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SWELLING OF URANIUM AND URANIUM ALLOYS ON POSTIRRADIATION ANNEALING

by

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Metallurgy Division

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ABSTRACT

The swelling of uranium and of a few selected uranium alloys on postirradiation annealing was investigated by utilizing density measurements in conjunction with the observation of pores in the microstructures of annealed specimens. Specimens were irradiated to about 0.3 a/o burnup in a constrained condition at approximately 275°C and were subsequently pulse annealed. The amount of swelling was found to be less than 1% for uranium specimens that were pulse annealed up to 75 hr at temperatures below 550°C; the amount of swelling, however, increased considerably on annealing at temperatures between 550°C and 650°C. Specimens pulse annealed up to 75 hr at 618°C decreased in density by approximately 18%. The swelling was accompanied by the formation of bubbles on grain boundaries in recrystallized regions. The observations suggest that recrystallization is a necessary prerequisite for pronounced swelling in the alpha phase.

Uranium specimens pulse annealed up to 75 hr at temperatures between 650°C and 750°C in the beta phase decreased in density by about 5%. Specimens annealed in the beta phase, in contrast with those annealed at 618°C in the alpha phase, were badly cracked and contained pores of a smaller diameter, which were uniformly distributed within the grains.

A specimen pulse annealed up to 16 hr at 822°C decreased in density by about 20%. This heat treatment produced pores of large diameter, located along grain boundaries, as well as pores of smaller diameter, distributed uniformly within the grains.

Uranium alloys containing between 1 w/o and 9 w/o of either titanium, zirconium, niobium, or molybdenum generally swelled more than pure uranium on pulse annealing up to 75 hr at 618°C and 740°C. An exception was the behavior of a U-4.0 w/o Nb alloy, which swelled less than uranium on annealing at 618°C. A carbon addition of 0.11 w/o to uranium substantially decreased the swelling on pulse annealing up to 75 hr at 618°C, whereas the effect of 0.02 w/o N was small; at 740°C, a nitrogen addition of 0.02 w/o to uranium caused an appreciable increase in the swelling, but the effect of 0.11 w/o C was slight.

INTRODUCTION

Several investigators[1,2] have determined that the density of uranium decreases when irradiated at temperatures above approximately 400°C with neutrons, or as a result of annealing at elevated temperatures following irradiation at temperatures below 400°C. The phenomenon has been called swelling. The decrease in density has been attributed primarily to the presence of bubbles which were generally believed to result from the diffusion of fission product atoms, krypton and xenon, through the lattice and their nucleation on suitable sites for bubbles.

The nature of the nucleation sites, the mechanism of growth, and the factors that control the size and distribution of bubbles have continued to be a subject for speculative comment. Homogeneous nucleation, nucleation on dislocations, and nucleation of bubbles on impurity atoms have been considered by various investigators.[3,4] It has been suggested that the bubbles grow by vacancy diffusion,[3] creep of the surrounding matrix,[5,6] plastic yielding,[3,7] re-solution of gas from small bubbles which results in growth of larger ones,[8] and joining of bubbles.[8] Some of the factors which have been suggested to influence the magnitude of swelling are temperature, amount of fission gas, time required to produce the gaseous fission products, and the presence of second phases.[2]

Much of the existing data on swelling in uranium were obtained with material which contained appreciable quantities of impurities and under experimental conditions which were not precisely defined, such as the amount of fission product gas in the material and irradiation temperature. Furthermore, no systematic studies have been made on the time dependence of the swelling process under isothermal conditions at temperatures extending into the beta- and gamma-phase regions. The studies described below were undertaken to study the possible effects of these variables and to carry out isothermal anneals from which one might hope to deduce information on the kinetics of the swelling process. The studies were made with high-purity unalloyed material and with a few selected alloys, largely the former. The methods of investigation were measurements of density variation and examinations of microstructures by optical and electron microscopy.

EXPERIMENTAL MATERIALS AND PROCEDURE

Castings of high-purity uranium and uranium alloys with either titanium, zirconium, niobium, molybdenum, carbon, or nitrogen were prepared by melting the appropriate materials in a thoria crucible in an evacuated, induction-heated furnace and pouring into a water-cooled copper mold. The carbon and nitrogen alloys were prepared by adding uranium-carbon and uranium-nitrogen arc-melted master alloy buttons. The castings contained 1.85 ± 0.12 w/o U^{235}, and they were extruded to an 83% reduction in area.

The extruded unalloyed uranium and the uranium-carbon and uranium-nitrogen alloys were heat treated at 725°C for 10 min, water quenched, and then further annealed at 620°C for one hour and cooled to room temperature. The resulting average grain diameter was 60 μ. The uranium alloys containing metallic additions were annealed at 800°C for 3 days, slowly cooled to 525°C, and annealed at this temperature for 14 days and cooled to room temperature. The chemical analyses and densities of the materials before irradiation are listed in Table I. The alloys listed in Table I were selected for study because of the dissimilar distribution of second phases in their microstructures prior to irradiation.

Table I

CHEMICAL ANALYSES AND DENSITIES OF URANIUM AND URANIUM ALLOYS BEFORE IRRADIATION

Material	Nonmetallic Impurities (w/o)			Density (gm/cc)
	O	N	C	
Uranium*	0.0025	0.0028	0.0017	19.02
U-2.2 w/o Ti	0.0037	0.0014	0.0014	17.94
U-1.8 w/o Mo	0.0019	0.0035	0.0021	18.64
U-4.1 w/o Mo	0.0032	-	0.0025	18.31
U-6.5 w/o Mo	0.0030	0.0019	0.0022	17.91
U-9.0 w/o Mo	0.0027	0.0016	0.0019	17.49
U-4.3 w/o Zr	0.0110	0.0022	0.0020	17.67
U-4.0 w/o Nb	0.0059	0.0103	0.0101	18.10
Uranium	0.0061	0.0190	0.0024	19.01
Uranium	0.0084	0.0027	0.1107	18.82

*The uranium also contained 0.0007 w/o Al, 0.0001 w/o Cu, 0.0001 w/o Mg, and 0.0015 w/o Si.

Specimens, 0.635 cm in diameter and 1.270 cm in length, were cut from the heat-treated materials and inserted in tight-fitting stainless steel irradiation capsules in groups of eight and sealed in a helium atmosphere. The capsules were irradiated in the Materials Test Reactor at an estimated central metal temperature of 275°C. Although the specimens were not completely constrained by the capsule before irradiation, this condition occurred during irradiation because of irradiation-induced growth. After irradiation, the specimens were removed from the capsule by parting the capsule wall along its length.

The irradiated specimens were annealed in a tantalum cup which was suspended in an Inconel tube evacuated to 0.01-μ pressure and heated

by a resistance furnace. Gases which were evolved from the specimens during heating were adsorbed on activated charcoal cooled with liquid nitrogen. The activity of the gas was continuously monitored by an end-window Geiger-Müller counter, and approximately 10^{-6} cc of Kr^{85} (STP) per cc of specimen could be detected with the apparatus. The annealing temperatures were measured with a calibrated chromel-alumel thermocouple located about one cm from the specimen and were controlled to ±0.5°C. The specimens were heated to and cooled from the annealing temperature at 4°C/min.

The density of an irradiated specimen was determined after each annealing treatment by weighing the specimen in air and in carbon tetrachloride by means of a remotely operated analytical balance capable of weighing with a precision of 0.05 mg. The temperature of the carbon tetrachloride was measured remotely with a calibrated thermister that was located about one cm from the specimen and was capable of detecting temperature changes of 0.01°C. Prior to weighing in the carbon tetrachloride, the specimen was left immersed for 30 min to 2 hr, the elapsed time depending on the amount of beta and gamma heating of the liquid and on the amount of swelling of the specimen. The maximum deviation of the density values from the average was ±0.02 gm/cc. The amount of swelling was expressed as the ratio of the change in density on annealing to the density of the specimen after irradiation.

After the annealing treatments of the irradiated specimens were completed, they were cut in two pieces. One piece was used for determining the number of fissions which had occurred in the sample, and the other was ground on silicon carbide and polished with 3- and 1-μ diamond paste. Worked metal which formed on the uranium specimens during mechanical polishing was removed by electrolytic polishing for 2 min in a solution containing five parts orthophosphoric acid, five parts ethylene glycol, and eight parts ethyl alcohol at a current density of 30 ma/cm^2. The specimens were then cathodically etched in an argon atmosphere at a pressure of 20 μ and a current density of about 0.3 ma/cm^2 at 4 kv. The specimens were cooled during etching by conduction through an aluminum tube containing ice water. The unirradiated specimens of uranium with metallic additions were electrolytically polished in a solution of eight parts orthophosphoric acid, five parts ethylene glycol, and five parts ethyl alcohol at a current density of 30 ma/cm^2 to reveal the distribution of the second phases.

The microstructures of the irradiated and cathodically etched specimens at magnifications up to 750 diameters were examined in the optical microscope by means of negative replicas prepared with cellulose acetate, or by direct observation in a beta- and gamma-shielded optical microscope. For examination of the microstructures at higher magnifications, the negative cellulose acetate replicas were shadowed with a

Pt-20 w/o Pd alloy and backed with carbon. The cellulose acetate on the carbon replicas was dissolved in methyl acetate, and the negative carbon replicas were examined in a Siemens Elmiskop I electron microscope. Hence, pores in the surface of the original specimen were mounds on the negative carbon replica, with shadows extending from them, whereas mounds on the surface of the original specimen were depressions in the negative carbon replica, with shadows within them.

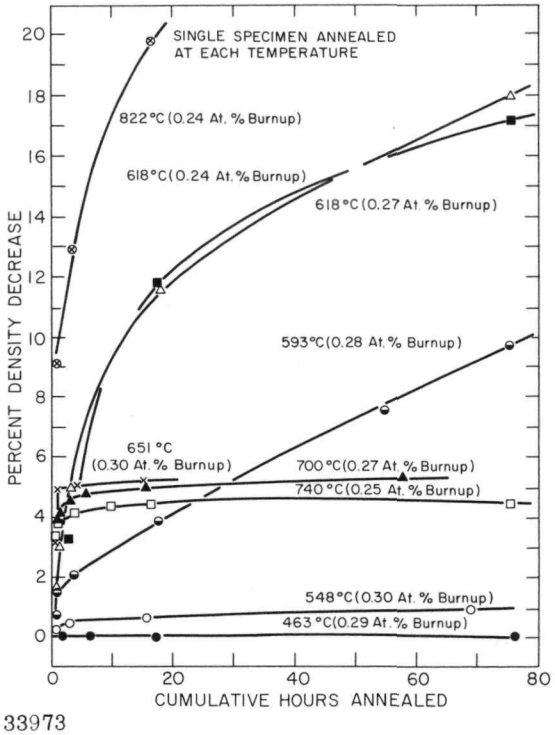
The exposure of the specimens to the neutrons is reported in terms of the fraction of all atoms which had undergone fission or, as expressed more briefly, a/o burnup. The burnup was determined from an analysis of the irradiated specimens for fission product Cs^{137} and uranium isotopes.

The amounts of krypton and xenon in the irradiated and annealed specimens were not determined experimentally. However, from experimental data on the isotopic yields of krypton and xenon from the fission of U^{235} reported by Blades, Fleming, and Thode,[9] 1 cc of uranium at 1 a/o burnup would contain 4.6 cc of gas (STP).

