during deformation. The cold-worked samples were sectioned from a tensile specimen that had been elongated 40 per cent in a vacuum.

A uranium-4 weight per cent molybdenum alloy, in the water-quenched condition, was examined by X-ray diffraction to determine if the crystal structure differed from the uranium-5 weight per cent molybdenum alloy.

Nickel-filtered copper $K\alpha$ radiation was used in all of the X-ray examinations.

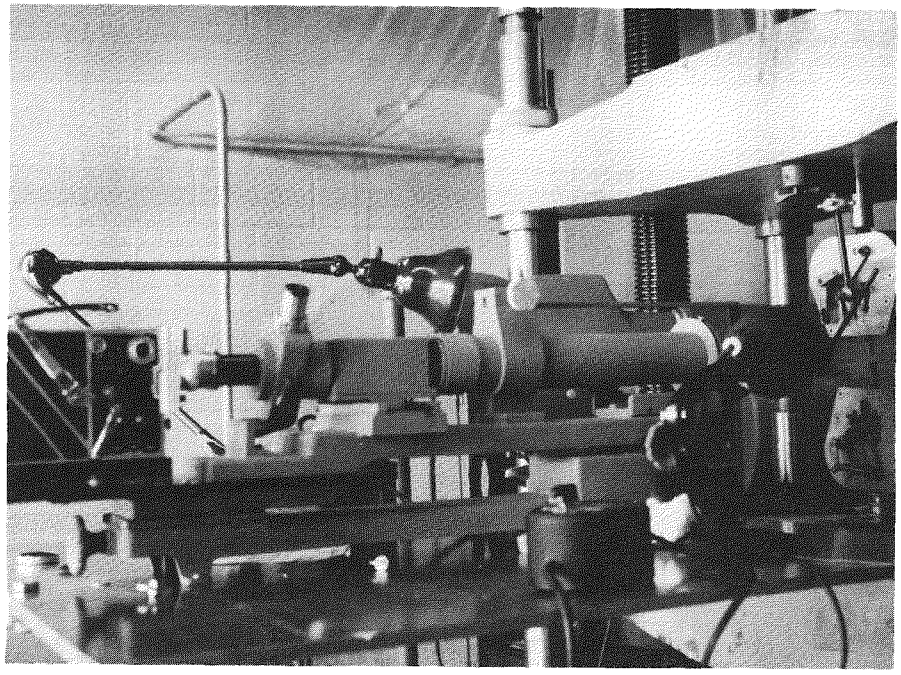


FIGURE 4

MOTION PICTURE CAMERA AND MICROSCOPE MOUNTED
ON 120,000-POUND TENSILE MACHINE

IX PREPARATION OF MATERIAL TO PRODUCE VARIOUS GRAIN SIZES

The effect of grain size on the cracking stress was determined on the uranium-5 weight per cent molybdenum alloy. Two billets were cast to supply the necessary material for rolling. One billet was annealed at 900° C for 16 hours in an argon atmosphere and sectioned into four pieces. Two, 4-inch x 1 1/2 x 0.600-inch sections were annealed at 830° C for an additional two hours and water quenched to room temperature. The remaining two sections of the billet were rolled at 700° and 900° C, respectively, with a reduction in thickness of 67 per cent. They were then annealed at 800° C in an argon atmosphere and water quenched to room temperature. Grain sizes of 0.186, 0.031, and 0.037 millimeter, respectively, were produced by the three procedures. A second casting was sectioned into two pieces. One piece was rolled at 900° C, reheating after every pass, with a total reduction in thickness of 67 per cent. The piece was then annealed in argon at 900° C for two hours and water quenched to room temperature. This method produced a grain size of 0.071 millimeter. The remaining section of the casting was rolled at 700° C with the same reduction in thickness. The rolled plate was sectioned into three pieces, and these were annealed in argon at 700° C for 1 hour, 800° C for 1 1/4 hours, and 980° C for 1 1/2 hours, respectively. All of the pieces were water quenched to room temperature. Grain sizes of 0.023, 0.030, and 0.031 millimeter were produced in the alloy by the three heat treatments. Grain sizes were measured by the intercept method.

Tensile specimens were machined from the various grain-sized materials. The specimens were etched in concentrated nitric acid and then electropolished in a chromic acid-phosphoric acid bath to remove worked material introduced by machining. The stress which caused cracking for each grain size was determined by stressing a sample to an arbitrary stress level, holding for approximately three minutes, then unloading and examinining at a magnification of 100X to see if cracking occurred. If cracking did occur, the next specimen was loaded to a lower stress and examined for cracking. Specimens were loaded to a higher stress if cracking did not occur and, by examining many tensile specimens loaded to various stress levels, the stress to cause cracking was determined.

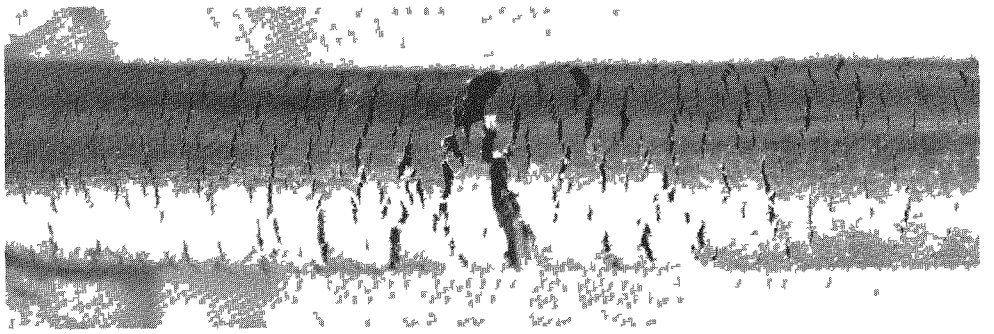
CHAPTER IV

EXPERIMENTAL RESULTS

This chapter presents the results of the experiments described in Chapter III, along with additional results from experiments that did not warrant a description under experimental procedure.

I EFFECT OF ENVIRONMENT

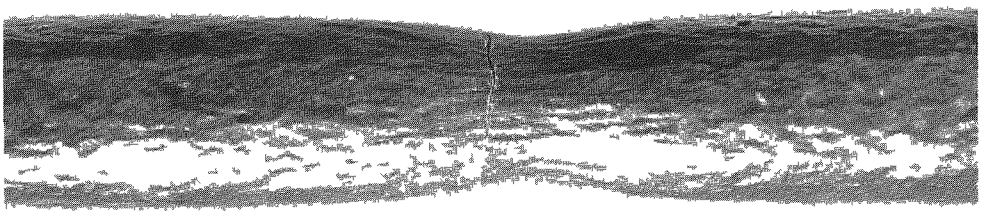
The mechanical properties of uranium-5 weight per cent molybdenum depended on the environment that surrounded the specimens during testing. When specimens were tested in air or oxygen, at room temperature, severe surface cracking occurred. This cracking was visible to the naked eye when the crosshead speed of the tensile machine was less than 10 in/min. Figure 5A shows the typical appearance of the cracks on the surface when the specimens were tested in air at a crosshead speed of 0.05 in/min. The specimen shown in Figure 5B came from the same heat-treated billet as the specimen shown in Figure 5A, but it was tested in a vacuum chamber with an air pressure less than 10^{-2} millimeters of mercury. It can be seen from the photograph that no cracking occurred, and considerable necking down did occur in the specimen. The surface roughness was due to the large grain size of the specimen. Figure 6 shows the typical appearance of the fracture when testing was done in air or oxygen. An area of discoloration, or attack, can be seen extending from the outside surface into the specimen.



5X

TESTED IN AIR

A



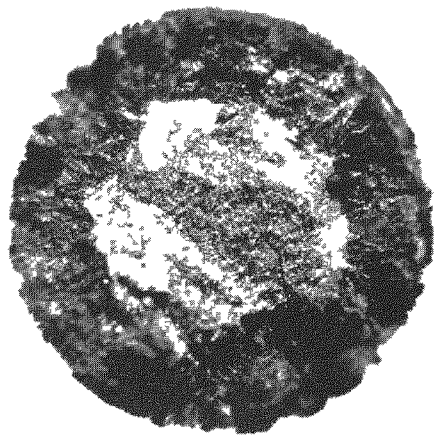
5X

TESTED IN A VACUUM

B

FIGURE 5

SURFACE OF A BROKEN TENSILE SPECIMEN OF A WATER-QUENCHED URANIUM-5 WEIGHT PER CENT MOLYBDENUM ALLOY



10X

FIGURE 6

FRACTURE SURFACE OF A WATER-QUENCHED URANIUM-5 WEIGHT PER CENT MOLYBDENUM ALLOY TENSILE SPECIMEN TESTED IN AIR

In order to determine if oxygen was the only constituent of air responsible for the cracking, tensile tests were performed in an atmosphere of nitrogen. The first tests were done using nitrogen directly from the gas cylinder, and a samll amount of cracking was observed. Subsequent tensile tests were done in nitrogen that was passed over copper chips at 550° C to remove oxygen, and no cracking was observed.

Mechanical properties were obtained on uranium-5 weight per cent molybdenum tested in helium, oxygen, and nitrogen. These tests were done in plastic bags with atmospheres, obtained directly from gas cylinders, flowing through them. Table II gives the results of the tests.

Stress-corrosion cracking has been observed only in alloys when the material was in tension. In order to determine if the uranium-5 weight per cent molybdenum alloy cracked only in tension, compression samples, with a diameter of 1/2 inch and a length of 1 inch, were machined from a rolled plate and tested in air. Two samples were compressed 20 and 50 per cent without surface cracking occurring. Figure 7 shows the sample that was compressed 20 per cent, along with a sample that was not compressed.

The results in Table II and the appearance of the specimens tested in air and oxygen indicated that oxygen embrittled the uranium-5 weight per cent molybdenum alloy. An experiment was carried out to determine what effect oxygen pressure had on the mechanical properties of the alloy. Tensile specimens were tested at a crosshead speed of 0.05 in/min in atmospheres of oxygen at pressures between 8×10^{-3}

TABLE II

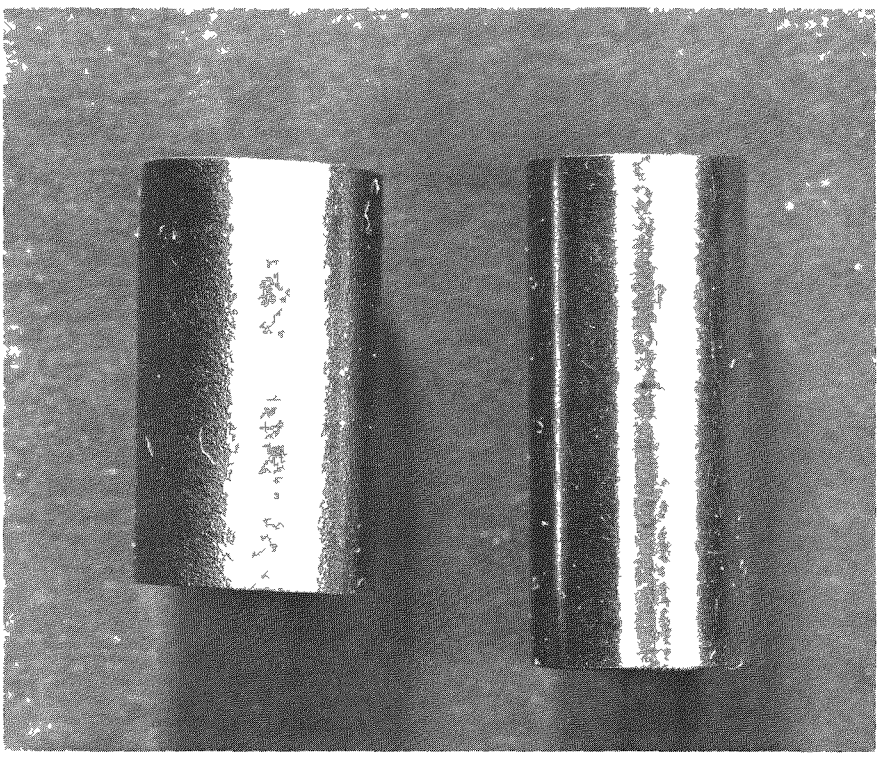
MECHANICAL PROPERTIES OF URANIUM-5 WEIGHT PER CENT MOLYBDENUM TESTED IN VARIOUS ATMOSPHERES[1]

Atmosphere	Tensile Strength (psi)	Yield Strength[2] (psi)	Elongation in One Inch (%)	Reduction in Area (%)
Helium	97,600	48,000	47	61
Oxygen	91,000	53,000	20	17
Nitrogen[3]	95,000	49,000	35	31

(1) Tested at a crosshead speed of 0.1 inch/minute.

