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OXIDATION PROPERTIES OF TWO URANIUM ALLOYS
(U-16.6 At % Nb-5.6 At % Zr and U-21 At % Nb)

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UNION CARBIDE CORPORATION
NUCLEAR DIVISION
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ABSTRACT

The fundamental oxidation characteristics of two uranium-base alloys (U-16.6 at % Nb-5.6 at % Zr and U-21 at % Nb) in the temperature range from 500 to 1,000° C in oxygen at 0.05 torr have been determined. Both alloys undergo large dimensional changes during oxidation at temperatures above 650° C due to stresses generated in the oxide during oxidation. Stresses estimated at one million psi are shown to develop in the oxidizing specimens. A mechanism for the generation of these stresses has been proposed.

CONTENTS

SUMMARY	7
INTRODUCTION	8
OXIDATION BEHAVIOR OF TWO URANIUM ALLOYS	9
Experimental Procedures	9
Surface Area Increase	9
Oxidation-Rate Measurements	11
Hot-Stage Microscopy	14
Oxide Morphology	16
Marker Experiments	19
Identity of the Oxide Phases	24
Mechanism of Stress Generation	28
Magnitude of the Stress Developed in the Oxide	29
Effect of Oxygen Pressure on Flexure	32
CONCLUSIONS	34
REFERENCES	35
ACKNOWLEDGEMENTS	37

SUMMARY

The fundamental oxidation characteristics of two uranium-base alloys (U-16.6 at % Nb-5.6 at % Zr and U-21 at % Nb) in the temperature range from 500 to 1,000° C in oxygen at 0.05 torr have been determined. Both alloys undergo large dimensional changes during oxidation at temperatures above 650° C due to stresses generated in the oxide during oxidation. Oxidation-rate curves for both alloys were determined at 100-degree intervals between 500 and 1,000° C. The activation energy for the process is shown to be small. The morphology of the oxide scale formed on the two alloys was found to be complex. Stresses estimated at one million psi are shown to develop in the oxidizing specimens. A mechanism for the generation of these stresses has been proposed.

INTRODUCTION

Knowledge was needed concerning the fundamental oxidation characteristics of two uranium-base alloys (nominal compositions: U-16.6 at % Nb-5.6 at % Zr and U-21 at % Nb) in the temperature range from 500 to 1,000° C in oxygen at a pressure of 0.05 torr. The oxidation process for the two alloys is quite involved and is illustrative, in many instances in exaggerated fashion, of many of the factors important to the oxidation of alloys generally. For example, the oxide scale is multiphased and the oxide morphology intricate. A complex interrelationship exists between this morphology, the mode of material transport across the film, and the extraordinarily large stresses which develop in the oxidizing specimens. These stresses, in turn, produce very large changes in the linear dimensions of the specimens. The mechanical properties of both oxide scale and substrate metal appear to have an important role in the oxidation mechanism. Thus, the results reported here bear not only on the oxidation processes for uranium-base alloys, but may be of general interest as well.

Both of these alloys are body-centered-cubic (bcc) at high temperatures. At 634 and 650° C, respectively, the binary and ternary alloys undergo a monotectoid transformation to a two-phase system consisting of a nearly pure α uranium (orthorhombic) and a niobium-rich phase designated as γ_3 .⁽¹⁾ Both alloys, however, may be quenched to room temperature in the bcc form. They then reach the equilibrium $\alpha + \gamma_3$ structure, upon suitable annealing, through a complicated series of transition phases.^(2,3) This study is concerned with the effects of these transformations only in the case of experiments performed at 500 to 600° C.

OXIDATION BEHAVIOR OF TWO URANIUM ALLOYS

EXPERIMENTAL PROCEDURES

Test specimens were usually in the form of coupons (1 cm W x 2 cms L x 0.05 cm T), although cylindrical specimens 0.5 centimeter in diameter and 0.75 centimeter long were used in the hot-stage microscope studies. Unless otherwise noted, the specimens were annealed in vacuum for one hour at 800° C, quenched in water to room temperature, and then mechanically polished and electro-polished in either concentrated phosphoric acid or a six volume percent solution of perchloric acid in methanol cooled to dry ice temperatures. The current density in both baths was approximately 0.1 ampere per square centimeter.

A gravimetric technique was used to measure the oxidation rate of the alloys between 500 and 1,000° C. A sensitive spring made of SAE Type 1095 piano wire served to measure the weight changes. The spring, which consisted of 48 turns, was fabricated by winding the wire around a graphite mandrel and annealing it in argon for two hours at 840° C. After a water quench from the annealing temperature, the spring was tempered for four hours at 370° C. The resulting spring constant was 20.8 milligrams per centimeter, which made it possible to detect oxide thickness changes of about 0.1 micron on the specimens when using a cathetometer with a sensitivity of 10 microns.