EXPERIMENTAL RESULTS

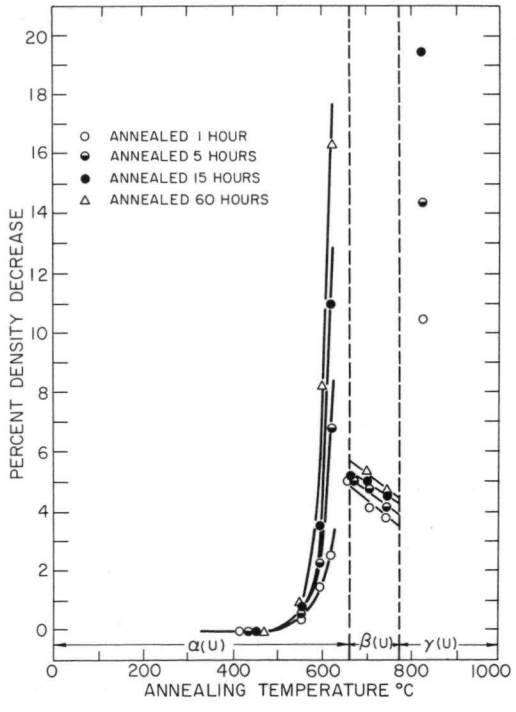
Swelling of Unalloyed High-purity Uranium

Density measurements. The density decrease of irradiated uranium specimens on pulse annealing up to 75 hr at various temperatures is shown in Figures 1 and 2. In Figure 1 the density decrease is plotted



33973

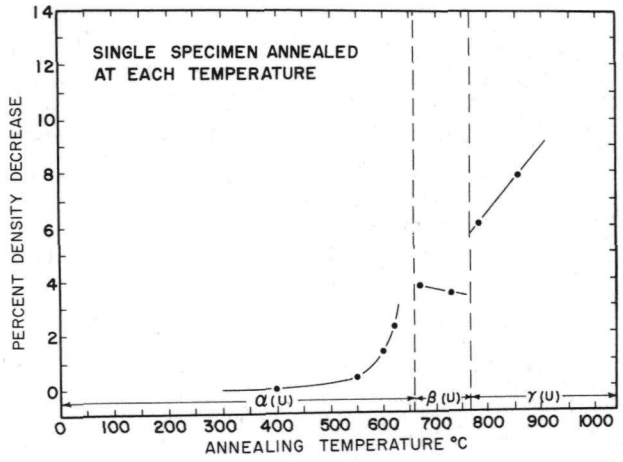
Figure 1. Effect of Annealing on the Swelling of Irradiated Uranium



33974

Figure 2. Effect of Annealing Temperature on the Swelling of Irradiated Uranium

against the annealing time for specimens annealed at the indicated temperature. Each curve represents the cumulative density decrease of a single specimen, and each point on a curve represents the total time that the specimen was annealed at the indicated temperature. The annealing times plotted do not include the times required for the specimen to heat to or to cool from the annealing temperature for each density determination. In Figure 2 the density decrease is plotted against the annealing temperatures for various periods of annealing time. These curves were constructed from those in Figure 1 by selecting the indicated annealing times.



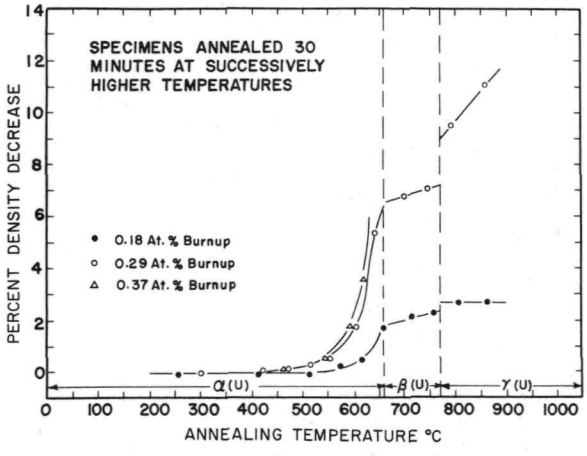
34111

Figure 3. Swelling of Uranium Specimens Irradiated about 0.30 a/o Burnup and Annealed 30 min at Various Temperatures

The swelling of individual specimens after annealing 30 min at various temperatures is shown in Figure 3. Each specimen was irradiated between 0.28 and 0.31 a/o burnup.

The swelling of irradiated uranium specimens with different burnups on annealing 30 min at successively higher temperatures is shown in Figure 4. Each point on a curve represents the cumulative density decrease of the specimen.

It is apparent from the curves in Figures 2, 3, and 4 that a pronounced increase in the swelling of uranium commences at about 600°C, regardless of whether the specimens were annealed for extended periods of time at temperature (see Figure 2), annealed only 30 min at temperature (see Figure 3), or annealed 30 min at successively higher temperatures (see Figure 4). The amount of swelling was less than 1% for specimens pulse annealed up to 75 hr at temperatures less than 550°C, but the amount of swelling increased appreciably for specimens annealed at temperatures between 550°C and 650°C.



34112

Figure 4. Swelling of Uranium Specimens on Annealing 30 min at Successively Higher Temperatures

Also, it is apparent that the amount of swelling is dependent on the allotropic structure of the uranium at the annealing temperature and on the allotropic transformations. Specimens on pulse annealing up to 75 hr at 618°C in the alpha orthorhombic phase decreased in density by approximately 18%, whereas pulse annealing up to 75 hr at temperatures between 650°C and 750°C in the beta tetragonal phase produced a decrease in the density of only about 5%, and a specimen pulse annealed up to 16 hr at 822°C in the gamma cubic phase decreased in density by about 20%.

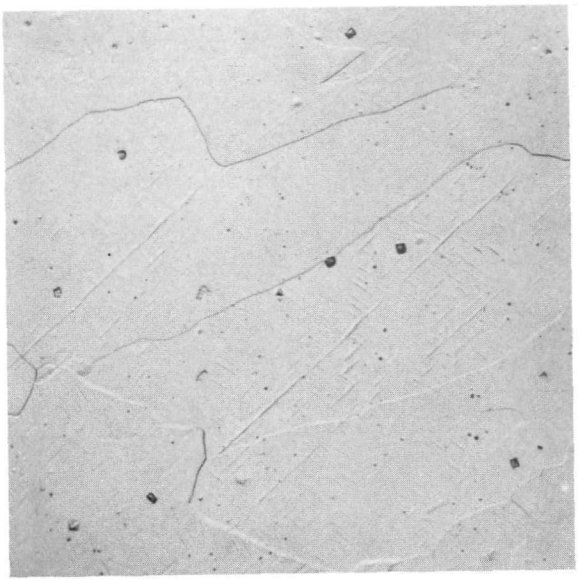
The rate of swelling was highest during the first few hours of annealing. In the case of specimens annealed between 650°C and 750°C, the rate of swelling decreased with time to the extent that after the first 3 hr of annealing the density decreased by less than 1% on further annealing up to 75 hr.

The dimensions of the swelled specimens were uniformly larger as compared with the dimensions of the as-irradiated specimens prior to annealing.

Microstructures before and after irradiation. Pores between 0.02 and 0.06 μ in diameter and in concentrations of approximately $10^{10}/cm^2$ were observed in the microstructures both before and after irradiation (see Figures 5c and 6b); pores with a diameter greater than 0.06 μ were almost nonexistent (see Figures 5 and 6). The pores in the as-irradiated uranium were surrounded by a darkened area which was not present around the pores in the unirradiated uranium. The 0.02- to 0.06-μ pores in the unirradiated and as-irradiated uranium were distinguishable only at magnifications greater than 32,000X; the effect of annealing was to make pores with diameters less than 0.06 μ easily distinguishable at much lower magnifications (see Figure 8d). Cracks were not evident in the microstructure of the as-irradiated uranium although the material appeared severely distorted (see Figure 6a).

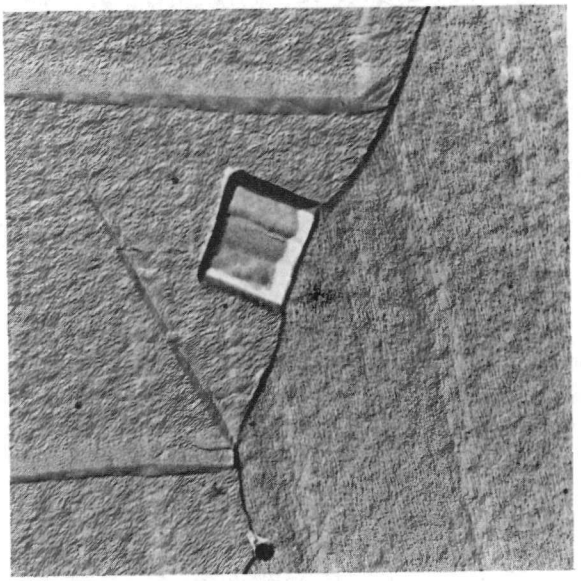
Microstructures after annealing at temperatures up to 650°C in the alpha phase. The microstructure of a uranium specimen irradiated to 0.29 a/o burnup and annealed 75 hr at 463°C appeared similar to the microstructure of the as-irradiated material. The density of this specimen decreased by 0.11%.

Pores between 0.02 and 0.3 μ in diameter were observed in the microstructure of a specimen irradiated to 0.30 a/o burnup and annealed 69 hr at 548°C (see Figure 7). The largest pores were located on grain boundaries or subgrain boundaries. Also, strings of pores were observed in the microstructure of this specimen (see Figure 7a), which were presumably formed on the boundaries of elongated grains present in the as-irradiated material (see Figure 6a). It could not be ascertained whether



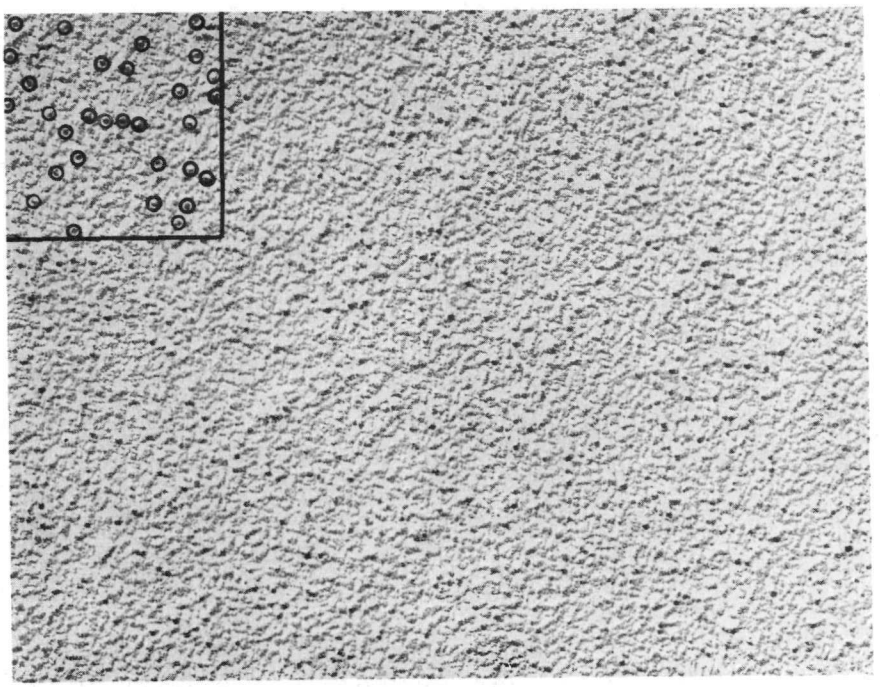
33971 Bright Field 500X

(a)



102529 Negative Replica 5200X

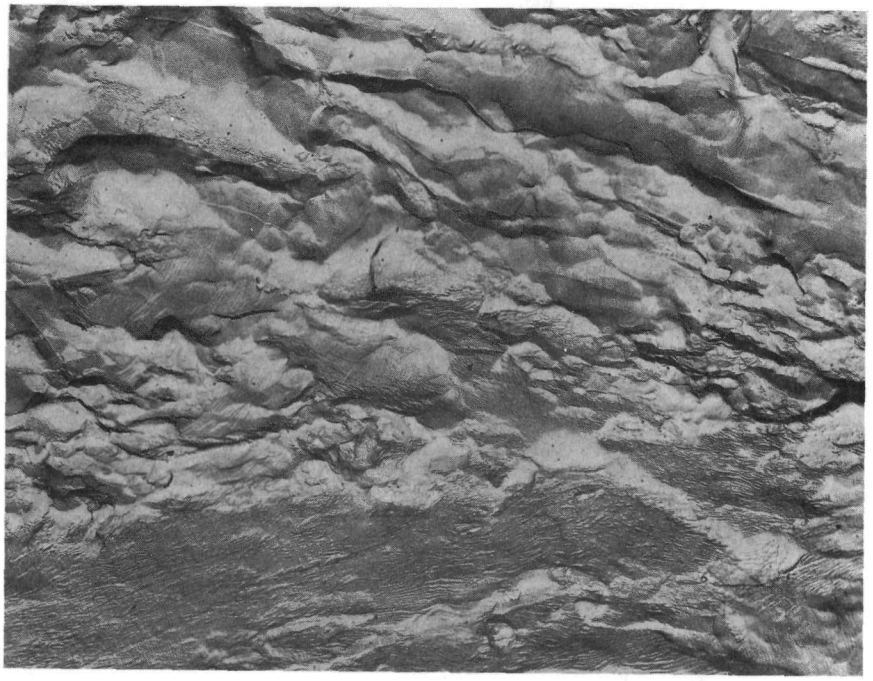
(b)