(2) 0.2 per cent offset.

(3) The nitrogen used in this test was not purified by passage over copper chips and, therefore, contained enough oxygen to cause cracking and to affect the mechanical properties.



2.5X

FIGURE 7

COMPRESSION SAMPLES OF A WATER-QUENCHED URANIUM-5 WEIGHT PER CENT MOLYBDENUM ALLOY BEFORE AND AFTER COMPRESSION IN AIR

and 760 millimeters of mercury. Figure 8 gives the elongation and ultimate tensile strength as functions of the oxygen pressure. Examination of the samples, after testing, revealed that the oxygen pressure necessary to cause cracking on the surface of the tensile specimens was between 8×10^{-3} and 130×10^{-3} millimeters of mercury.

II EFFECT OF TEMPERATURE

Mechanical properties were obtained on uranium-5 weight per cent molybdenum, at various temperatures, to determine what effect temperature had on the mechanical properties and also to indicate the severity of cracking at various temperatures. Tensile specimens from uranium-4 weight per cent molybdenum alloy were also tested at various temperatures to see if they cracked in a manner similar to the uranium-5 weight per cent alloy. The mechanical properties of the two alloys are listed in Tables III and IV. Cracking was observed on the surface of the uranium-5 weight per cent molybdenum alloy tensile specimens at all test temperatures except 0° C. The uranium-4 weight per cent molybdenum alloy showed surface cracking when the testing temperature was greater than 15° C. An increase in ultimate tensile strength, elongation, and reduction in area was observed in both alloys as the test temperature was lowered to a temperature where cracking did not occur.

In order to study the effect of temperature on time to fracture in a uranium-5 weight per cent molybdenum alloy, a series of tensile bars were machined from an

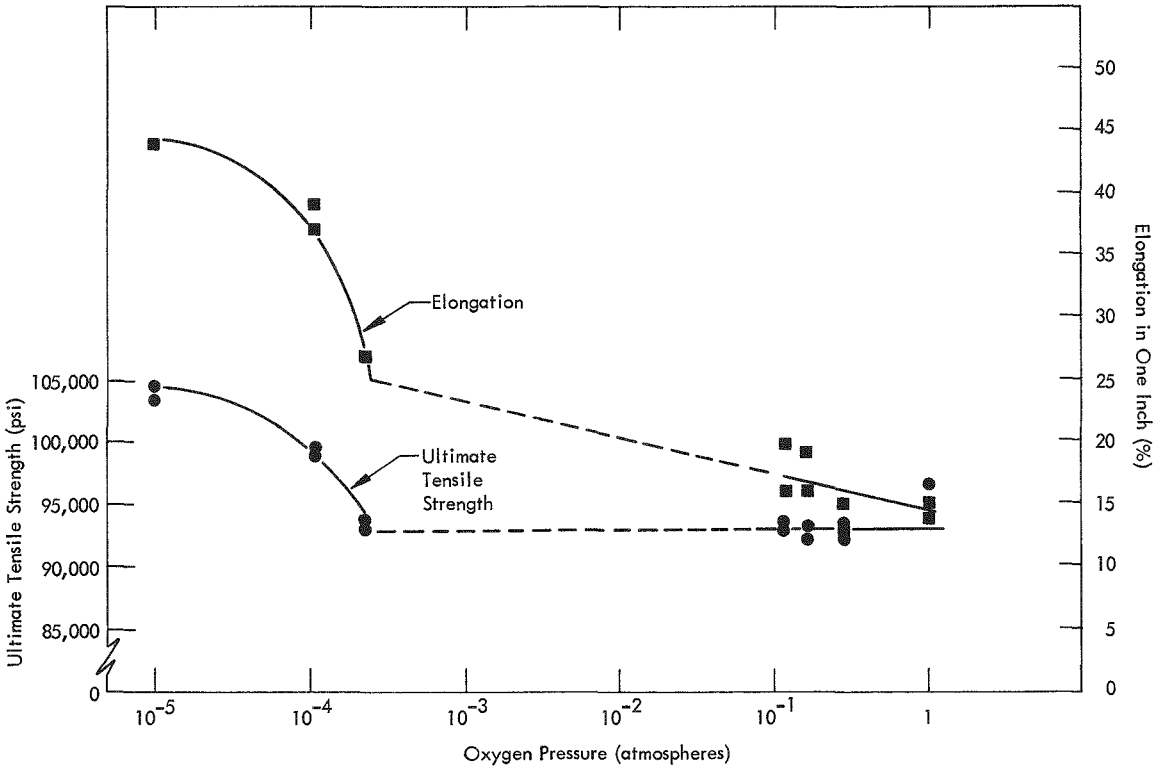


FIGURE 8

PLOT OF MECHANICAL PROPERTIES VERSUS THE OXYGEN PRESSURE

TABLE III

MECHANICAL PROPERTIES OF A URANIUM-5 WEIGHT PER CENT MOLYBDENUM ALLOY TESTED IN AIR AT VARIOUS TEMPERATURES

Test Temperature[1] (°C)	Ultimate Tensile Strength (psi)	Yield Strength[2] (psi)	Elongation (%)	Reduction in Area (%)	Comments
0	108,500	47,800	40	46	No cracks on surface.
15	104,200	41,200	30	22	Cracks on surface.
22	85,200	48,700	14	17	Severe cracking on surface.
40	76,200	48,000	11	10	Severe cracking on surface.
60	75,600	48,300	10	10	Severe cracking on surface.
80	68,500	43,800	7	6	Severe cracking on surface.
100	70,500	45,900	11	14	Severe cracking on surface.
120	69,500	42,500	10	9	Severe cracking on surface.
150	72,700	48,200	21	21	Severe cracking on surface.

(1) Tested at a crosshead speed of 0.05 inch/minute.

(2) 0.2 per cent offset.

TABLE IV

MECHANICAL PROPERTIES OF A URANIUM-4 WEIGHT PER CENT MOLYBDENUM ALLOY TESTED IN AIR AT VARIOUS TEMPERATURES

Test Temperature(1) (°C)	Ultimate Tensile Strength (psi)	Yield Strength(2) (psi)	Elongation (%)	Reduction in Area (%)	Comments
5	131,700	34,800	21	17	No cracks.
10	131,500	33,800	21	18	No cracks.
15	129,750	34,400	20	16	No cracks.
20	125,650	32,300	22	15	Few surface cracks.
25	106,300	34,400	11	11	Many surface cracks.

(1) Tested at a crosshead speed of 0.05 inch/minute.

(2) 0.2 per cent offset.

alloy plate. Each tensile specimen was loaded to a stress of 55,000 psi, and the time until fracture occurred was measured. Data were obtained at temperatures between 10° and 100° C. The data were fitted to the Arrhenius equation,

$$1/t = Ae^{\frac{Q}{RT}},$$

where:

t is the time to fracture in minutes,

A is a constant with units of 1/minutes,

Q is the temperature coefficient of the cracking reaction or an activation energy in cal/mol,

R is the universal gas constant (1.987 cal/°K mol),

and

T is the absolute temperature in °K.

By taking the natural logarithm of both sides of the equation and plotting ln 1/t versus 1/RT, an equation for a straight line results with a slope of Q. Since the time to fracture data did not fall exactly on a straight line, it was assumed that any error was connected with the time measurement. The experimental data (see Appendix, Table IV) were fitted by the least squares method, using the IBM 7090 computer. An activation energy, Q, of -6300 cal/mol was obtained with a standard error of 1580 cal/mol, and ln A was equal to 7.9 with a standard error of 1.2. Figure 9 is the plot of ln 1/t versus 1/RT showing the experimental points along with the straight line determined by least squares. Temperature versus time to fracture is plotted in Figure 10, using the constants obtained from the Arrhenius plot. Fracture did not occur at 10° C after 16 hours under stress.

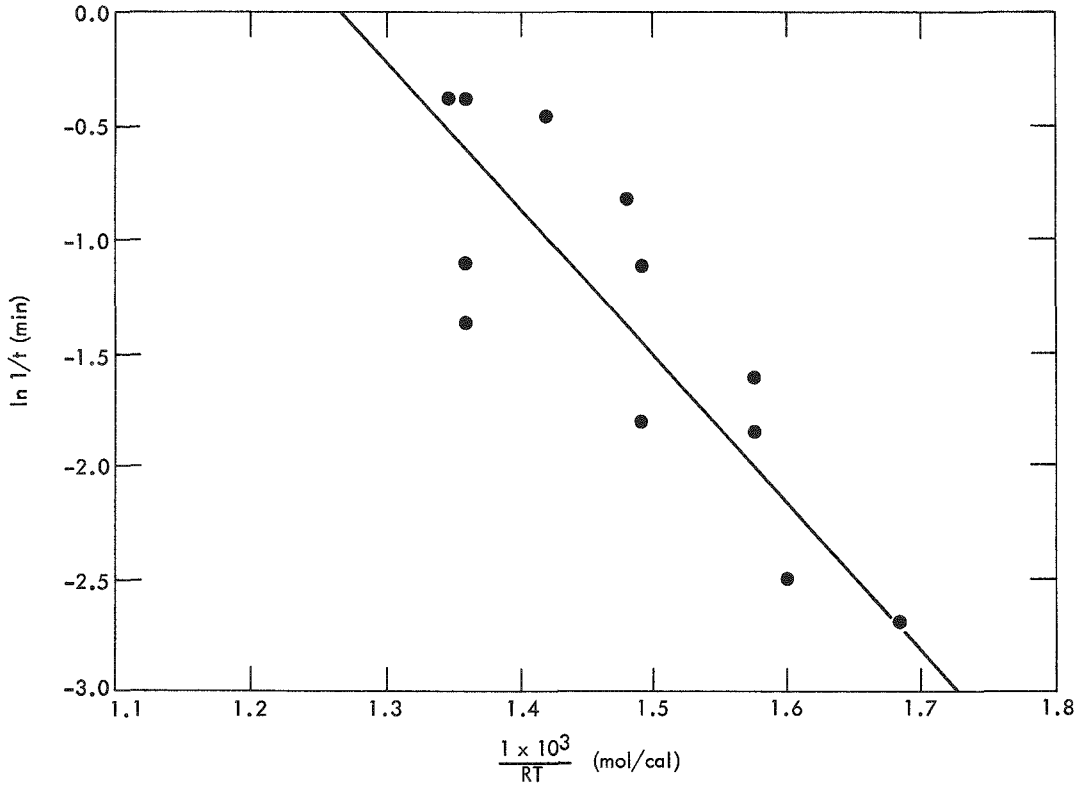


FIGURE 9

PLOT OF LN 1/T VERSUS 1/RT FOR A WATER-QUENCHED URANIUM-5 WEIGHT PER CENT MOLYBDENUM ALLOY

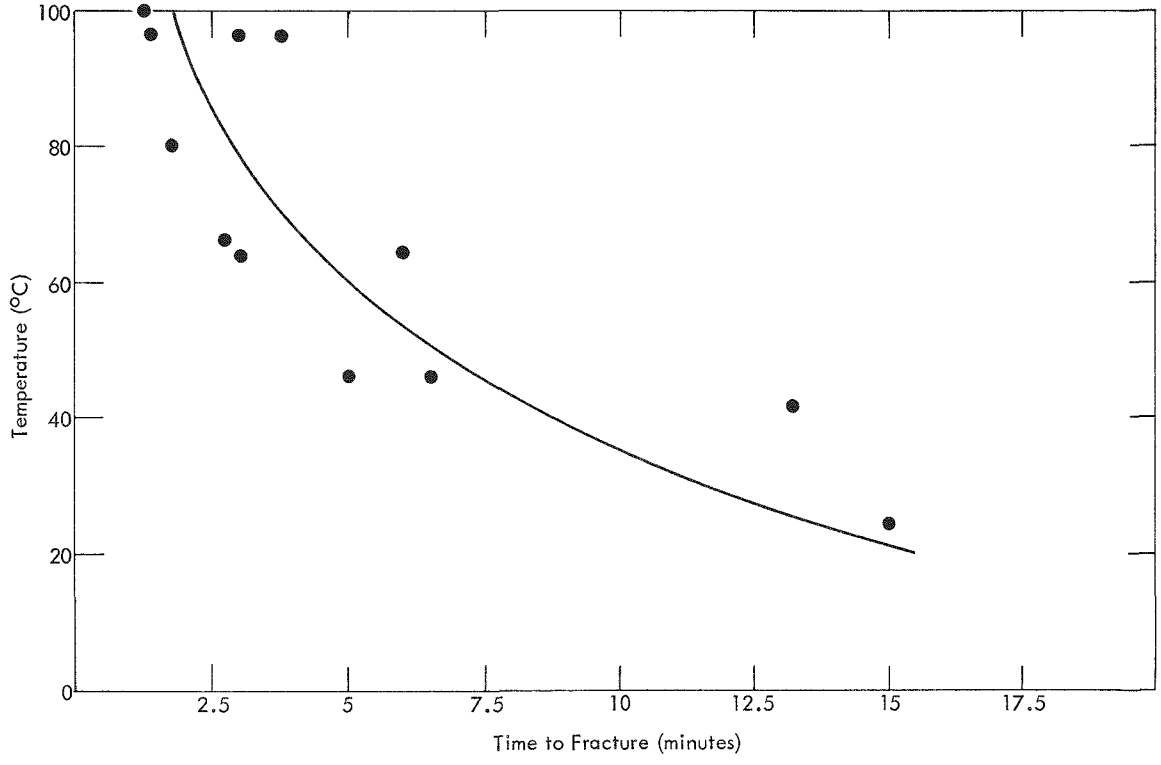


FIGURE 10

PLOT OF TEMPERATURE VERSUS TIME TO FRACTURE FOR A WATER-QUENCHED URANIUM-5 WEIGHT PER CENT MOLYBDENUM ALLOY

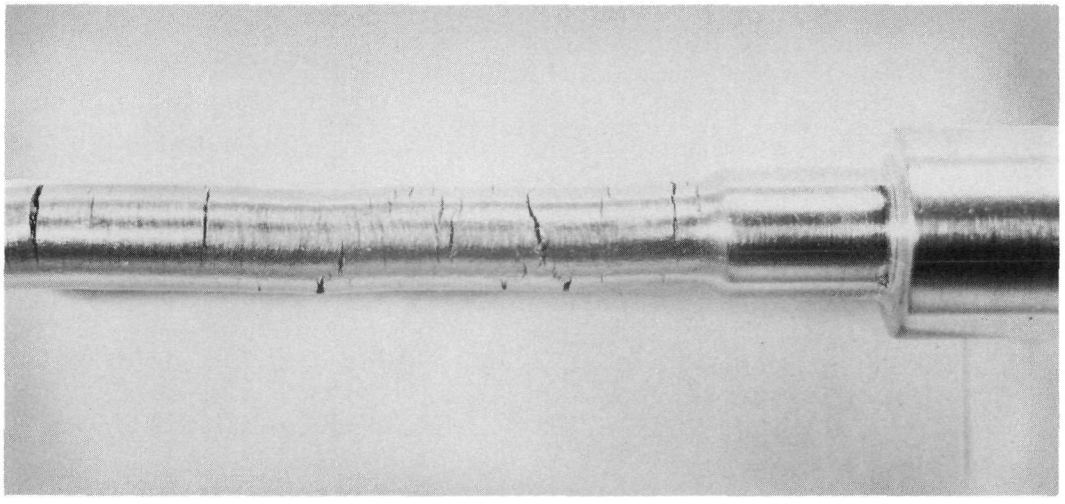
III EFFECT OF DEFORMATION SPEED

Figure 11 shows the appearance of the surface of tensile bars after testing, at 25° C, at crosshead speeds of 0.025 and 10 in/min. At a deformation speed of 0.025 in/min, cracking was severe. The amount of cracking was observed to decrease as the strain rate increased until only a small amount was observed on the surface of the specimen tested at 10 in/min; cracking did not occur at a strain rate of 12 in/min. The mechanical properties at various crosshead speeds are tabulated in Table V for a uranium-5 weight per cent molybdenum alloy.

IV EFFECT OF STRESS ON TIME TO FRACTURE

It is generally observed, in alloys that are subject to stress-corrosion cracking, that there is a minimum stress below which cracking does not occur. As the stress is increased above this minimum stress, the time until fracture decreases.

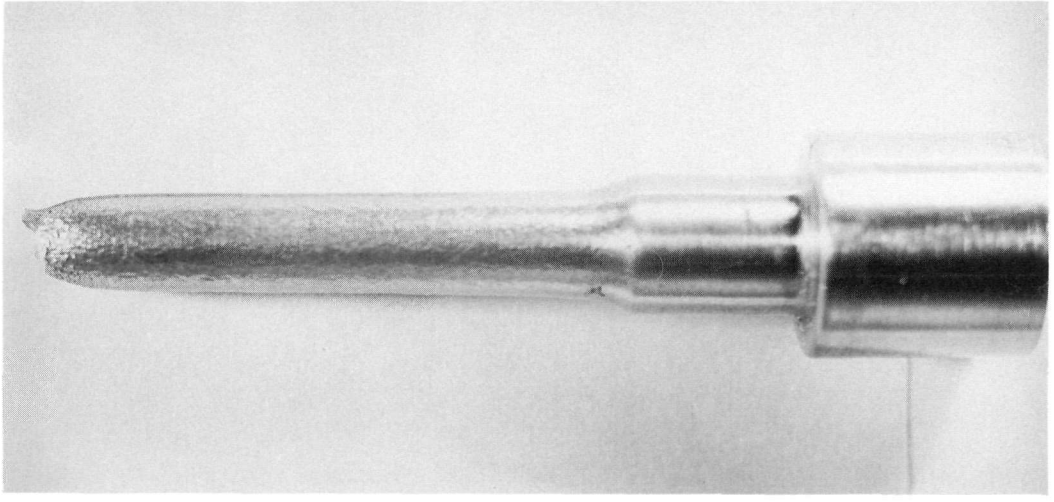
The time for fracture to occur in 0.252-inch-diameter tensile specimens was measured for a uranium-5 weight per cent molybdenum alloy, and the results are plotted in Figure 12. At a stress of 44,000 lbs/in^2, fracture occurred in 35 minutes, but at 42,000 lbs/in^2, fracture did not occur in 16 hours. It is presumed that the test specimen would have held the load indefinitely. At a stress between 46,000 and 56,000 lbs/in^2, the time to fracture was independent of the stress, and the samples failed in 20 minutes. Above 60,000 lbs/in^2, the time to fracture decreased as the stress increased, and at 74,000 lbs/in^2 (the highest stress-time measurement),



2X

CROSSHEAD SPEED OF 0.025 INCH PER MINUTE

A



2X

CROSSHEAD SPEED OF 10 INCHES PER MINUTE

B

FIGURE 11

SURFACE OF A WATER-QUENCHED URANIUM-5 WEIGHT PER CENT MOLYBDENUM TENSILE SPECIMEN TESTED IN AIR

TABLE V

MECHANICAL PROPERTIES OF A URANIUM-5 WEIGHT PER CENT MOLYBDENUM ALLOY TESTED AT VARIOUS STRAIN RATES

Speed of Deformation (in/min)	Tensile Strength (psi)	Yield Strength(1) (psi)	Elongation in One Inch (%)	Reduction in Area (%)	Comments
0.025	70,900	-	8	5	Cracked severely on surface.
0.1	80,500	49,000	24	27	Cracked on surface
2.0	89,800	-	36	64	Cracks visible on surface.
5.0	89,400	-	41	67	Small amount of cracking on surface.
10.0	89,900	-	44	70	Little cracking.
12.0	90,000	-	37.5	69	No cracks on surface.
16.0	80,100	-	37.5	71	No cracks on surface.
20.0	73,200	-	37.5	67	No cracks on surface.

(1) 0.2 per cent offset.