120159 Negative Replica 64,000X

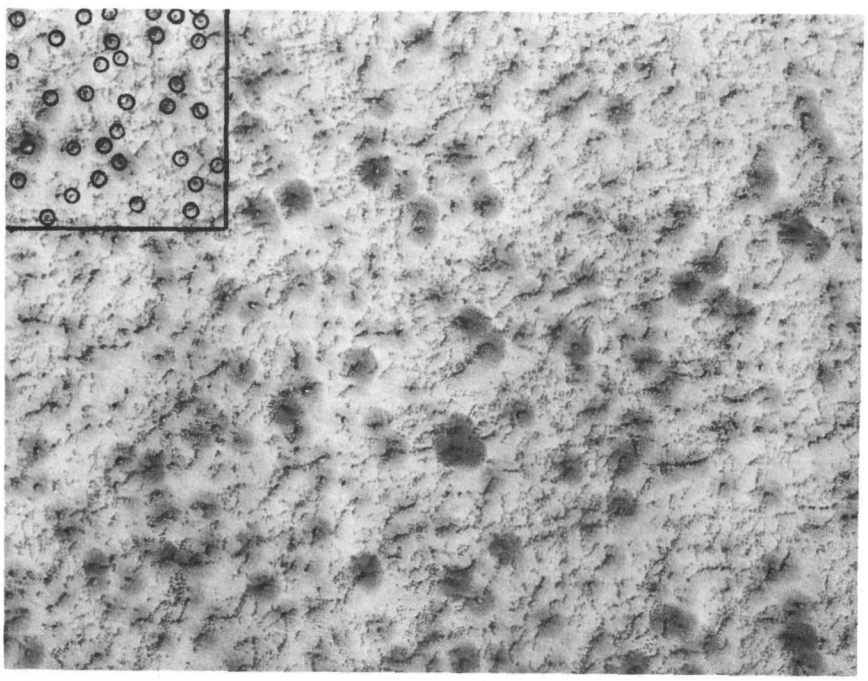
(c)

Figure 5. Microstructures of Uranium before Irradiation



(a)

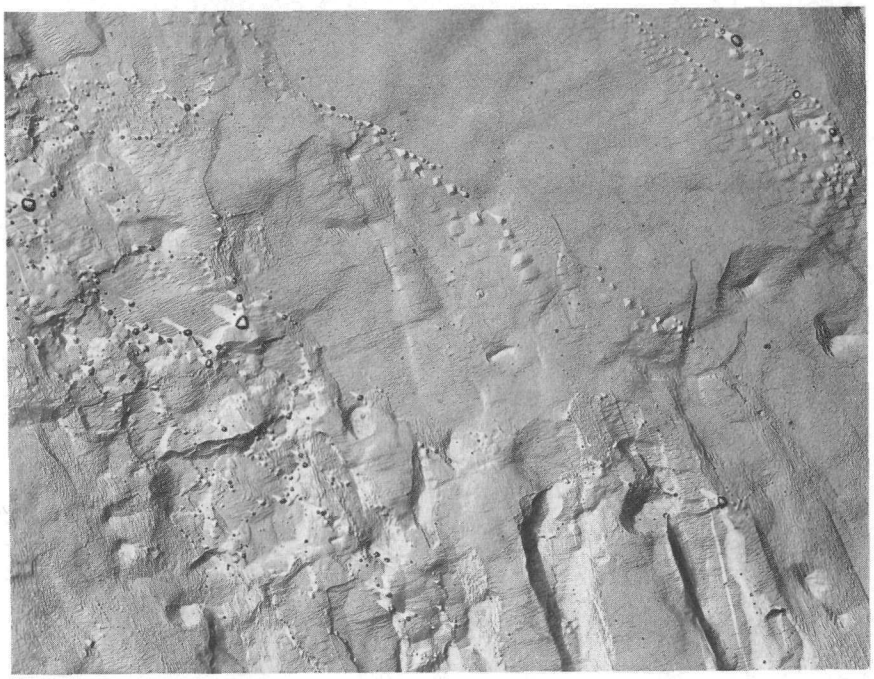
102473 Negative Replica 5200X



(b)

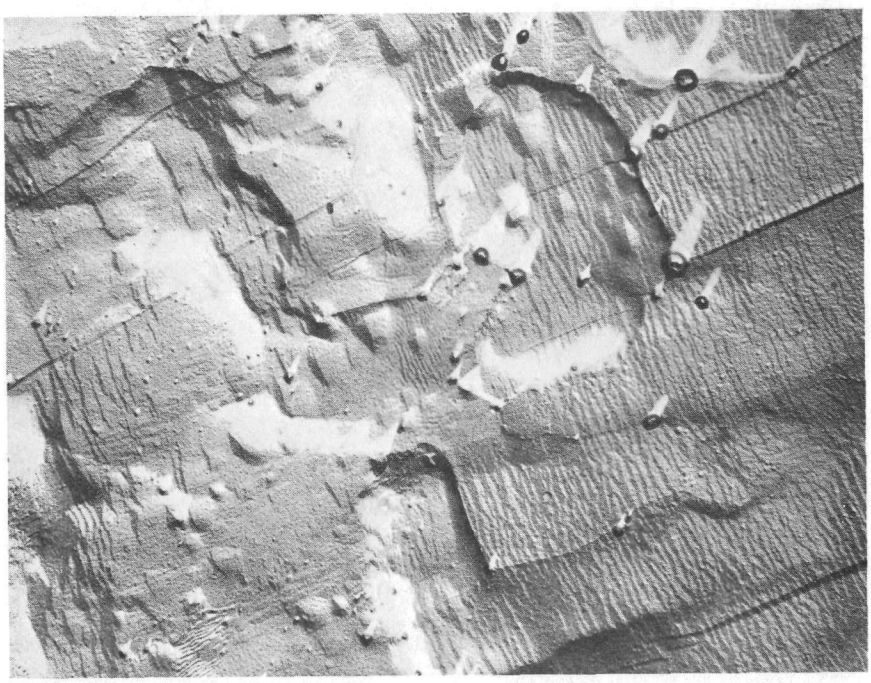
120063 Negative Replica 64,000X

Figure 6. Microstructures of Uranium after Irradiation to 0.30 a/o Burnup



(a)

102277 Negative Replica 5200X



(b)

102474 Negative Replica 16,000X

Figure 7. Microstructures of Uranium Irradiated to 0.30 a/o Burnup and Annealed 69 hr at 548°C.

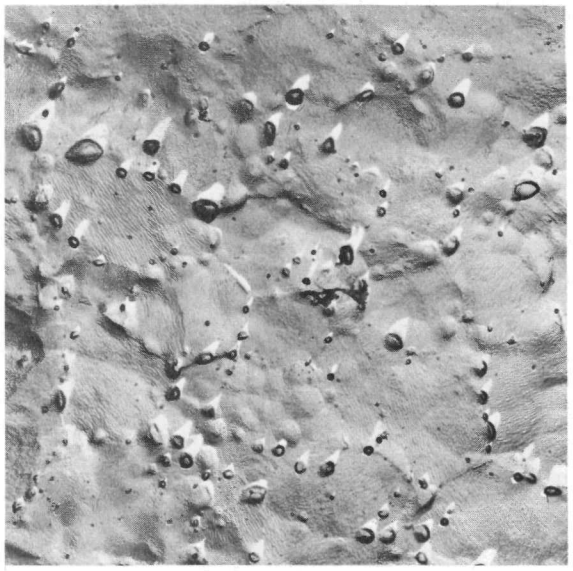
the more regularly shaped grains with pores on their boundaries were grains of recrystallized material, subgrains formed by recovery of the irradiated material, or grains present in the as-irradiated condition. This specimen decreased in density by 1.01%.

There was evidence of partial recrystallization in the microstructure of a specimen irradiated to 0.30 a/o burnup and annealed 30 min at 625°C (see Figure 8). The evidence for this is the shape of the grains and the different orientation within the neighboring grains of the striated structure which was produced by the cathodic etching (see Figure 8a). The diameters of the pores in this specimen ranged from 0.02 to 1.3 μ, and the largest pores were situated mostly on grain boundaries (see Figures 8a, 8b, and 8c). In those areas of Figure 8b which were relatively free from large-diameter pores, numerous pores with diameters between 0.02 and 0.06 μ were present (see Figure 8d). This specimen decreased in density by 2.28%.

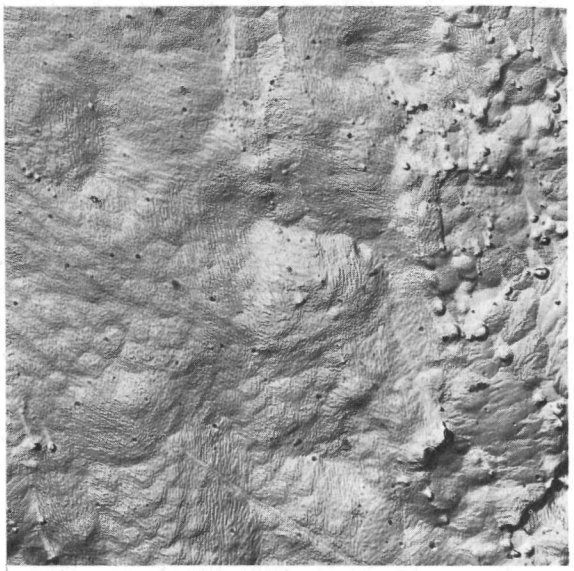
Specimens irradiated to 0.24 or 0.27 a/o burnup and annealed 75 hr at 618°C were determined, from measurements on photomicrographs of areas in which there were large diameter pores, to be about 75% recrystallized, and the diameter of the grains was approximately 6 μ (see Figures 9 and 10). The pores in these specimens had diameters between 0.02 and 2.5 μ, and the pores with the largest diameter were mostly located on grain boundaries. The number of pores was significantly reduced or were not present at all within the recrystallized grains (see Figures 9b and 10). In the unrecrystallized areas of Figures 9a and 9b, which were relatively free of large-diameter pores, the microstructure appeared similar to that shown in Figure 8d. Cracks were almost nonexistent in specimens annealed at 618°C or at lower temperatures. The decrease in density of specimens annealed 75 hr at 618°C was about 18%.

Microstructures after annealing at temperatures between 650°C and 750°C in the beta phase. Pores with diameters between 0.02 and 1.3 μ were uniformly distributed in the microstructures of specimens annealed between 650°C and 750°C in the beta phase (see Figures 11b and 12), and cracks were prevalent along grain boundaries (see Figure 11a). The pores adjacent to cracks or along grain boundaries did not appear to be substantially larger than the pores within the grains. The amount of grain boundary cracking did not appreciably increase on extending the annealing time from 30 min at 670°C to 75 hr at 740°C.

A specimen annealed at 651°C had a microstructure similar to specimens annealed at higher temperatures in the beta phase, even though for high-purity uranium this temperature is well within the alpha phase. Also, the specimen decreased in density in a manner similar to other specimens annealed at 700°C and 740°C (see Figure 1). The decrease in density of specimens annealed up to 75 hr at temperatures in the beta phase was about 5%.