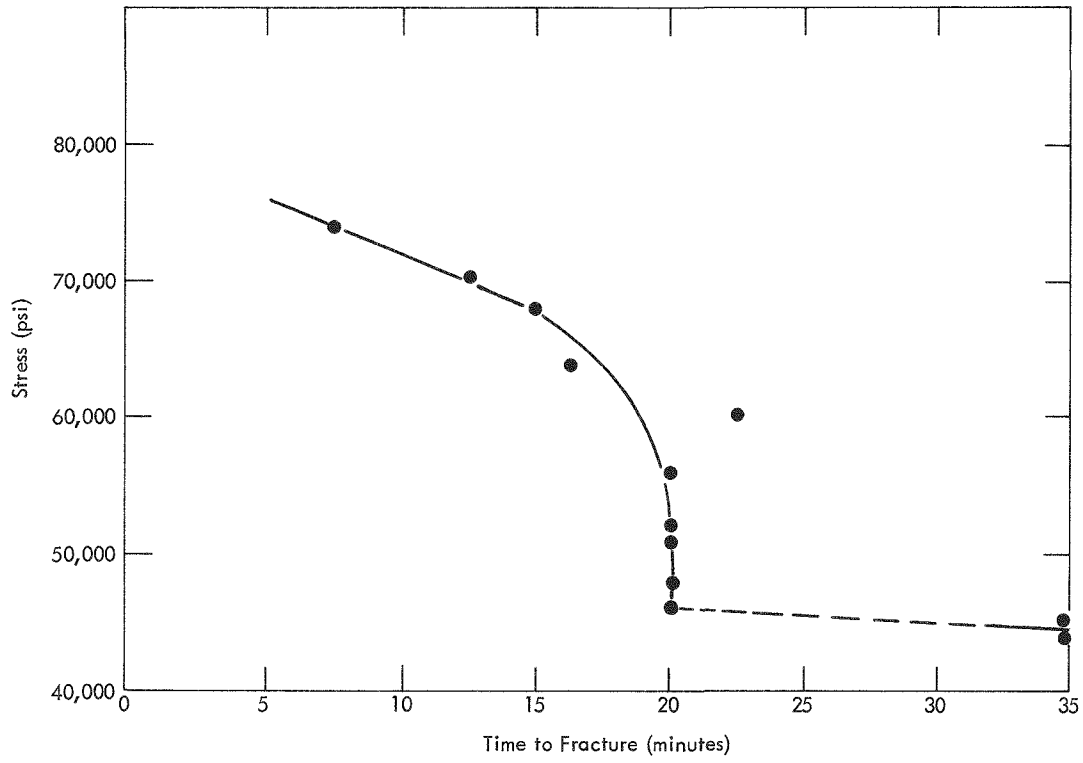


FIGURE 12

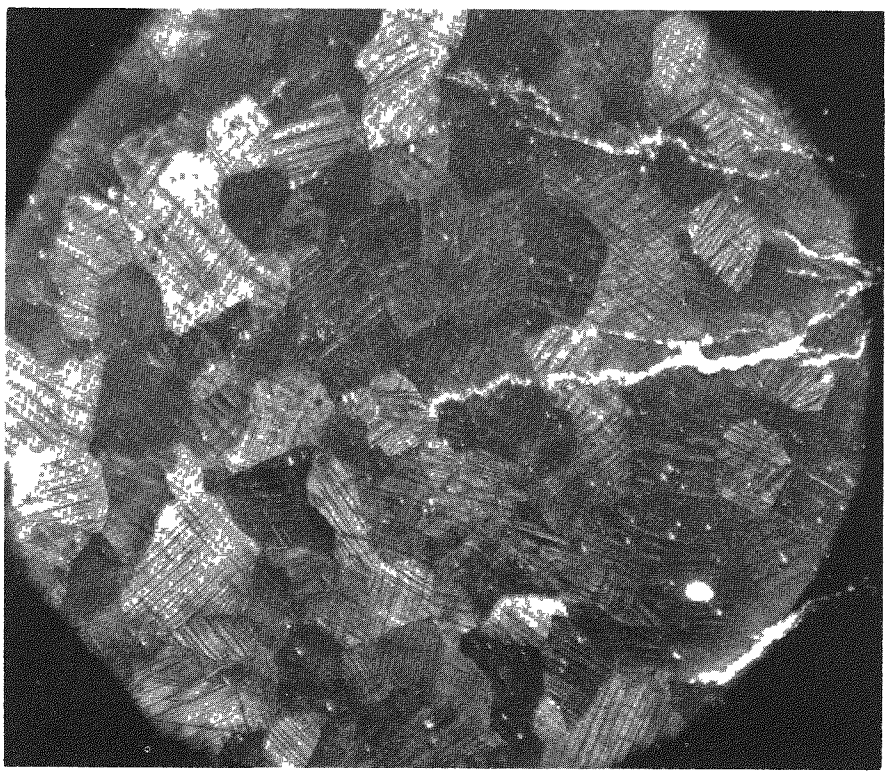
PLOT OF STRESS VERSUS TIME TO FRACTURE IN AIR FOR 0.252-INCH-DIAMETER TENSILE SPECIMENS OF A WATER-QUENCHED URANIUM-5 WEIGHT PER CENT MOLYBDENUM ALLOY

fracture occurred in 7.5 minutes. The 0.2 per cent offset yield strength was 45,000 lbs/in^2 for this particular alloy, and a stress of 74,000 lbs/in^2 would produce a strain of approximately 0.004 in/in. It was observed in another experiment that the grain size affected the minimum stress at which fracture would occur, and the curve shown in Figure 12 would be shifted up or down depending on the grain size of the alloy investigated.

V PATH OF FRACTURE

The path of cracking was always transgranular, as can be seen in Figure 13. Deformation markings on polished samples occurred in two shapes. One type was straight and typical of slip. The other type was lenticular in shape, typical of a twin or a deformation-induced transformation product. The two types are shown in Figures 14 and 15. Figure 16 shows that the deformation markings were also visible in the grains, under polarized light, after the sample was sectioned and polished for metallographic examination. Figure 17 shows the path of fracture is random relative to the deformation markings.

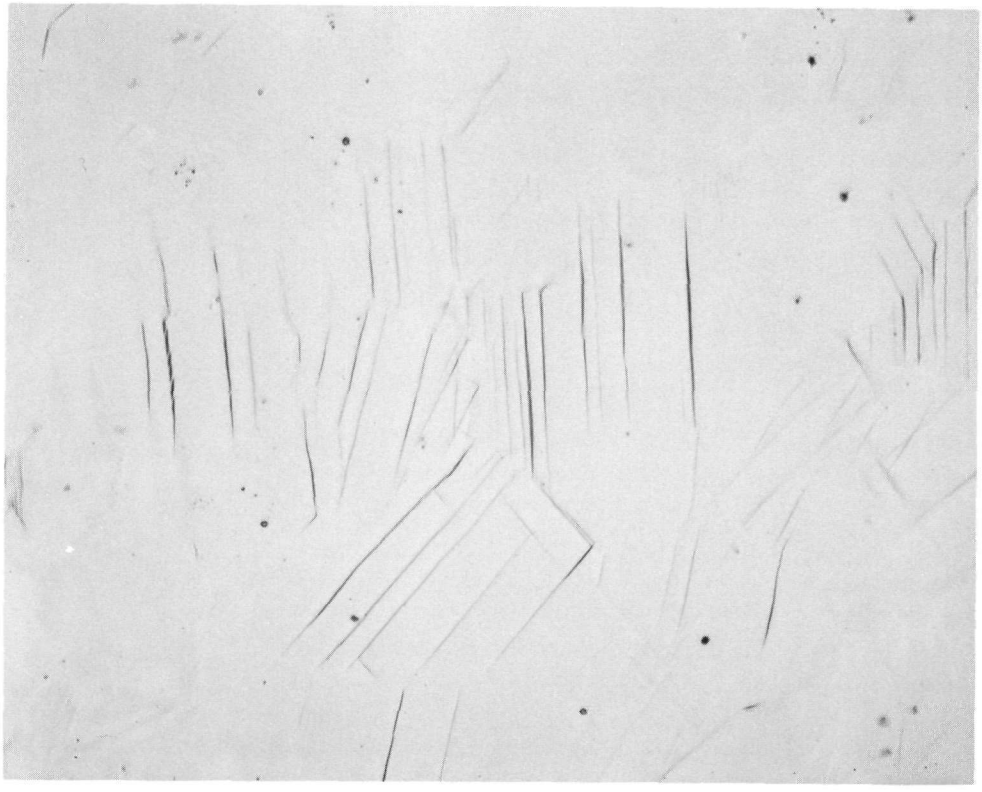
Nine motion pictures, at a magnification of 100X, were taken of the surface of tensile specimens during deformation. Only one motion picture showed a crack propagating. In that particular film deformation bands, spaced a small distance apart, were observed in one area, and a crack propagated from an area approximately 0.005 inch from the deformation bands. The crack did not start at these deformation bands, not did it propagate through them, but it propagated through an



100X

FIGURE 13

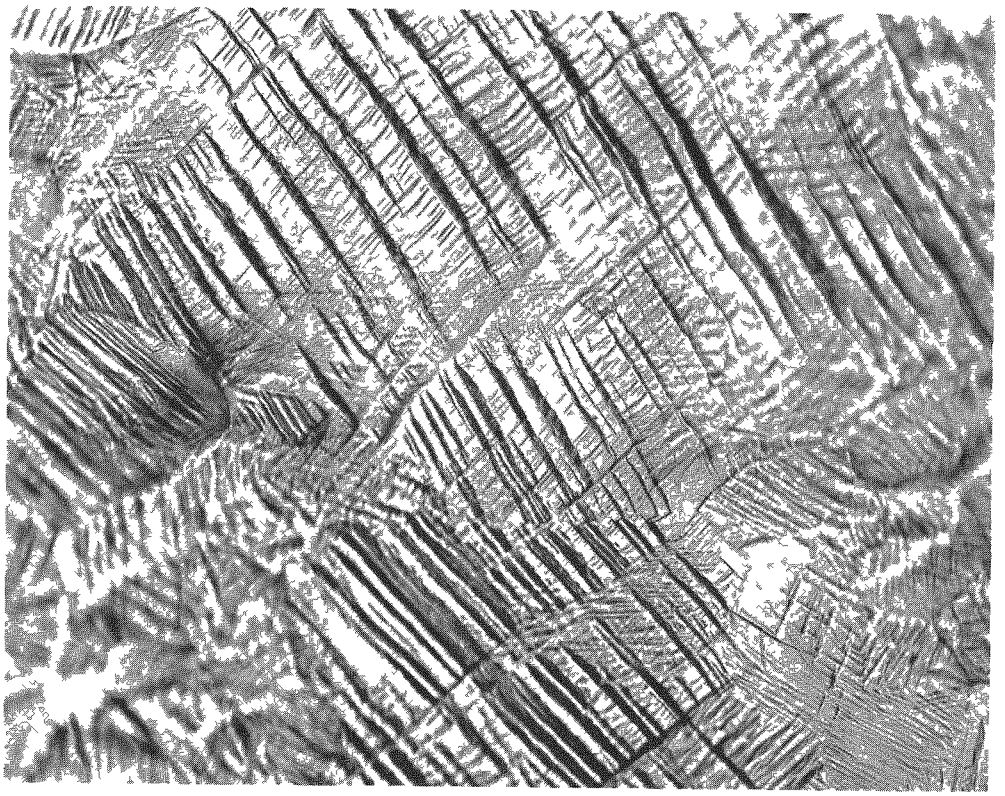
RELATION OF CRACKS TO THE MICROSTRUCTURE OF A WATER-QUENCHED URANIUM-5 WEIGHT PER CENT MOLYBDENUM ALLOY STRESSED IN AIR



500X

FIGURE 14

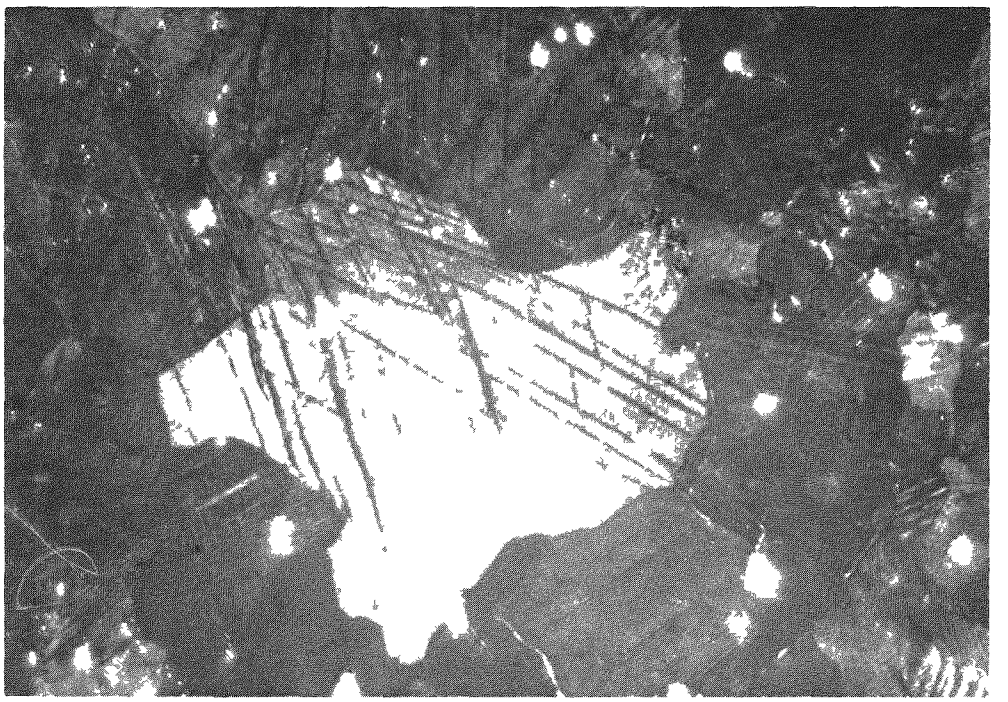
DEFORMATION MARKINGS TYPICAL OF SLIP IN A WATER-QUENCHED URANIUM-5 WEIGHT PER CENT MOLYBDENUM ALLOY