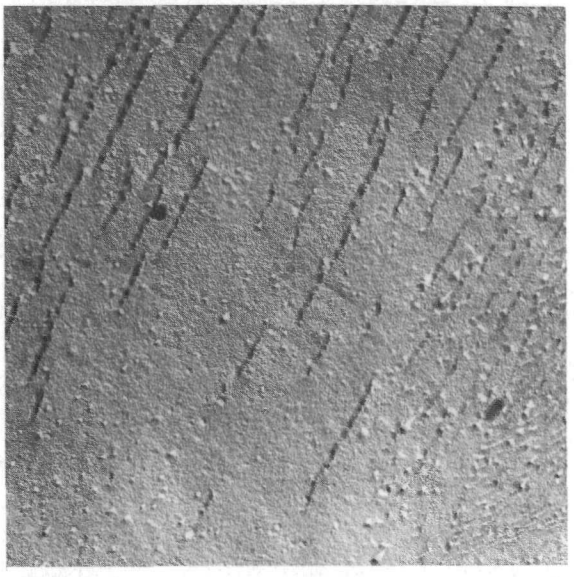


102860 Negative Replica 5200X
(a)



102864 Negative Replica 5200X
(b)

102861 Negative Replica 16,000X
(c)

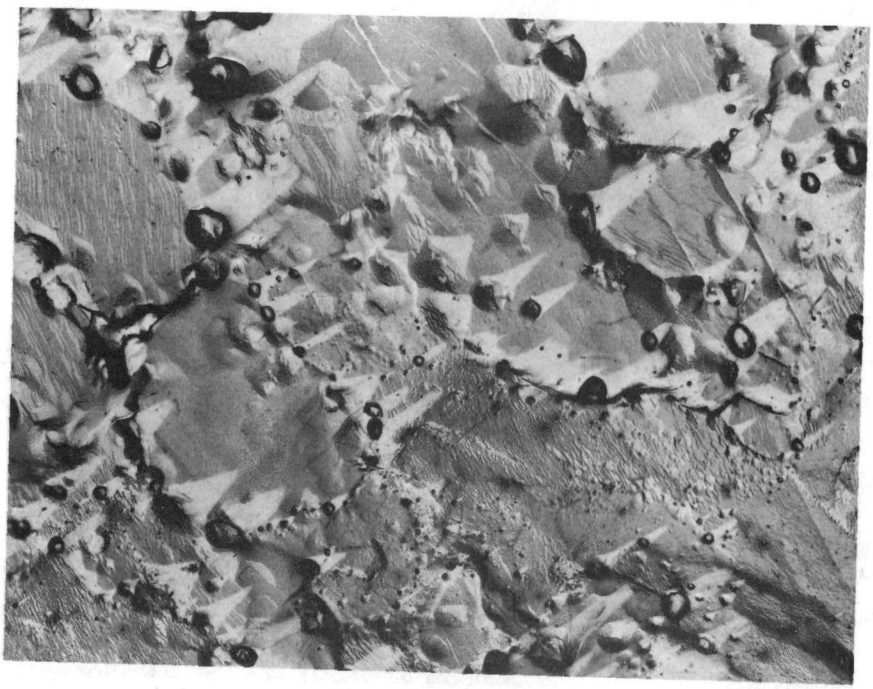


102349 Negative Replica 16,000X
(d)

Figure 8. Microstructures of Uranium Irradiated to 0.30 a/o Burnup and Annealed 30 min at 625°C

(a)

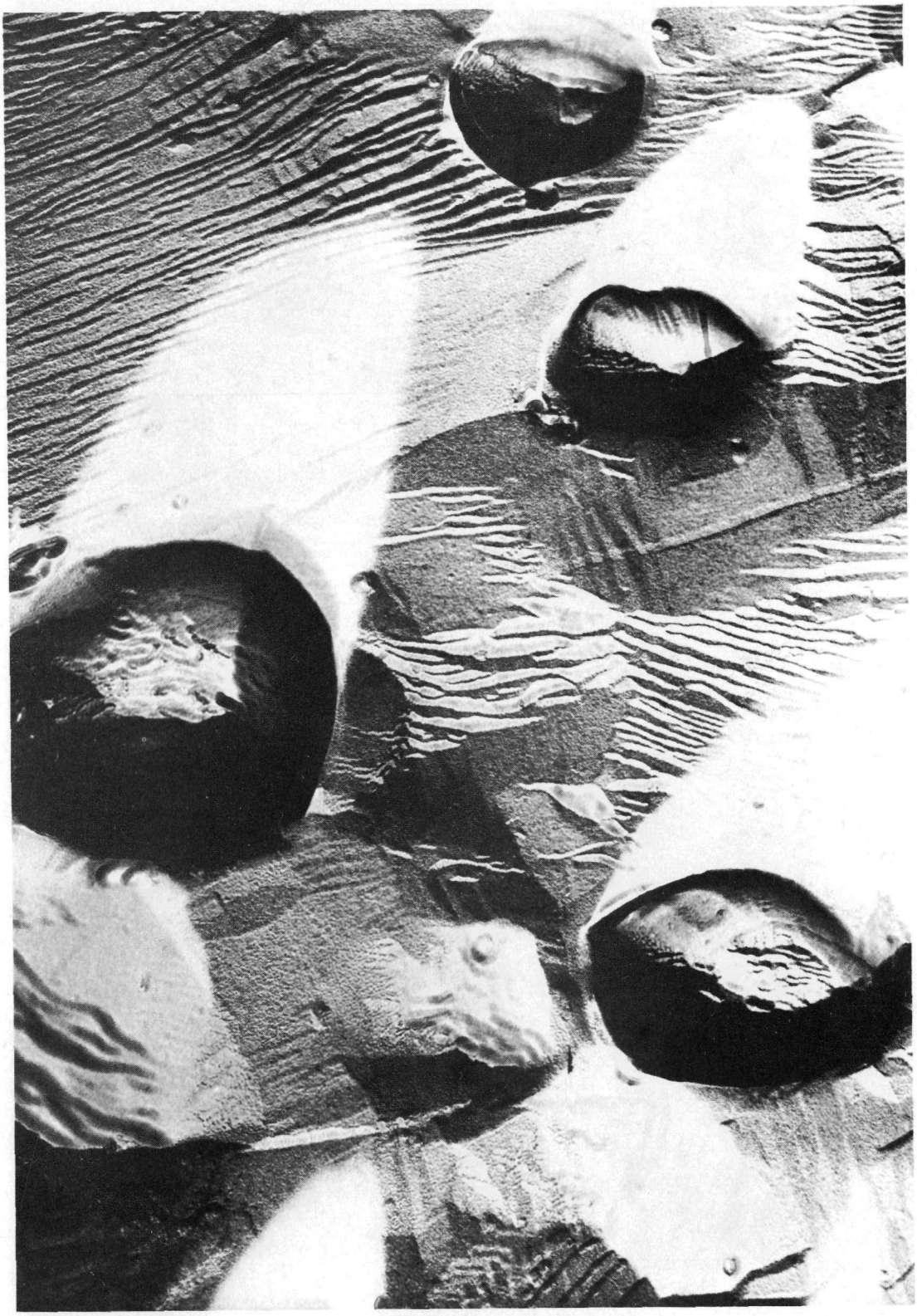
110492 Negative Replica 768X



(b)

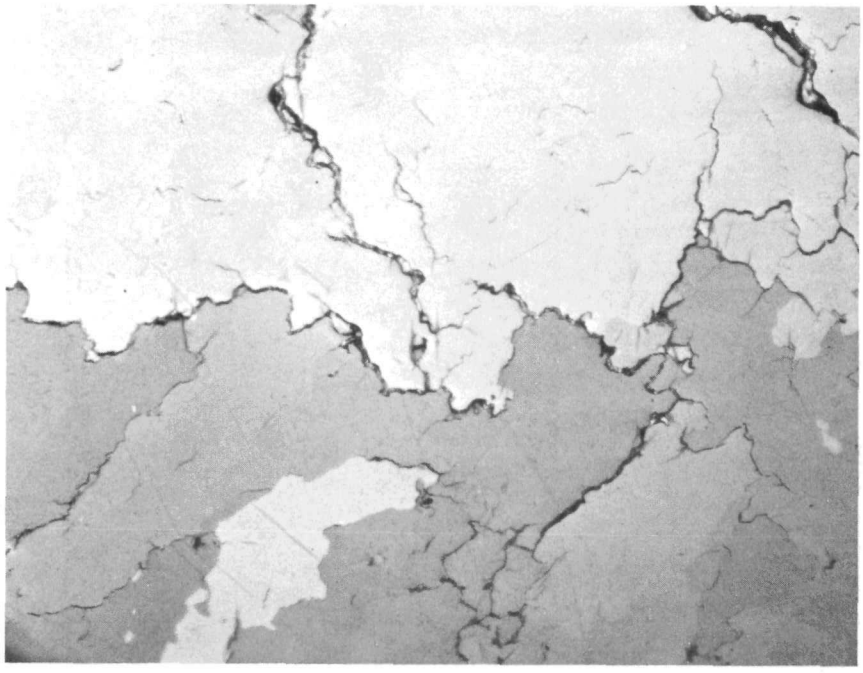
102406 Negative Replica 5200X

Figure 9. Microstructures of Uranium Irradiated to 0.24 a/o Burnup and Annealed 75 hr at 618°C



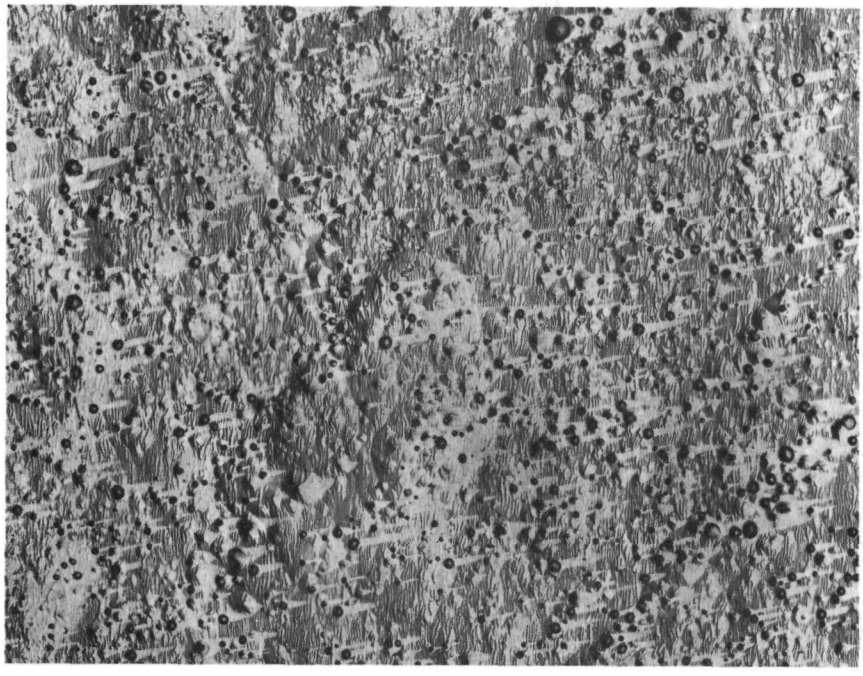
102359 Negative Replica 20,000X

Figure 10. Microstructure of Uranium Irradiated to 0.27 a/o Burnup and Annealed 75 hr at 618°C



(a)

33402 Polarized Light 100X



(b)

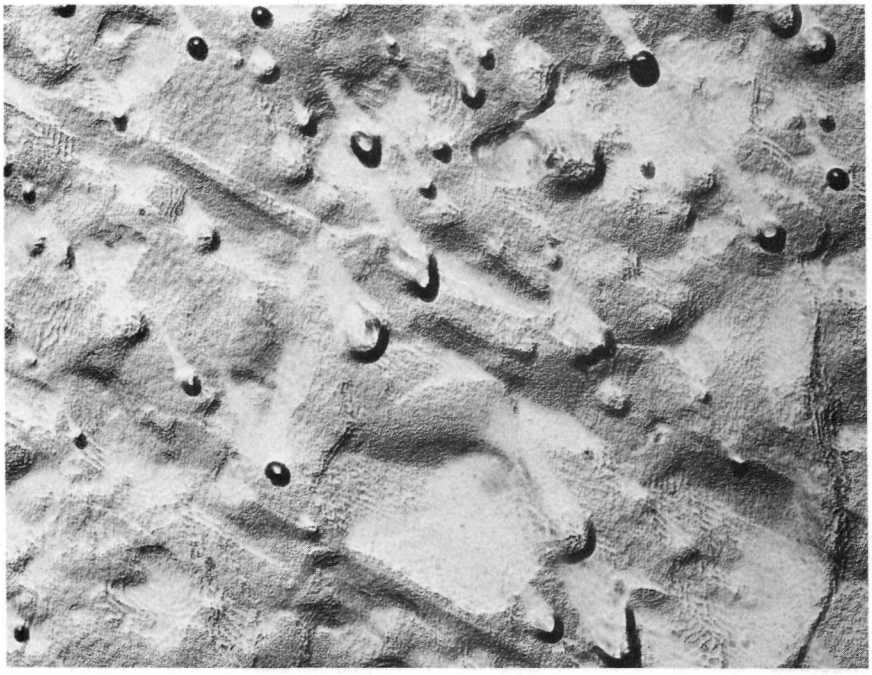
102355 Negative Replica 5200X

Figure 11. (a) Microstructure of Uranium Irradiated to 0.30 a/o Burnup and Annealed 30 min at 731°C.

(b) Microstructure of Uranium Irradiated to 0.28 a/o Burnup and Annealed 30 min at 670°C.

(a)

102868 Negative Replica 5200X



(b)

102866 Negative Replica 16,000X

Figure 12. Microstructures of Uranium Irradiated to 0.25 a/o Burnup and Annealed 75 hr at 740°C

Microstructures after annealing at temperatures in the gamma phase. Pores with diameters between 0.02 and 2.5 μ were present in the microstructure of a specimen irradiated to 0.31 a/o burnup and annealed 30 min at 860°C (see Figure 13). Areas about 2 μ in width and denuded of pores were observed to course through the microstructure. The configuration of these areas suggests that they are associated with grain boundaries in the gamma phase. Pores on one side of the denuded areas were more regularly spaced and generally larger in diameter than pores on the other side. The pores within the grains were uniformly distributed, and the diameters of the pores were about the same as those along the areas denuded of pores. The decrease in density of this specimen was 7.84%.

A specimen irradiated 0.24 a/o burnup and annealed 16 hr at 822°C contained large pores with diameters up to 21 μ arranged in a configuration which suggests that they are associated with grain boundaries in the gamma phase (see Figure 14). Many of the large pores along the grain boundaries joined to form elongated pores, and the pore diameter and interpore spacing generally decreased with distance from the grain boundaries. The areas along grain boundaries denuded of pores were not so well defined as in the specimen annealed 30 min at 860°C. There was some evidence of plastic deformation in the vicinity of the large pores on grain boundaries. Deformation twins appeared to emanate from these pores, and the matrix adjacent to the pores appeared deformed (see Figure 15). The plastic deformation of the uranium matrix may have resulted from cooling the specimen to ambient temperature. There were numerous cracks visible in the microstructure of this specimen, but cracking was not so extensive as in specimens annealed in the beta phase. The decrease in density of this specimen was 19.86%.

Sizes and distribution of pores. The effect of the different annealing treatments on the number and size of the pores was determined by examining approximately 10^3 pores in the microstructures of several specimens. The number of pores with diameters in exponentially increasing size ranges is presented for these specimens in Table II, and histograms for these data are presented in Figures 16 and 17.

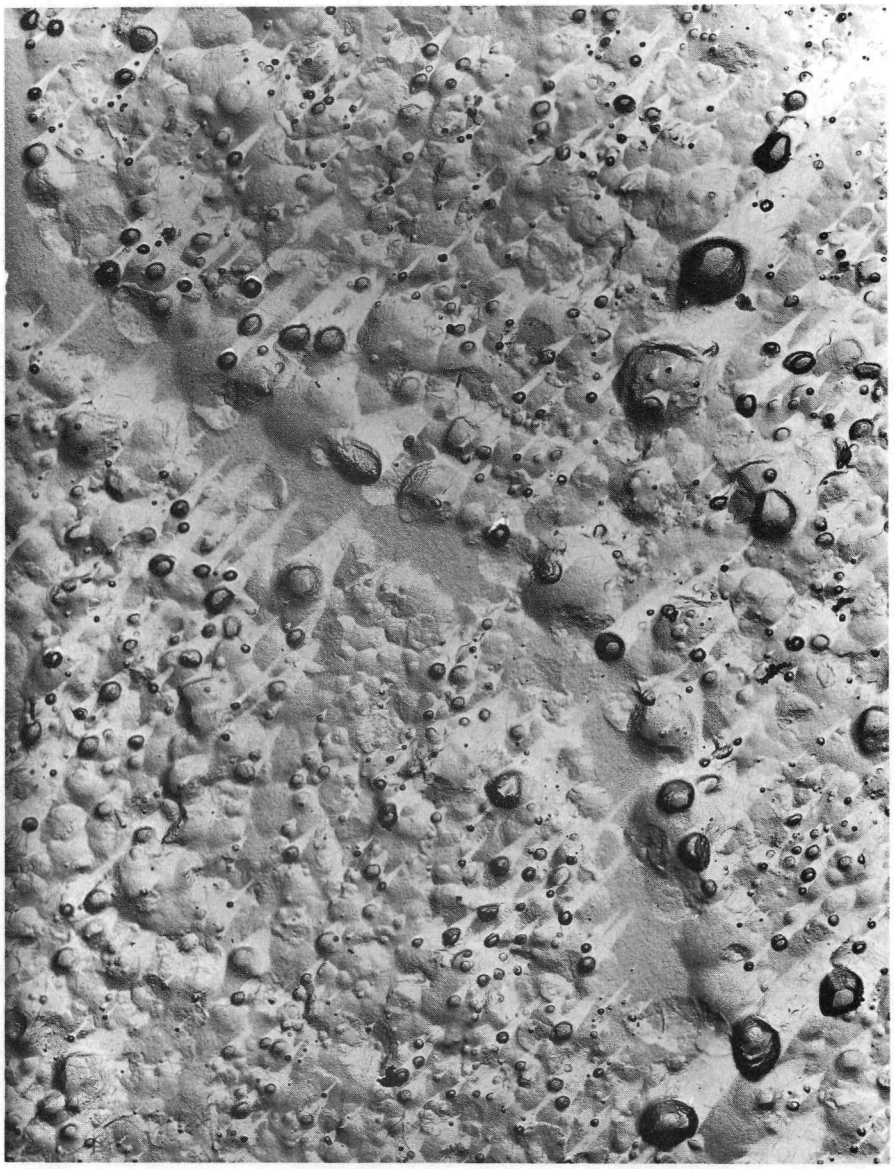
Table II

DISTRIBUTION OF POROSITY IN IRRADIATED AND ANNEALED URANIUM SPECIMENS

Specimen Heat Treatment	Number of Pores Per cm^2 in Given Size Ranges (μ)									$\Sigma\pi/(4n_i d_i^2)$* (%)	Density** Decrease (%)
	0.02 to 0.06	0.06 to 0.15	0.15 to 0.3	0.3 to 0.6	0.6 to 1.3	1.3 to 2.5	2.5 to 5.1	5.1 to 10.2	10.2 to 21.0		
30 min at 625°C	$\sim 1 \times 10^9$	2×10^7	1×10^7	5×10^6	6×10^5					3.1	2.28
75 hr at 618°C	$\sim 1 \times 10^9$	3×10^6	6×10^6	9×10^6	9×10^6	1×10^6				12.1	17.20
30 min at 670°C	$\sim 3 \times 10^7$	8×10^7	5×10^7	9×10^6	5×10^5					4.4	3.66
75 hr at 740°C	$\sim 1 \times 10^7$	5×10^7	5×10^7	1×10^7	2×10^6					5.4	4.53
30 min at 860°C	$\sim 3 \times 10^7$	4×10^7	5×10^7	2×10^7	2×10^6	5×10^5				8.3	7.84
16 hr at 822°C	$\sim 3 \times 10^7$	3×10^7	3×10^7	2×10^7	5×10^6	7×10^5	3×10^5	8×10^4	1×10^4	19.3	19.86

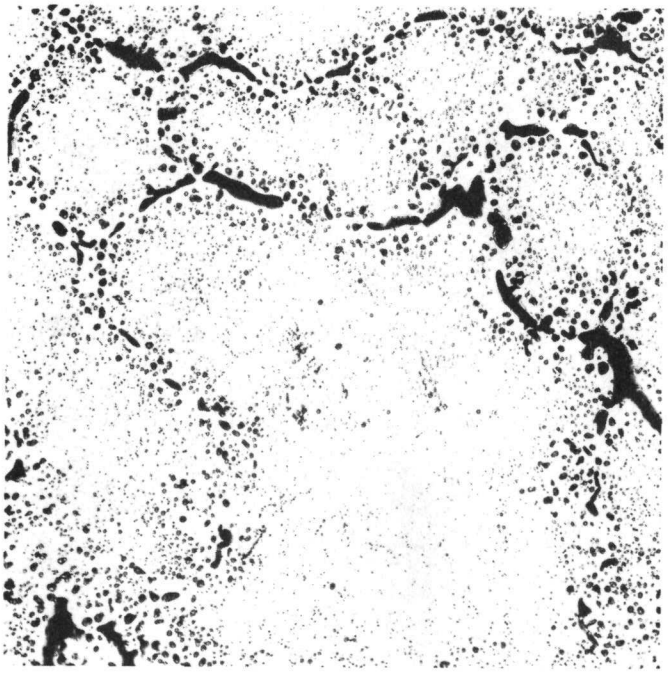
* The ratio of the change in density to the initial density = $\Sigma\pi/(4n_i d_i^2)$.

** The ratio of the change in density to the initial density as determined by the buoyancy technique.



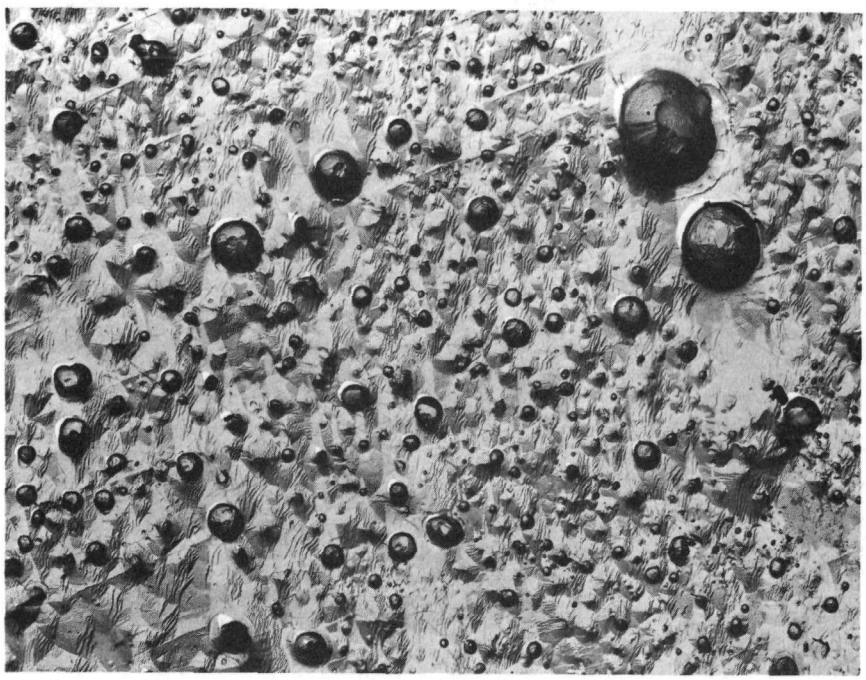
102458 Negative Replica 5200X

Figure 13. Microstructure of Uranium Irradiated to 0.31 a/o Burnup and Annealed 30 min at 860°C