500X

FIGURE 15

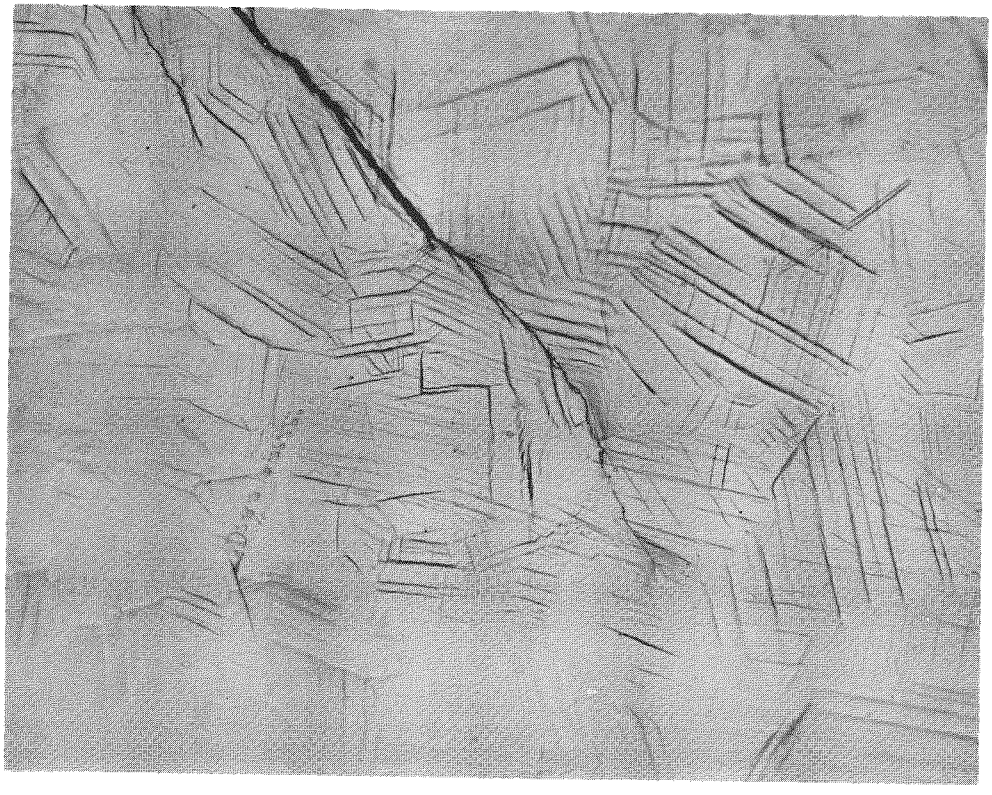
DEFORMATION BANDS IN A WATER-QUENCHED URANIUM-5 WEIGHT PER CENT MOLYBDENUM ALLOY



500X

FIGURE 16

DEFORMATION MARKINGS VISIBLE IN THE GRAINS OF A WATER-QUENCHED URANIUM-5 WEIGHT PER CENT MOLYBDENUM ALLOY



250X

FIGURE 17

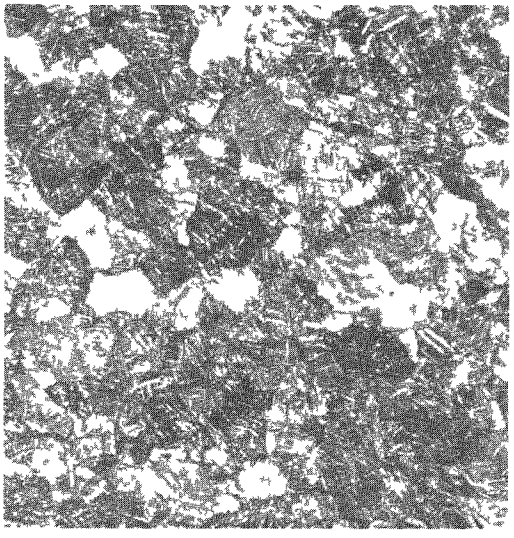
PATH OF FRACTURE RELATIVE TO THE DEFORMATION MARKINGS

area where no strain markings were visible. It is not known if there was a defect, or strain marking, at the origin of the crack. The crack had propagated a very short distance before it passed into the camera field. Further work, by motion picture, on the origin of the crack proved fruitless.

VI COMPARISON OF STRUCTURES OF URANIUM-5 WEIGHT PER CENT MOLYBDENUM AND URANIUM-4 WEIGHT PER CENT MOLYBDENUM

From Tables III and IV (Chapter IV, Pages 33 and 34), it can be seen that uranium-4 weight per cent molybdenum cracks in a manner similar to the uranium-5 weight per cent molybdenum alloy. There was an increase in the mechanical properties as the temperature was lowered below room temperature, and then a complete disappearance of cracking at a temperature of 10° C for the uranium-5 weight per cent molybdenum alloy and at a temperature of 15° C for the uranium-4 weight per cent molybdenum alloy. The literature states that the two alloys have different crystal structures in the water-quenched condition.[2,3,4] Therefore, when cracking was observed in both alloys, examination of their microstructures and X-ray diffraction traces were carried out to see what differences existed between the two alloys.

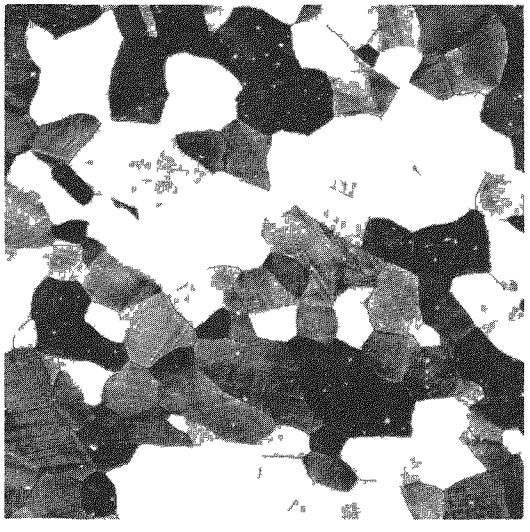
The microstructures of uranium-4 weight per cent molybdenum and uranium-5 weight per cent molybdenum, both in the water-quenched condition, are shown in Figure 18. A difference between the two structures is evident; the uranium-4 weight per cent molybdenum alloy appears to be typical of an alloy that has undergone a martensitic transformation, while the uranium-5 weight per cent molybdenum



100X

URANIUM-4 WEIGHT PER CENT MOLYBDENUM

A



100X

URANIUM-5 WEIGHT PER CENT MOLYBDENUM

B

FIGURE 18

MICROSTRUCTURES OF URANIUM-MOLYBDENUM ALLOYS
IN THE WATER-QUENCHED CONDITION

alloy does not show this effect. X-ray diffraction spectrometer traces, shown in Figures 19 and 20, demonstrate that there was a difference in crystal structure also. The trace in Figure 19 may be interpreted in terms of the structure of the equilibrium α phase, the (002) and (021) reflections of the α phase have merged into one, and the (110), (111), and the (112) have split into doublets.[2] The pattern obtained for the uranium-4 weight per cent molybdenum alloy is typical of the X-ray diffraction pattern for α'' as described by Hills, et al[2] and α'_b shown by Lehmann[14] where she found that α'_b could be indexed with a monoclinic structure, thus agreeing with Tangri's[3] observation of the crystal structure of α''. The uranium-5 weight per cent molybdenum alloy X-ray diffractometer trace, shown in Figure 20, is based on the body-centered cubic γ phase, but from the literature, the structure can be identified as the crystal structure of the γ_o phase.[2,3] It was explained in Chapter II that Hills, et al[2] found that γ_o was body-centered tetragonal, while Tangri[3] stated it was base-centered tetragonal due to ordering in the alloy. These effects are not easily observed in an X-ray diffractometer trace due to the c/a ratio that approaches 1 when the structure is identified as body-centered tetragonal. From the X-ray diffractometer traces obtained for the uranium-4 weight per cent and the uranium-5 weight per cent molybdenum alloys, it can be concluded that the crystal structures were different, and that cracking was not associated with one particular metastable phase in the uranium-molybdenum system.

The thick lenticular bands formed in the uranium-5 weight per cent molybdenum alloy microstructure suggested that a deformation-induced transformation was