(a)

33417 Bright Field 100X



(b)

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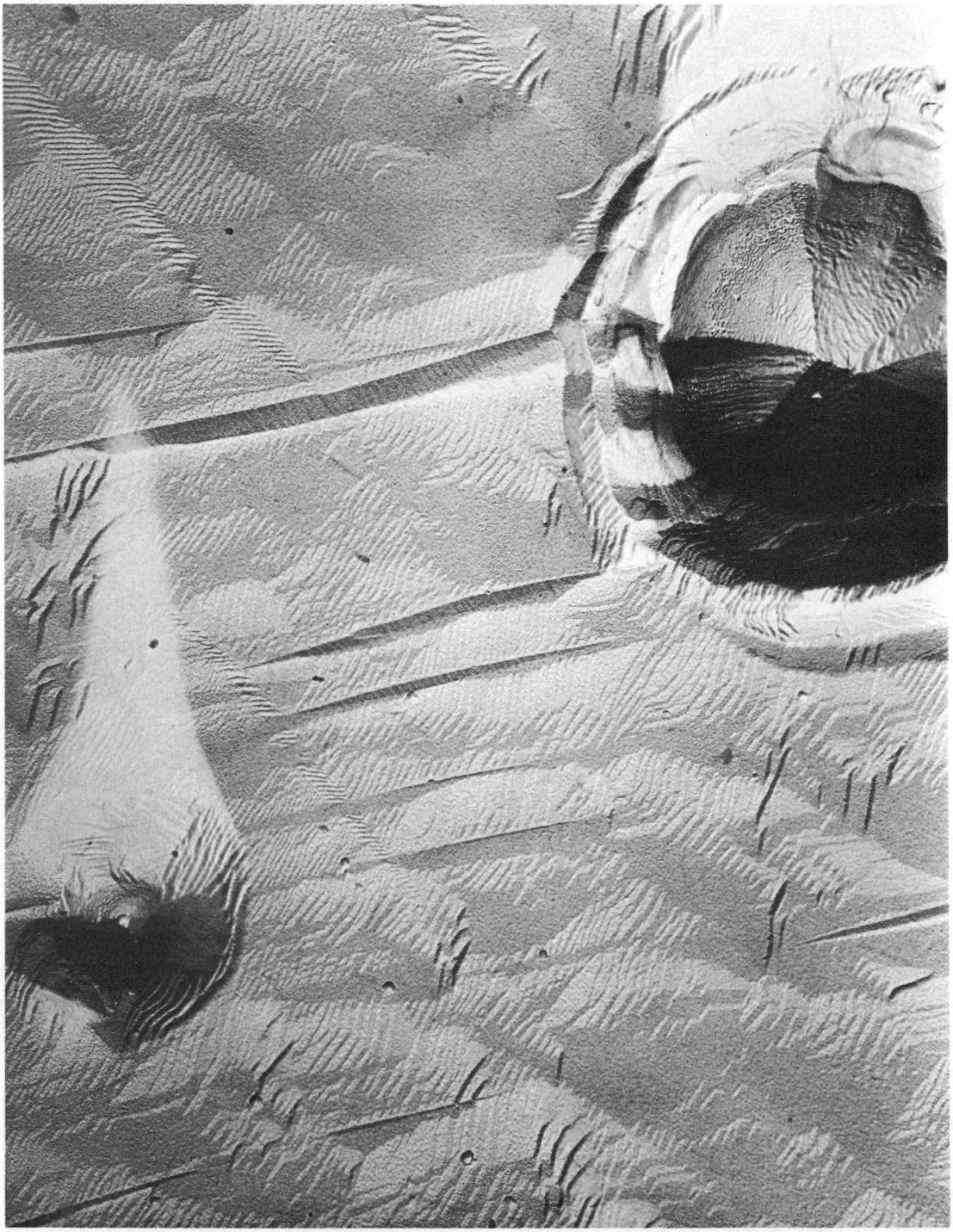
Figure 14. Microstructures of Uranium Irradiated to 0.24 a/o Burnup and Annealed 16 hr at 822°C



102469 Negative Replica 20,000X

Figure 15. Pores on Grain Boundary of Uranium Irradiated to 0.24 a/o Burnup and Annealed 16 hr at 822°C

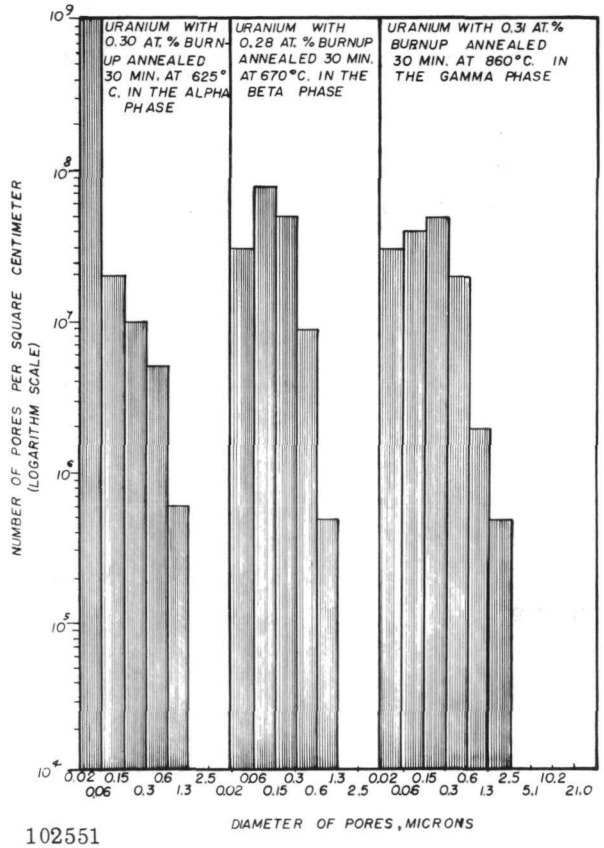


Figure 16. Histograms Showing Distribution of Porosity in Irradiated Uranium Specimens after Annealing 30 min at 625°C, 670°C, or 860°C.

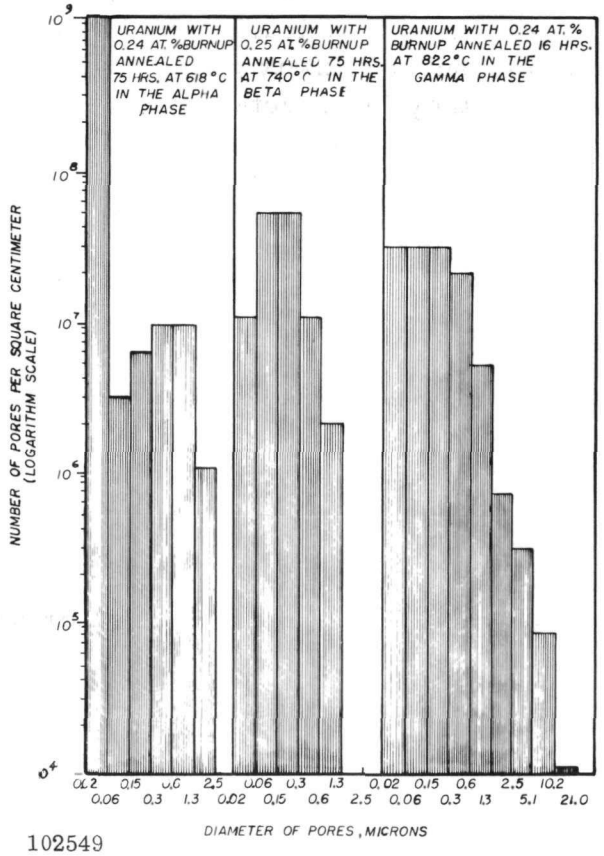


Figure 17. Histograms Showing Distribution of Porosity in Irradiated Uranium Specimens after Annealing for Extended Times at 618°C, 740°C, or 822°C

The total number of pores in specimens annealed in either the alpha, beta, or gamma phase did not decrease significantly on extending the annealing time from 30 min to 16 or 75 hr. However, the total number of pores in specimens annealed in the beta or gamma phase was about an order of magnitude less than when annealed in the alpha phase. Extension of the annealing times at temperatures in the alpha and gamma phase had the effect of extension of the size ranges to higher values; however, this was not the case on annealing in the beta phase. Thus, the diameter of the largest pores in specimens annealed about 620°C in the alpha phase increased from 1.3 μ to 2.5 μ on extending the annealing time from 30 min to 75 hr, whereas the largest pores in specimens annealed in the beta phase had a diameter about 1.3 μ regardless of the annealing time or temperature. The diameter of the largest pores in specimens annealed at temperatures in the gamma phase increased from 2.5 μ to 21 μ on extending the annealing time from 30 min at 860°C to 16 hr at 822°C.

The sizes and distributions of pores in the annealed specimens can also be used to calculate the volume changes and to compare these with the measured density changes. Since it was possible to observe bubbles only as they intersected a plane section, it was assumed that there were $N_1, N_2, \ldots N_i$ bubbles per unit volume of specimen with radii of $r_1, r_2, \ldots r_i$. The number of bubbles per unit volume of specimen was deduced from the number of pores per cm^2, n_i, observed in the microstructure by means of the equation[10]

$$N_i = n_i/2r_i \quad .$$

The pore diameters d_i observed in the microstructures were related to the true bubble radii r_i by[10]

$$r_i = \sqrt{3/8}\ d_i \quad .$$

The ratio of the volume increase of the specimens, ΔV, to the final specimen volume V_f (V_f = volume after annealing) is given by

$$\frac{\Delta V}{V_f} = \sum_i \frac{4\pi}{3} N_i r_i^3 \quad .$$

The ratio of the volume increase of the specimen to the final specimen volume is equivalent to the ratio of the decrease in density of the specimen, $\Delta\rho$, to the initial specimen density ρ_i (ρ_i = density before annealing). The substitution for N_i and r_i in terms of n_i and d_i yields the expression

$$\frac{\Delta V}{V_f} = \frac{\Delta\rho}{\rho_i} = \sum_i \frac{\pi}{4} n_i d_i^2 \quad .$$

This expression was evaluated for several annealed specimens, and the results are presented in Table II. The decrease in density calculated from the distribution of the number and sizes of pores observed in the specimens agrees reasonably well with the density decrease determined experimentally, considering the very large number of pores to be counted to obtain representative distributions, the lack of direct observation of true bubble sizes, the nonuniform distribution of porosity in localized areas, and the difficulty in measuring nonspherical pores.

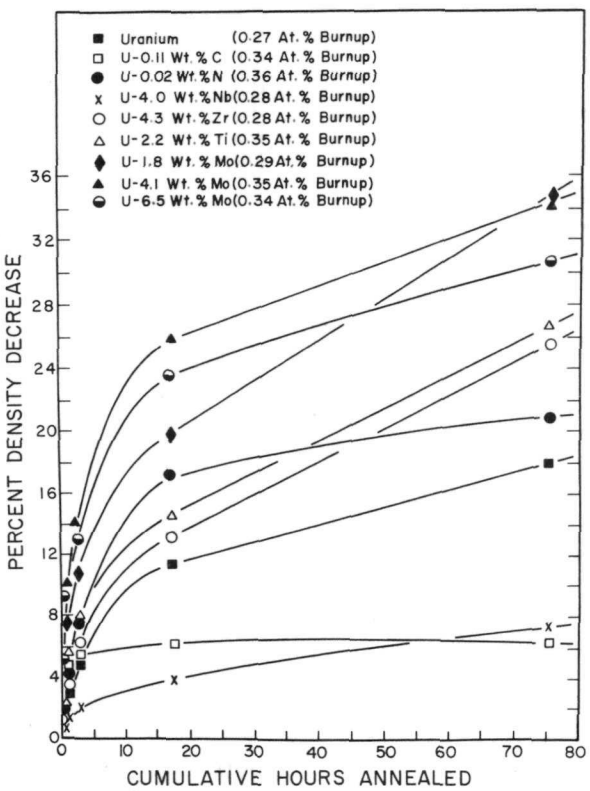
The sizes and distributions of pores were approximately the same at the center and near the surface of the specimens.