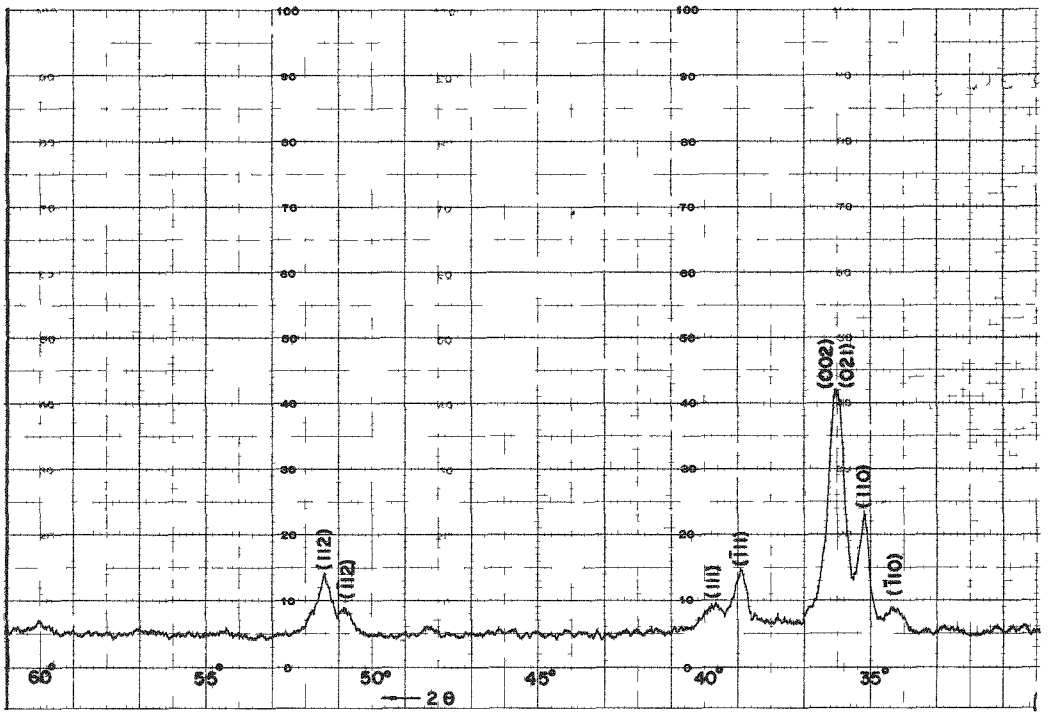


FIGURE 19

X-RAY DIFFRACTION SPECTROMETER TRACE FOR URANIUM-4 WEIGHT PER CENT MOLYBDENUM IN THE WATER-QUENCHED CONDITION

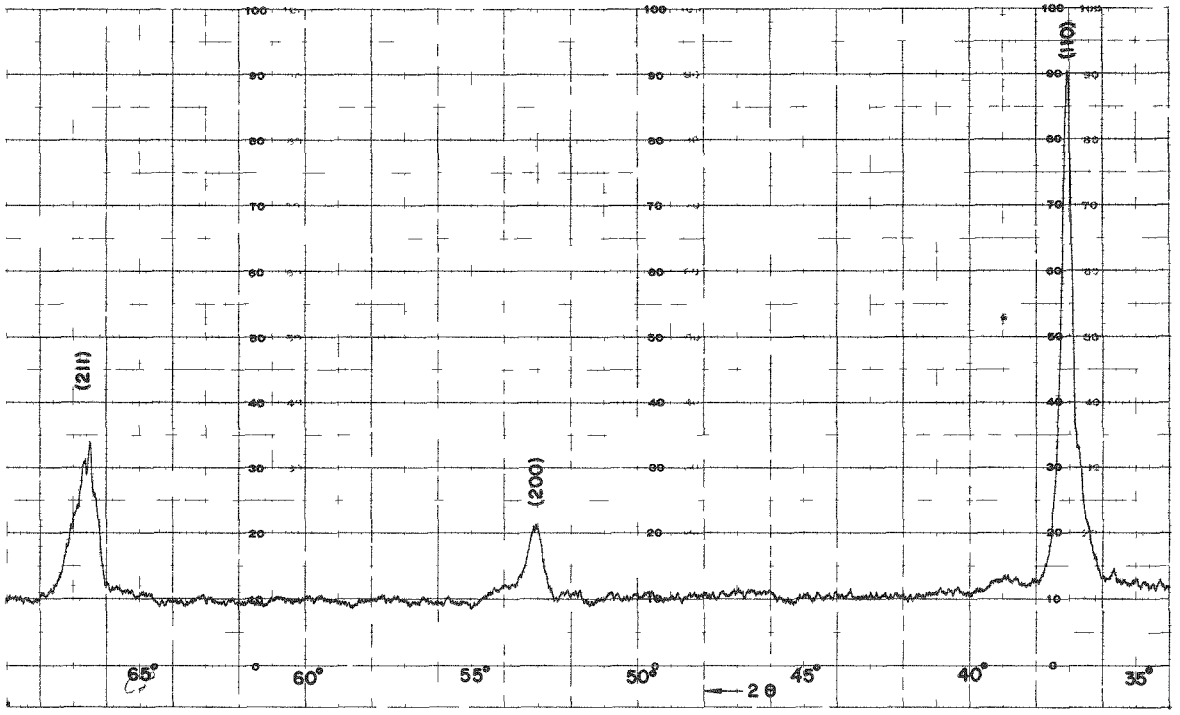


FIGURE 20

X-RAY DIFFRACTION SPECTROMETER TRACE FOR URANIUM-5 WEIGHT PER CENT MOLYBDENUM IN THE WATER-QUENCHED CONDITION

occurring. No phase change, however, was observed in the alloy by X-ray diffraction from a cold-worked sample. The sample was obtained from a tensile specimen that was elongated 40 per cent in a vacuum of 8×10^{-3} millimeters of mercury. A vacuum was used to eliminate cracking in the sample in order to obtain a higher elongation. Figure 21 shows the X-ray spectrometer trace for the worked sample and can be compared to Figure 20, the trace for the alloy in the water-quenched condition. The diffractometer trace from the worked sample showed no new reflections, indicating a new phase was present. The (110) reflection was broadened and the (200) and (211) reflections decreased in intensity.

The sudden stopping of the cracking at 10° C suggested a phase change in the vicinity of 10° C to a phase that was not sensitive to stress-corrosion cracking in oxygen. This theory was disproved by obtaining diffractometer traces at temperatures between 28° and -70° C. No phase change was observed in this temperature range. Figure 22 is the diffractometer trace at -70° C and is identical to the trace obtained at 28° C.

VII ANELASTIC BEHAVIOUR

Anelastic behaviour indicates that atomic displacements are occurring, while the specimen is under stress, that are not produced instantaneously when the stress is applied or are not recovered instantaneously when the stress is removed. Therefore, the atom movements responsible for the anelastic effects may be responsible for providing the heterogeneities in composition that Dix[7] and

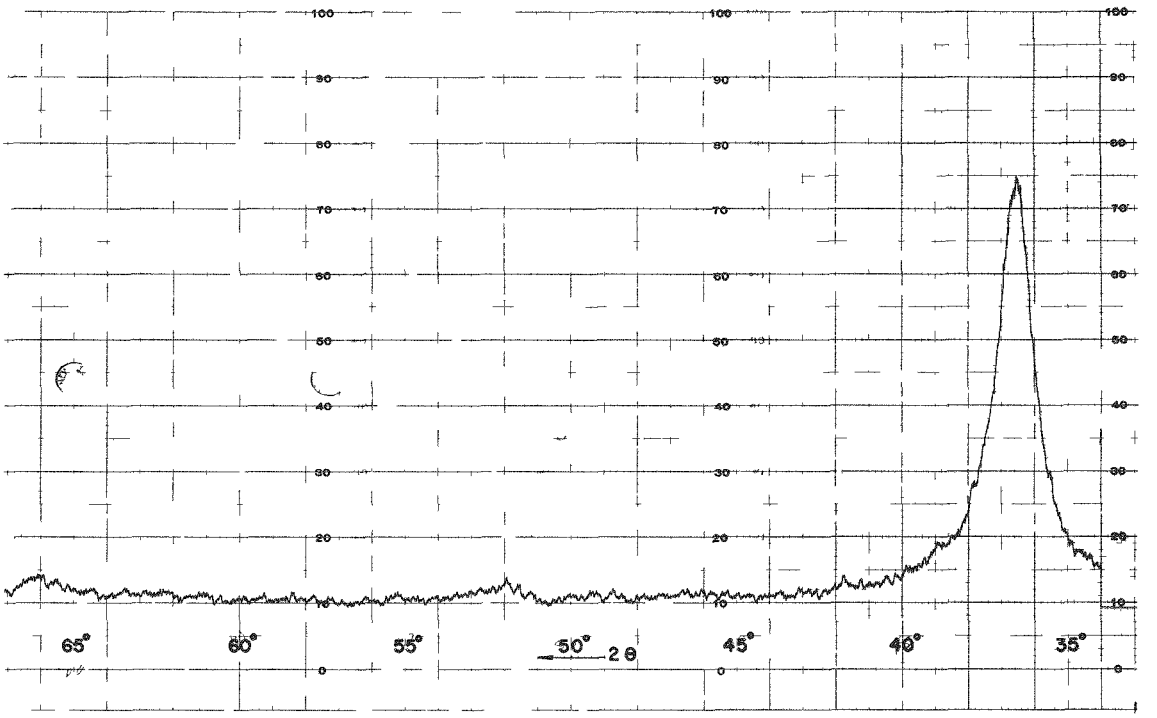
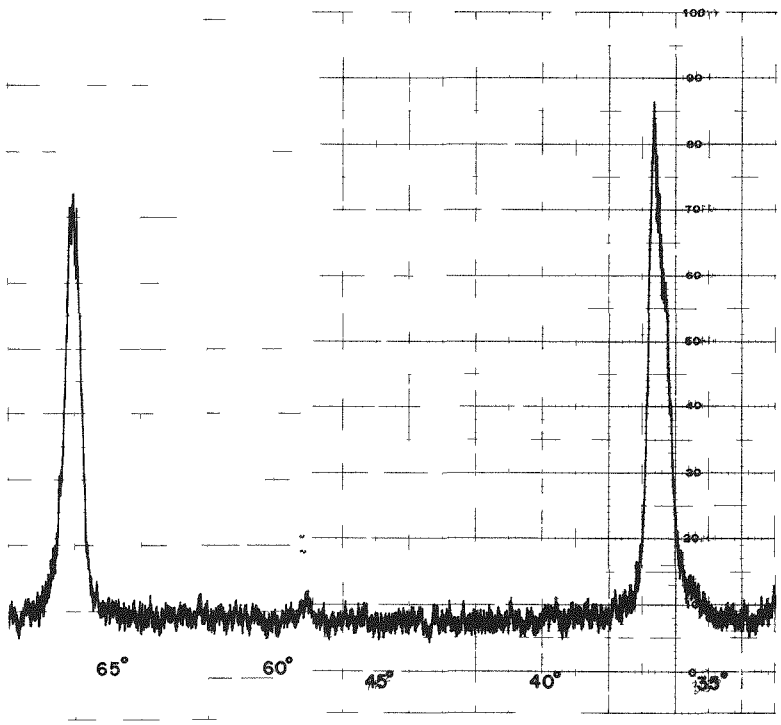


FIGURE 21

X-RAY DIFFRACTION SPECTROMETER TRACE FOR A WATER-QUENCHED URANIUM-5 WEIGHT PER CENT MOLYBDENUM ALLOY THAT WAS ELONGATED 40 PER CENT IN TENSION


65°
60°
45°
40°
35°

Uhlig[7] propose must be present in an alloy that undergoes stress-corrosion cracking.

Figure 23 shows the hysteretic loop, in the stress-strain diagram, formed on loading and unloading the alloy in a tensile test. An elastic after effect was observed in the uranium-5 weight per cent molybdenum alloy. This effect can be seen in Figure 24(A), where the testing machine was stopped at the maximum load shown on the load-elongation curve, and the sample continued to elongate, causing a decrease in load. On unloading, the machine was again stopped, and the specimen continued to contract, causing the load on the machine to increase. This is the discontinuity in the unloading curve in Figure 24(A).

If the anelastic behaviour provides the rearrangement of atoms necessary to cause the alloy to undergo stress-corrosion cracking by oxygen, then the disappearance of cracking at 10° C would also result in a disappearance of the anelastic behaviour. This theory was disproved, as can be seen in Figure 24(B), which shows the same type of hysteretic loop and elastic after effect at -5° C.

Figure 25 shows the load-elongation curve for a sample that was held under stress and cracked. The first drop in load, with increasing elongation, was caused by the elastic after effect. The remaining portion of the curve, which shows an additional drop in load with increasing elongation, was caused by the cracking of the sample.