Fission gas release. No detectable amount of radioactive fission gas was evolved from specimens of irradiated uranium or uranium alloy during annealing. Since approximately 10^{-6} cc of Kr^{85} per cc of specimen

could be detected with the apparatus, the volume of krypton and xenon gas released from the specimens at annealing temperatures up to 860°C was probably less than 10^{-4} cc per cc of specimen.(9)

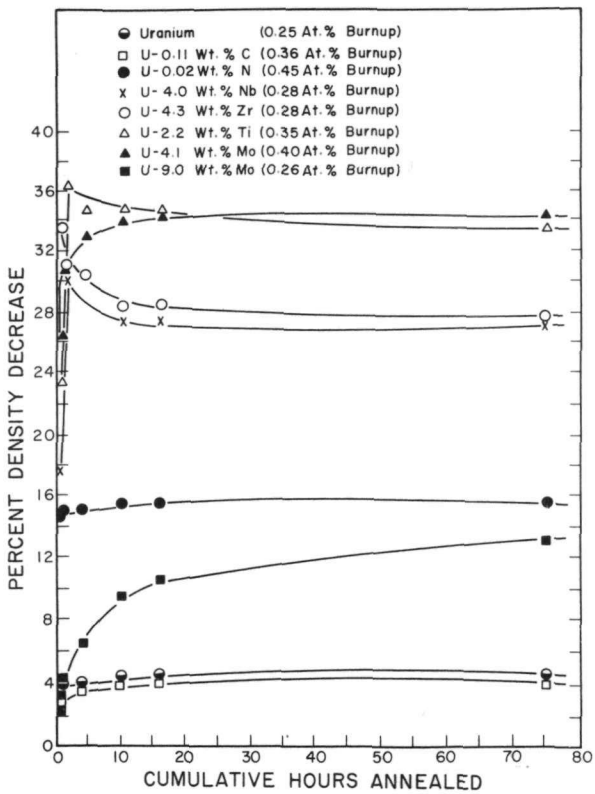
Swelling of Uranium Alloys

Density measurements. The density decrease of several uranium alloys on annealing up to 75 hr at 618°C and 740°C is shown in Figures 18 and 19, respectively. Each curve represents the cumulative density decrease of a single specimen, and each point on a curve represents the total cumulative time that the specimen was at the indicated temperature. The density decrease of an unalloyed uranium specimen is included for comparison.



34114

Figure 18. Effect of Annealing at 618°C on the Swelling of Irradiated Uranium Alloys



34115

Figure 19. Effect of Annealing at 740°C on the Swelling of Irradiated Uranium Alloys

The swelling behavior of U-6.5 w/o Mo alloy specimens irradiated to 0.19, 0.35, 0.48, and 0.73 a/o burnup is shown in Figure 20. Each curve represents the cumulative density decrease of a single specimen on annealing for 30 min at successively higher temperatures.

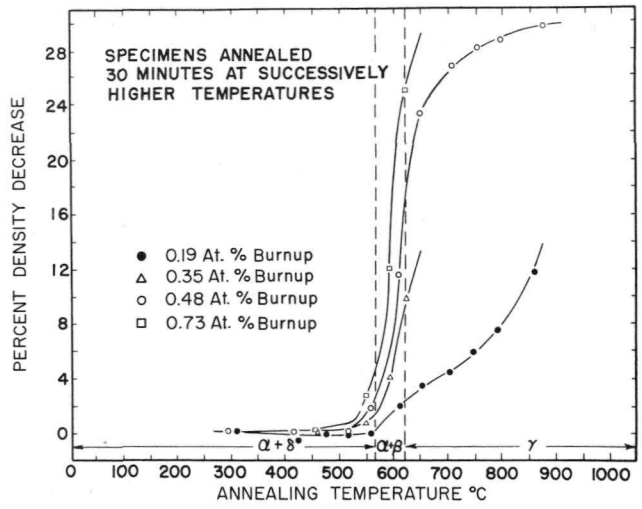


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Figure 20

Effect of Annealing Temperature on the Swelling of Irradiated U-6.5 w/o Mo Alloy Specimens with Different Burnups

Alloying with metallic elements apparently resulted in increased swelling. An exception was the behavior of the U-4.0 w/o Nb alloy at 618°C. The effect of nitrogen was small at 618°C, but it substantially increased the swelling at 740°C. Carbon, on the other hand, substantially decreased the swelling at 618°C, but had only a slight effect at 740°C. The major amount of swelling occurred within the first 15 hr of annealing.

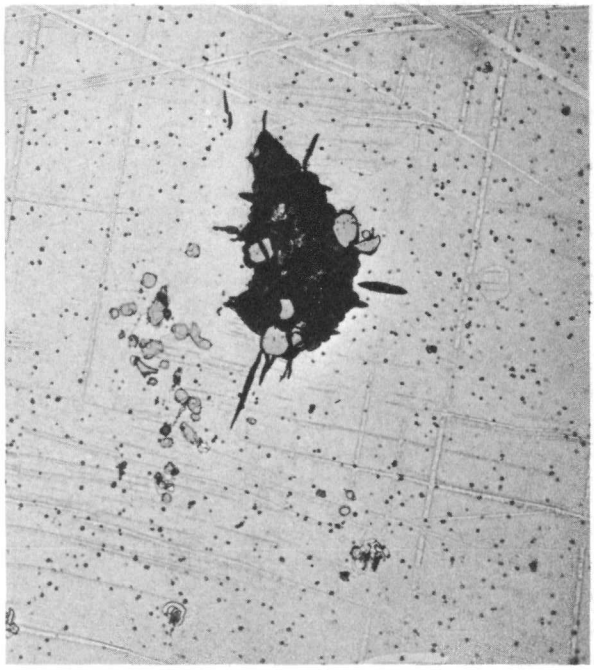
Microstructures before irradiation. The microstructures of the uranium alloys before irradiation are shown in Figures 21, 22, and 23. The microstructures of the alloys after irradiation were not examined.

DISCUSSION OF RESULTS

High-purity Uranium

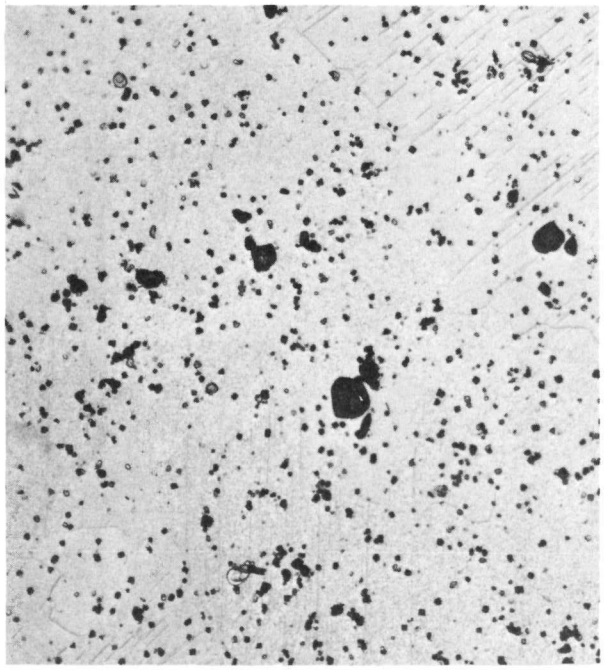
Annealing in alpha phase. The significant aspect of the swelling behavior in the alpha phase of uranium is the sharp rise in swelling as the annealing temperature is raised above about 550°C. Below this temperature, 75 hr of annealing produced a density decrease of 1% or less, whereas at 618°C density decreases of about 18% were observed. In this latter respect the results differ from those of Pugh,[2] who reports swelling only of the order of 1% on annealing in the alpha phase. Bierlein, Leggett, Mastel, and Weber,[11] however, likewise report that the density decreases appreciably on annealing at 600°C.

The pronounced increase in swelling at about 600°C is associated with the presence of numerous bubbles with diameters up to 2.5 μ. Bubbles with the largest diameters were noted to form in areas which had recrystallized to produce grains with diameters of about 6 μ, and the bubbles were observed to be located mostly on grain boundaries. These observations suggest that recrystallization is a necessary prerequisite for



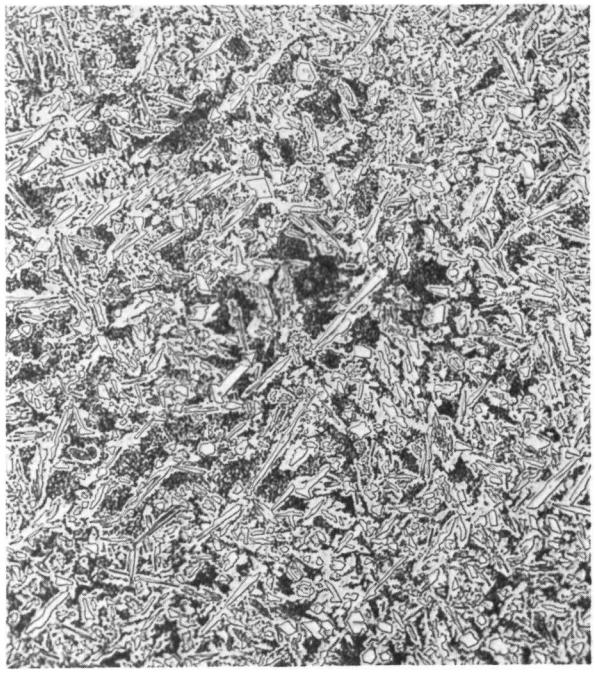
34616 Bright Field 250X

(a)



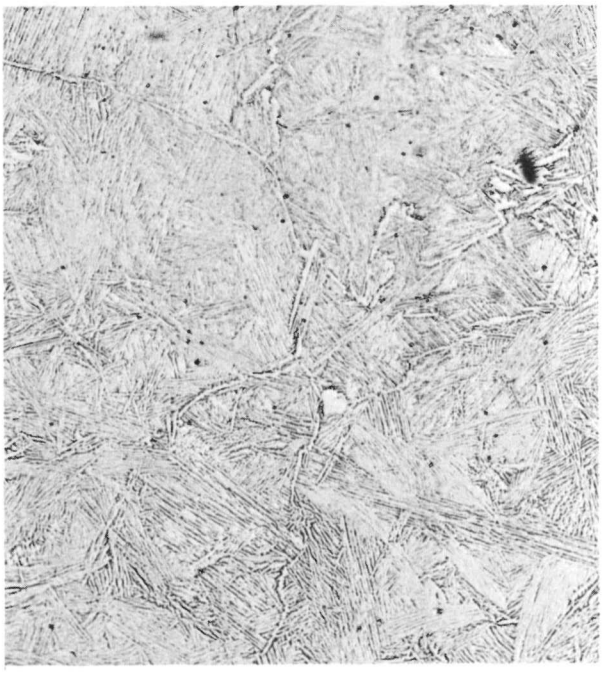
34615 Bright Field 250X

(b)



25704 Bright Field 250X

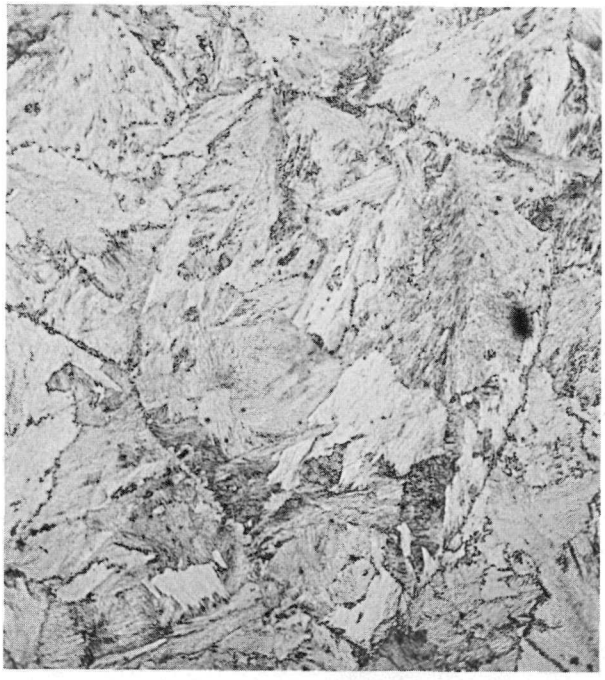
(c)