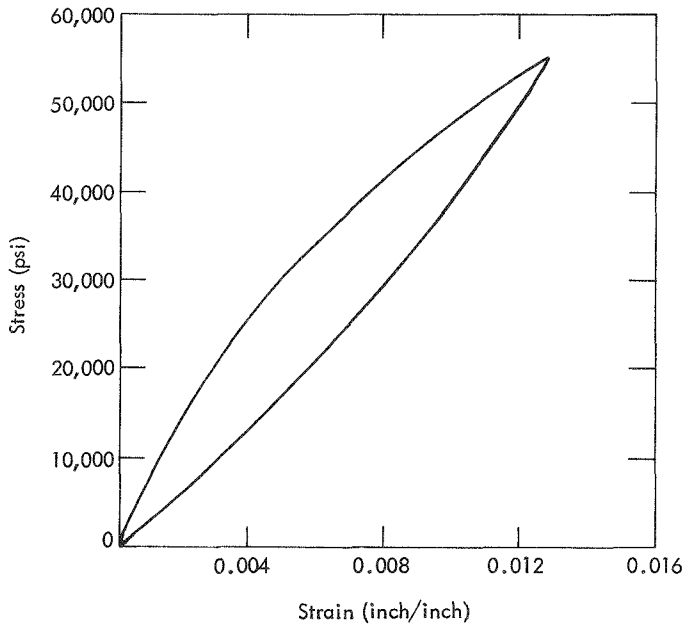
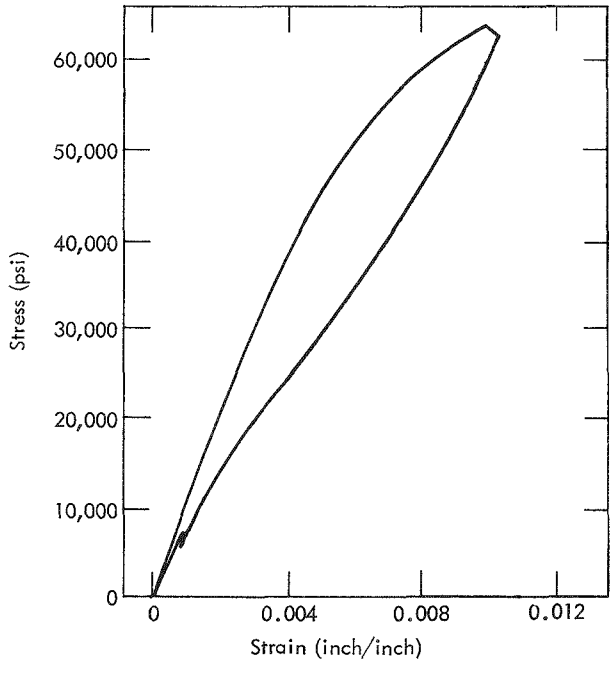


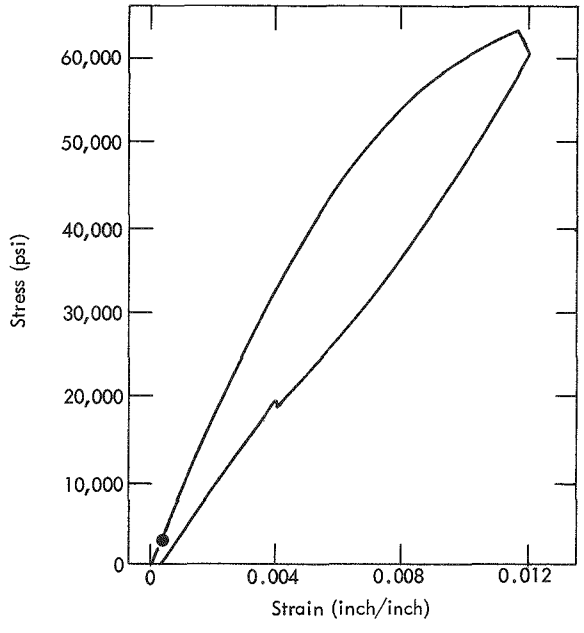
FIGURE 23

MECHANICAL HYSTERESIS IN A WATER-QUENCHED URANIUM-5 WEIGHT PER CENT MOLYBDENUM ALLOY



AT 25° C

A



AT -5° C

B

FIGURE 24

ELASTIC AFTER EFFECT IN A WATER-QUENCHED URANIUM-5 WEIGHT PER CENT MOLYBDENUM ALLOY

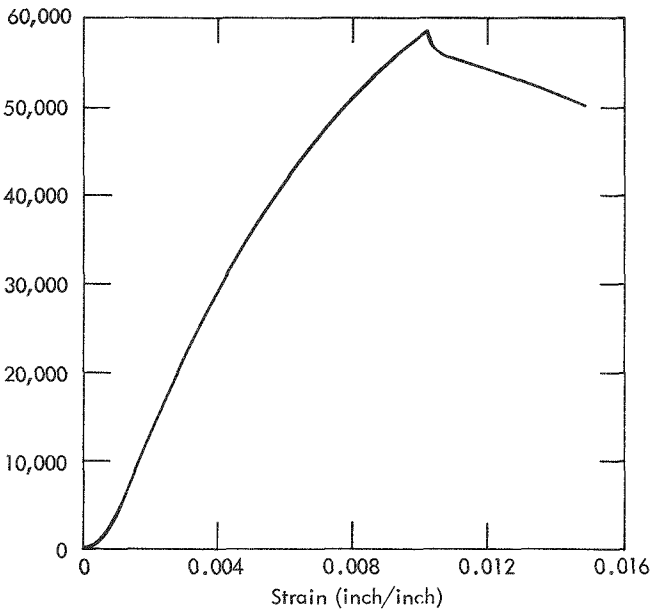


FIGURE 25

LOAD-ELONGATION CURVE SHOWING ANELASTIC BEHAVIOUR AND CRACKING IN A WATER-QUENCHED URANIUM-5 WEIGHT PER CENT MOLYBDENUM ALLOY

VIII THE EFFECT OF GRAIN SIZE ON FRACTURE

Since the Stroh-Petch equation (Chapter II, Page 9) states a relationship between fracture stress and grain size, a series of samples composed of groups of specimens with different grain sizes were tested in tension, and the stress to cause cracking was determined. The stress to cause cracking was fitted to the Stroh-Petch fracture-stress equation by the method of least squares, using the IBM 7090 computer, and assuming any error was in the stress measurement. Figure 26 is the plot of fracture stress versus (grain diameter)$^{-1/2}$ showing the experimental points (see Appendix, Table VII) along with the straight line determined by least squares. The slope, K, of the line was found to be 8485 lbs mm$^{1/2}$/in^2 with a standard error of 1380 lbs mm$^{1/2}$/in^2 and the intercept σ_o was 15,865 lbs/in^2 with a standard error of 7120 lbs/in^2. Using the preceding constants, a plot of fracture stress versus grain size is shown in Figure 27.

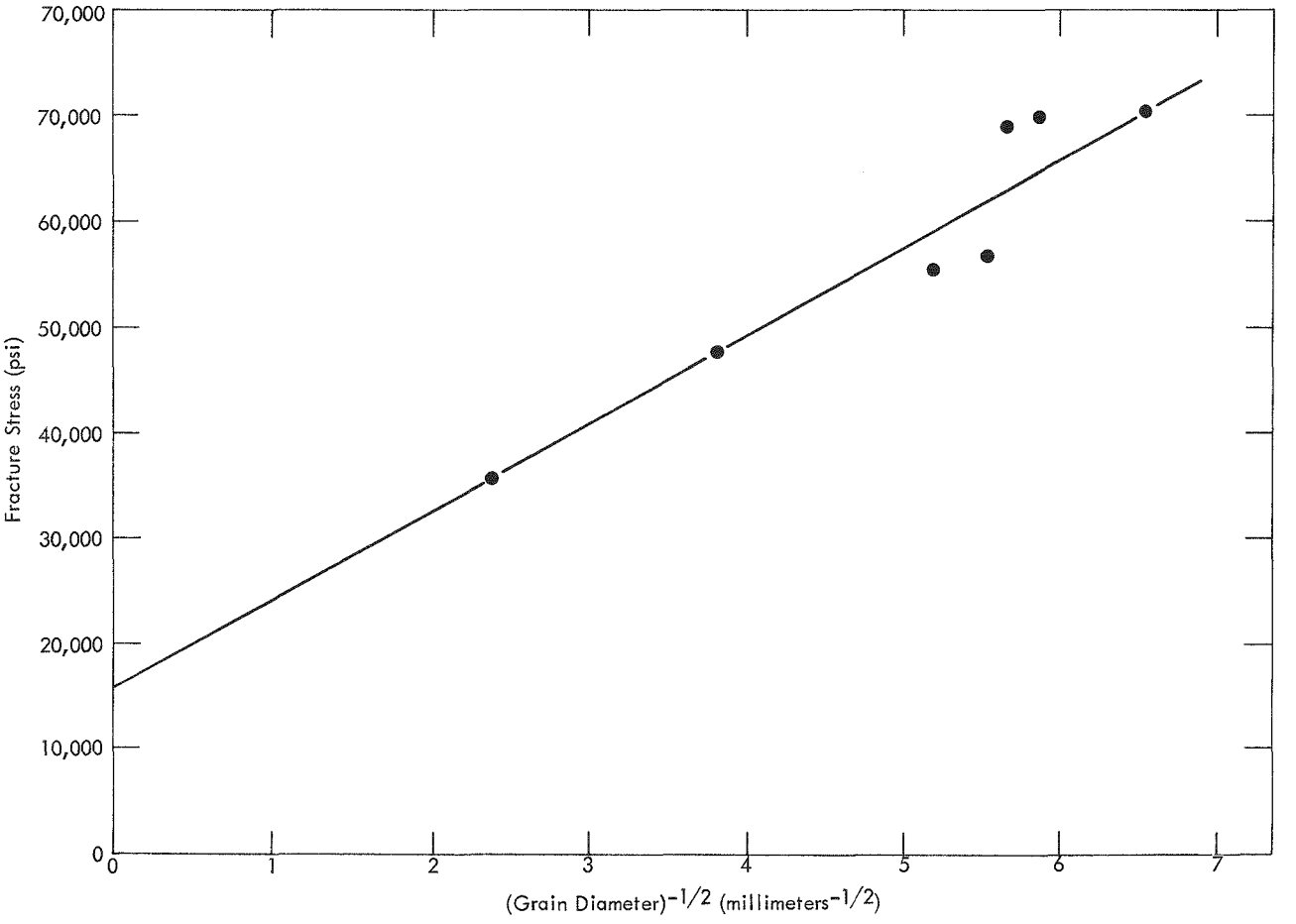


FIGURE 26

PLOT OF FRACTURE STRESS VERSUS (GRAIN DIAMETER)$^{-1/2}$ FOR A WATER-QUENCHED URANIUM-5 WEIGHT PER CENT MOLYBDENUM ALLOY

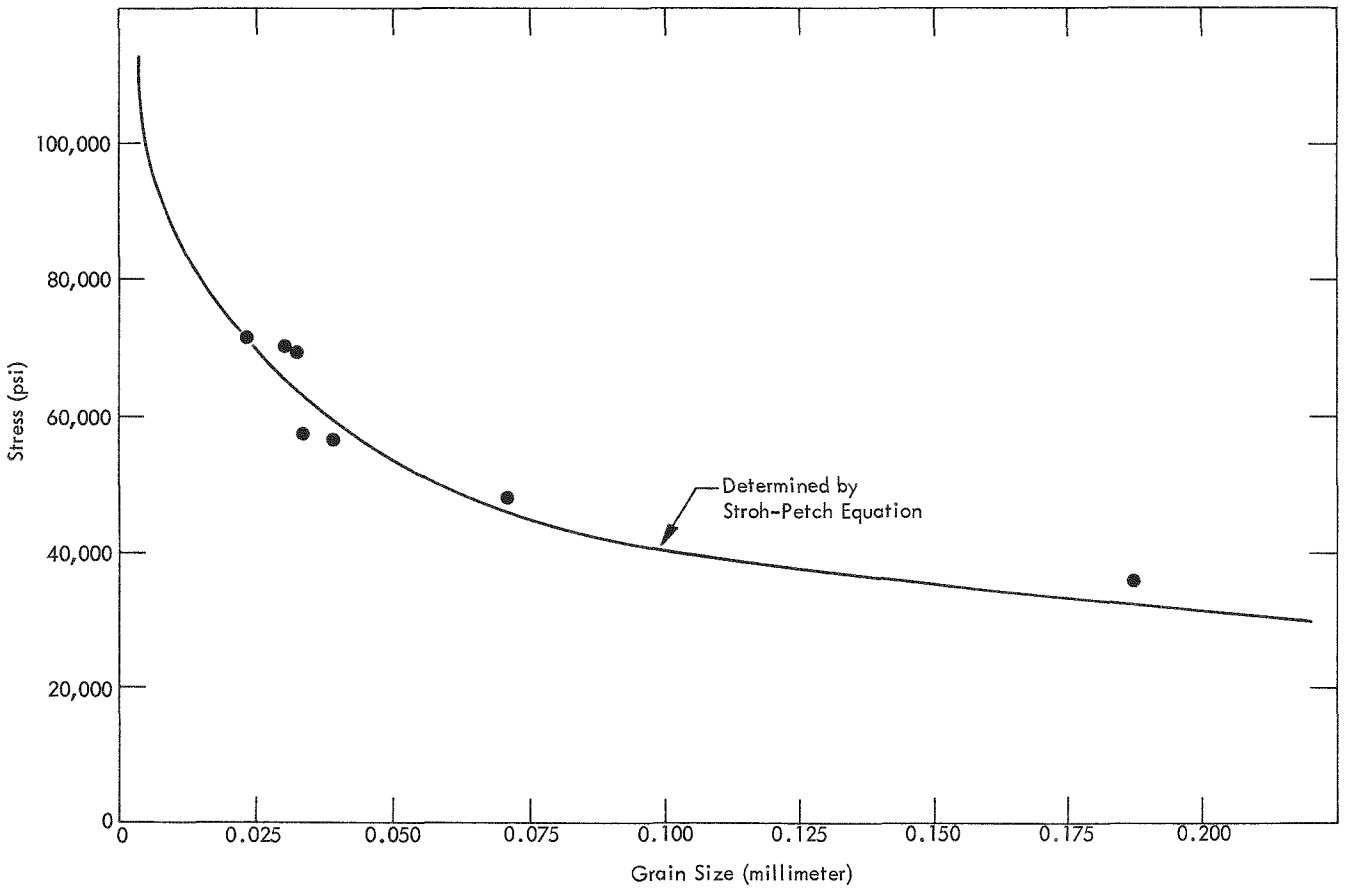


FIGURE 27

PLOT OF FRACTURE STRESS VERSUS GRAIN SIZE FOR A WATER-QUENCHED URANIUM-5 WEIGHT PER CENT MOLYBDENUM ALLOY

CHAPTER V

DISCUSSION

Oxygen in the atmosphere was found to be the gas that caused cracking in the uranium-5 weight per cent molybdenum alloy. An area of discoloration was observed on the fracture surfaces of the broken tensile bars that differed from the rest of the fracture. The discolored area has been attributed to oxidation, although no positive identification of an oxide on the attacked surface could be made to verify this conclusion.

The drop in ultimate tensile strength, elongation, and reduction in area, as the temperature was increased above 0° C in the uranium-5 weight per cent molybdenum alloy, was due to the depth of cracking that occurred. At 0° C, no cracking was observed, and the mechanical properties were equal to the properties obtained in an inert atmosphere, or vacuum, at 25° C. At temperatures of 15° C and above, the cracking caused the load carrying cross-sectional area of the sample to decrease, and this was indicated by a decrease in the conventional ultimate tensile strength. The presence of the cracks produced a notch effect such that the sample elongated only a small amount in the reduced cross section before failure occurred.

Tensile tests, at various temperatures in air, demonstrated that, as the temperature increased, the rate of cracking increased. An Arrhenius plot was made from the experimental data, and an activation energy for the cracking reaction was calculated. The activation energy could not be compared to any known

activation energy, thus identifying the rate-controlling mechanism for the reaction, but had to be described as the temperature coefficient of the cracking reaction. At 10° C, the cracking suddenly stopped, although an extrapolation of the Arrhenius equation to 10° C indicated fracture should have occurred in approximately 25 minutes.

A uranium-4 weight per cent alloy cracked in air, although the crystal structure differed from the structure of the uranium-5 weight per cent molybdenum alloy. Therefore, the cracking was not associated with only one metastable phase in the uranium-molybdenum system but with at least two phases.

From studies on the effect of oxygen pressure on fracture, it was observed that cracking occurred at an oxygen pressure between 8×10^{-3} and 130×10^{-3} millimeters of mercury. Therefore, the observation of cracking in nitrogen that was not purified by passage over hot copper chips could be explained by the small amount of oxygen present in the nitrogen. Analyses of nitrogen taken from gas cylinders at the Y-12 Plant,previous to this investigation, have shown an oxygen content of 400 ppm by volume. At a pressure of 760 millimeters of mercury, 400 ppm, by volume, of oxygen would exert a pressure of 300×10^{-3} millimeters of mercury, which was enough to cause cracking.

The observation that the depth of cracking decreased as the deformation speed was increased, until cracking was not evident at crosshead speeds greater than 10 in/min may be rationalized in terms of the time each sample was under stress. At a crosshead speed of 10 in/min, the specimen elongated approximately

0.5 inch, and the time for the crosshead to travel this distance was three seconds. At a speed of 0.025 in/min, the sample elongated approximately 0.1 inch, and the time for the crosshead to move this distance was approximately four minutes. Therefore, the specimens were under stress a very short time at crosshead speeds greater than 10 in/min, and the cracking reaction acted only a short time.

During the investigation of the effect of temperature on cracking susceptibility, it was observed that the cracking did not occur below 10° C in the uranium-5 weight per cent molybdenum alloy. It was impossible to determine why the cracking did not occur below 10° C. It was proposed that a phase change occurred in the vicinity of 10° C, resulting in a new phase that was not sensitive to stress-corrosion cracking in oxygen. X-ray diffraction examination did not reveal a phase change between 28° and -70° C. The uranium-5 weight per cent molybdenum alloy behaved anelastically during the tensile test. It was proposed that atomic displacements, that were not produced instantaneously as the stress was applied, accounted for the anelastic behaviour and, also, could be the mechanism that might produce heterogeneities in composition causing stress-corrosion cracking in the alloy. Therefore, the disappearance of cracking at 10° C would be accounted for by a disappearance in the anelastic effects. This theory was disproved by loading and unloading tensile bars at various temperatures. The anelastic effects observed at room temperature were still evident at -5° C.

An examination of crack propagation, relative to the microstructure, revealed that the cracks were always transgranular in the uranium-5 weight per cent

alloy. They propagated in a random fashion, relative to deformation markings. Motion pictures failed to show where the cracks originated on the surface, but showed that the one crack observed propagated through an area of sample that showed no strain markings.

An investigation of the cracking phenomenon in uranium-5 weight per cent molybdenum alloys, with various grain sizes, revealed that as the grain size increased, the stress to cause cracking decreased. The results were analyzed using the Stroh-Petch equation. The Stroh-Petch equation has been used, by various investigators, in an attempt to explain the cause of stress-corrosion cracking,[6,9] hydrogen embrittlement,[6,9,16] and liquid-metal embrittlement.[9,15] By plotting σ_f versus $d^{-1/2}$ and measuring the slope of the line, K, the surface energy of the alloy was calculated. The investigators found that the calculated surface energy of the alloy investigated, with respect to its environment, was lower than the surface energy of the alloy surrounded by its own vapor. The conclusion was then made that the cause of premature failure, or cracks, was the lowering of surface energy due to adsorption of a species from the environment.

From the slope of the line in Figure 26, the surface energy for uranium-5 weight per cent molybdenum can be calculated. Using the constants, $G = 4.72 \times 10^6$ psi and $\nu = 0.36$, γ, the surface energy was calculated as 3580 ergs/cm^2. This value is two to three times the measured surface energy for most metals and alloys with respect to their vapors. It must be concluded that the Stroh-Petch equation gave an unreasonable value for the surface energy of uranium-5 weight per cent

molybdenum, with respect to its surface in air, and cannot be used to conclude that the cause of cracking was a lowering of surface energy due to the adsorption of oxygen.

Another factor that was not considered in using the Stroh-Petch equation was the presence of variables introduced through different fabrication schedules and heat treatments to produce the various grain sizes.

It was found in the study of the effect of grain size on fracture, that, generally, the minimum stress to cause cracking was the stress where plastic strain started. In the set of samples containing the largest grain size, the lowest stress to cause fracture was a stress where no permanent set occurred.

It was also observed in the investigation of grain size that the stress where cracking started could be increased by loading the sample in increments of 2000 lbs/in^2, starting at 50,000 lbs/in^2, and allowing 10 minutes at stress between increments. This was carried out on one sample from a group that normally cracked at 56,000 lbs/in^2; the stress to cause cracking in the incrementally loaded sample was 80,000 lbs/in^2. The results seemed to indicate that a very slow strain rate would eliminate cracking. One specimen was tested at a crosshead speed of 0.002 in/min, and the sample cracked. A lower strain rate could not be obtained on the available tensile machines. Further examination of this phenomenon was beyond the scope of this investigation.

CHAPTER VI

CONCLUSIONS

An investigation of cracking in uranium-5 weight per cent molybdenum was conclusive in finding the phenomenological cause of cracking, but did not provide a mechanism for explaining why the material was attacked selectively by oxygen. The results of the investigation permit the following conclusions to be made:

1. The cracking occurred only in tension, and can be considered as stress-corrosion cracking, due to the presence of oxygen in the atmosphere.
2. The cracking rate increased as the temperature was increased and could be fitted to the Arrhenius rate equation over the temperature range 25° to 100° C.
3. Below 10° C, cracking in uranium-5 weight per cent molybdenum was not observed.
4. A minimum oxygen pressure between 8×10^{-3} and 130×10^{-3} millimeters of mercury was required to produce cracks on the surface of tensile bars during tensile tests.
5. Elongations greater than 40 per cent (no cracking occurred) were obtained on uranium-5 weight per cent molydenum when (a) the testing was done in an atmosphere containing a small amount of oxygen, (b) the test temperature was below 10° C, and (c) the crosshead speed of the tensile machine was greater than 10 in/min.

6. The cracking was not associated with only one metastable phase because a uranium-4 weight per cent molybdenum alloy showed cracking on the surface of tensile specimens although its crystal structure was different from the structure of uranium-5 weight per cent molybdenum.
7. Uranium-5 weight per cent molybdenum behaved anelastically in the tension test, but the effect could not be related to the cracking mechanism.
8. The stress to cause cracking decreased as the grain size increased.
9. The cracks were always transgranular.

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APPENDIX

TABLE VI

TIME FOR FRACTURE TO OCCUR AT VARIOUS TEMPERATURES

Temperature (° K)	1/RT (mol/° K x 10^3)	Time to Fracture (min)	ln (1/time to fracture)
298	1.69	15	-2.659
298	1.69	15	-2.659
298	1.69	15	-2.659
298	1.69	15	-2.659
315	1.60	12.8	-2.525
319	1.58	5.0	-1.609
319	1.58	6.5	-1.897
338	1.49	3.0	-1.109
338	1.49	6.0	-1.772
340	1.48	2.3	-0.821
353	1.42	1.6	-0.462
369	1.36	1.4	-0.342
369	1.36	3.8	-1.347
369	1.36	3.0	-1.109
373	1.35	1.4	-0.342

TABLE VII

STRESS TO CAUSE CRACKING AT VARIOUS (GRAIN SIZES)$^{-1/2}$

(Grain Size)$^{-1/2}$ (millimeter)$^{-1/2}$	Fracture Stress (psi)
2.31	36,000
3.75	48,000
5.21	56,000
5.68	69,690
5.78	70,000
5.59	56,500
6.58	71,000