25718 Bright Field 250X

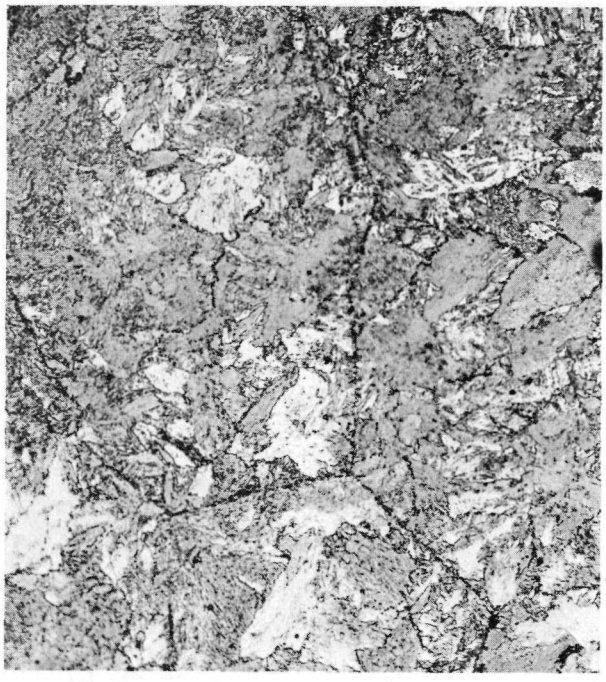
(d)

Figure 21. Microstructures of (a) U-0.02 w/o N, (b) U-0.11 w/o C, (c) U-2.2 w/o Ti, and (d) U-1.8 w/o Mo Alloys before Irradiation



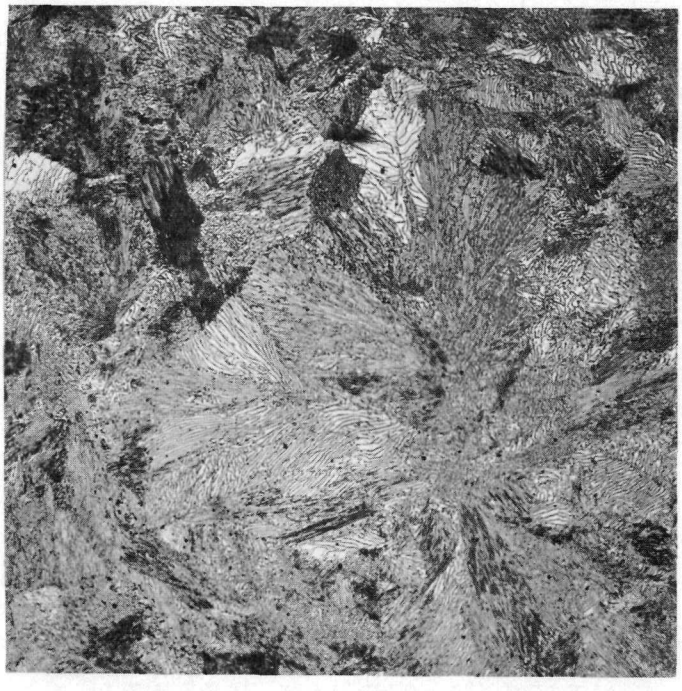
25706 Bright Field 250X

(a)



25708 Bright Field 250X

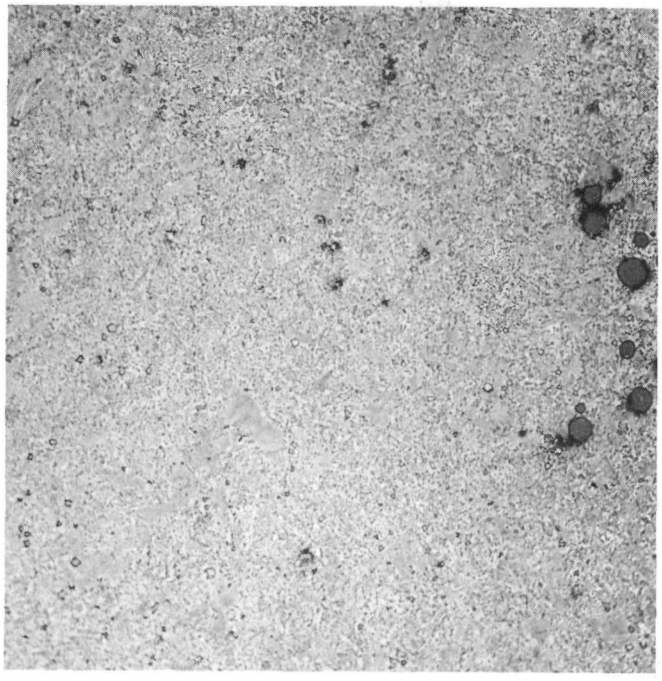
(b)



25710 Bright Field 250X

(c)

Figure 22. Microstructures of (a) U-4.1 w/o Mo, (b) U-6.5 w/o Mo, (c) U-9.0 w/o Mo Alloys before Irradiation



(a)

25714 Bright Field 250X

(b)

25712 Bright Field 250X

Figure 23. Microstructures of (a) U-4.0 w/o Nb and (b) U-4.3 w/o Zr Alloys before Irradiation

pronounced swelling to take place. Evidence for this is also provided by the observation that in unrecrystallized areas the majority of the pores had diameters of less than 0.1 μ. A recrystallized fine-grained structure has also been observed by Bierlein, Mastel, and Leggett[12] on annealing at 600°C.

The mechanism whereby the krypton and xenon fission product atoms change their relatively uniform distribution in the uranium matrix at some time during irradiation to a nonuniform distribution in the form of bubbles on grain boundaries during subsequent annealing is not altogether clear. The observation of the appearance of 0.02- to 0.06-μ pores with a concentration of about $10^{10}/cm^2$, which corresponds to the reported dislocation density in annealed uranium,[13] complied with the absence or significant reduction of porosity within recrystallized areas, which suggests the possibility of association of xenon and krypton atoms with dislocations during irradiation and their being subsequently swept to grain boundaries by the recrystallization and grain growth process.

The mechanism whereby the collection of gas atoms in microscopic bubbles on grain boundaries results in a macroscopic volume increase is also obscure. One possibility that suggests itself is that the volume increase proceeds by the deposition of uranium atoms at internal surfaces, i.e., grain boundaries. This could occur as a result of vacancies diffusing to existing gas-filled bubbles or some gas atom-vacancy complexes agglomerating at preferred sites on the grain boundaries. Greenwood[3] has shown from considerations of free energy that for vacancies to diffuse to a bubble the gas pressure in the bubble must be greater than the surface tension restraining pressure at the bubble/matrix interface. From the ideal gas law, the average gas pressure P_{av} in a bubble is given by

$$P_{av} \frac{(\Delta V)}{V_f} = qbT \quad ,$$

where q is a constant and b is the atomic per cent burnup. From the fission gas yield[9] the value of q was calculated to be 1.7×10^4 dynes cm^{-2} $(°K)^{-1}$ for one a/o burnup. The average surface tension restraining pressure P_r is given[14] as

$$P_r \sim 4\sqrt{2/3}\ \gamma \sum_i n_i d_i \Big/ \sum_i n_i d_i^2 \quad .$$

If for γ, the surface tension of the bubble/matrix interface, a value of approximately 10^3 dynes/cm[15] is used along with the data in Table II, the values of P_{av} and P_r for a specimen irradiated to 0.24 a/o burnup and annealed 75 hr at 618°C are 2×10^7 dynes/cm^2 and 1×10^8 dynes/cm^2, respectively. The corresponding values for a specimen irradiated to

0.30 a/o burnup and annealed for 30 min at 625°C are 2 x 10^8 dynes/cm^2 and 4 x 10^8 dynes/cm^2. Thus, the average gas pressure in the bubbles is less than the surface tension restraining pressure, and it is therefore difficult to see on the basis of Greenwood's concepts the reasons for vacancy migration to existing gas-filled bubbles. The suggested alternative of the formation of gas atom-vacancy complexes and their agglomeration at grain boundaries remains to be demonstrated.

If one assumes a relationship between swelling and recrystallization, as suggested by the microstructures, the decrease in the swelling rate with time can be readily interpreted in terms of the kinetics of the latter process. Similarly, it would also account for the observed effects of carbon additions, since uranium-carbon alloys have been reported to require higher temperatures for recrystallization.(16)

Annealing in the beta phase. The distribution of bubbles after annealing in the beta phase was not closely related to the presence of grain boundaries or other microstructural features, in contrast with specimens annealed at temperatures in the alpha phase. The bubbles were uniformly distributed and appeared to result from homogeneous nucleation and growth in the beta phase and/or the growth from pre-existing bubbles formed in the alpha phase on heating to the annealing temperature in the beta phase.

The most puzzling aspect of the swelling behavior in the beta phase is that the bubble size does not change appreciably on extended annealing. It is, perhaps, significant that, if one applies the same calculations as above, the average gas pressure in the bubbles is found to be slightly less than the surface tension restraining pressure. Under these conditions a driving force would not exist for vacancy diffusion to bubbles, but rather vacancies would tend to leave the bubbles.

Cracks were present along grain boundaries and were partly responsible for some of the swelling. Since no cracking occurred in specimens annealed in the alpha phase, it is estimated from the curve for the specimen with 0.29 a/o burnup in Figure 4 that cracks caused approximately a 1% decrease in density. The cracks probably formed as a result of the allotropic transformation stresses.

Annealing in the gamma phase. The presence of areas of approximately 2 μ in width and denuded of pores along the grain boundaries of a specimen annealed at 860°C might be explained by assuming that vacancies diffused from the grain boundaries to bubbles within the grains, and that uranium atoms were simultaneously deposited along the grain boundaries. Alternatively, the areas free of porosity could be due to the sweeping of small bubbles from these areas by movement of grain boundaries.

The large elongated pores observed in a specimen annealed for 16 hr at 822°C were evidently the result of bubbles joining up and were presumably situated on grain boundaries in the gamma phase. However, it is not certain whether the large bubbles adjacent to the grain boundaries are due to the diffusion of vacancies from the grain boundaries or to resolution of gas atoms from the smaller bubbles in favor of the growth of larger neighboring bubbles.[8] In either event, such a process did not occur to an appreciable extent within the grains.

CONCLUSIONS

1. Uranium irradiated between 0.24 and 0.30 a/o burnup at about 275°C swells and decreases in density on postirradiation annealing; the amount of swelling does not increase proportionally with increasing annealing temperatures.

2. The swelling rises sharply when the annealing temperature exceeds about 550°C; it is proposed that this is due to recrystallization and the formation of enlarged pores on grain boundaries.

3. The extent of swelling is dependent on the allotropic structure. Annealing in the beta tetragonal phase causes less swelling than annealing at high temperatures in the alpha orthorhombic phase or in the gamma cubic phase.

4. The rate of swelling is highest during the first few hours of annealing. In the case of specimens annealed in the beta phase, the rate of swelling decreases to the extent that after the first 3 hr of annealing the density decreases less than 1% on further annealing up to 75 hr.

5. Uranium alloys containing between 1 w/o and 9 w/o of either molybdenum, titanium, zirconium, or niobium generally swelled more than pure uranium on annealing up to 75 hr at 618°C or 740°C. The exception to this behavior was a U-4.0 w/o Nb alloy annealed at 618°C.

6. The alloying of pure uranium with 0.11 w/o C caused an appreciable reduction in swelling on postirradiation annealing at 618°C, but the effect of this amount of carbon was small in reducing the swelling at 740°C.

7. The alloying of pure uranium with 0.02 w/o N resulted in an appreciable increase in the swelling of uranium on postirradiation annealing at 740°C, but the effect was small on annealing at 618°C.

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