The spring assembly was enclosed in a tubular oxidation apparatus in which the atmosphere could be controlled. The upper portion of the apparatus contained the spring and was made of water-jacketed glass tube, the water serving to stabilize the temperature of the spring. The lower part of the apparatus, which contained the specimen, was made of Mullite and was separated from the rest of the system by a slotted heat baffle. Purified oxygen was admitted to the system through a controlled leak. Proper adjustment of the leak in conjunction with the operation of a mechanical vacuum pump made it possible to maintain a constant flow of oxygen through a system at a pressure of 0.05 torr.

SURFACE AREA INCREASE

A striking feature of the oxidation of the ternary alloy between 700 and 1,000° C was the very large increase in the surface area of the unoxidized portion of the metal which occurred during oxidation. Figure 1 presents a view of a standard unoxidized specimen next to a specimen oxidized for three hours at 800° C. During this period of time, only about 15 percent of the specimen was converted to oxide, yet there is a very obvious increase in the lateral dimensions of the oxidized specimen as well as the extensive bending and distortion which occurred.

Y-101054

Figure 1. COUPONS OF THE URANIUM-NIOBIUM-ZIRCONIUM ALLOY SHOWING THE DIMENSIONAL CHANGES PRODUCED BY OXIDATION.

As indicated by the graph of Figure 2, where the relative area increase is plotted as a function of the oxidation time, the gross surface area of a specimen such as this doubled in six hours of oxidation at this temperature.

This area increase was very much a function of the specimen geometry. The data shown in Figure 2 are for the standard coupon specimens. For the cylindrical specimens described previously, however, there was almost no change in the overall dimensions during oxidation. Nevertheless, the existence of large surface stresses in the specimen is suggested by the "earing" of the edges of the specimen, as illustrated in Figure 3, which shows a cylindrical specimen in cross section. The specimen was used as a sample on a hot-stage microscope and was originally a right cylinder with a small shoulder machined at the bottom in order to fit the sample onto the microscope stage. Similar earing was also evident at the edges of the "sheet" specimens.

This phenomenon was observed only when the specimens were oxidized at temperatures in the single-phase γ region of the phase diagram. For example, a specimen oxidized at 650°C (just above the transition temperature for the ternary alloy) exhibited earing very similar to that shown in Figure 3. At 625°C (just below the transformation temperature) no such earing occurred.

Surprisingly, the uranium-niobium alloy exhibited only a comparatively small increase in surface area. Increases of only 10 - 15 percent were noted after several hours of oxidation at $700 - 1,000^{\circ}\text{C}$, despite the fact that the total thickness of oxide formed was comparable to that on the ternary specimens.

The occurrence of large dimensional changes in the metal specimens during oxidation is an unusual phenomenon, but it has been observed previously. Phalnikar and Baldwin⁽⁴⁾ reported area increases on the order of twice that of the original specimen for zirconium specimens oxidized at 800 and 900° C. More recently, Rhines and Wolf⁽⁵⁾ observed a much smaller, but still measurable, change in the dimensions of oxidizing nickel samples.

Different stress-generating mechanisms were proposed in the two cases just cited, and still a third will be proposed for the uranium alloys. Regardless of the validity of any of these mechanistic proposals, however, it should be obvious that the magnitude of the observed dimensional changes is, in itself, *prima facie* evidence for the generation of very large stresses during the oxidation of these specimens.

OXIDATION-RATE MEASUREMENTS

A representative set of oxidation rate data for the ternary alloy obtained at 800° C and 0.05 torr oxygen pressure is given in Figure 4. The oxide-thickness values used in the upper curve were calculated on the basis of oxygen consumption per square centimeter of the original specimen surface area; for the lower curve, the points have been corrected for the surface area increase which

Figure 2. RELATIVE AREA INCREASE OF STANDARD COUPON SPECIMENS OF THE URANIUM-NIOBIUM-ZIRCONIUM ALLOY DURING OXIDATION AT 800° C IN OXYGEN AT 0.05 TORR AS A FUNCTION OF TIME.

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Figure 3. CROSS SECTION THROUGH A CYLINDRICAL URANIUM-NIOBIUM-ZIRCONIUM ALLOY SPECIMEN THAT HAS BEEN OXIDIZED FOR FOUR HOURS AT 800° C IN AIR AT 0.5 TORR. (Note the "Extrusion" of Metal which has Occurred around the Edges of the Specimen; 12X)

occurred as oxidation proceeded (see Figure 2). Thus, the corrected curve shows oxygen consumption per unit of the "instantaneous" surface area of the specimen.

Typical rate curves for the ternary and binary alloys are seen in Figures 5 and 6, respectively, for temperatures between 500 and 1,000° C. The oxygen pressure was again 0.05 torr; and, in all cases, the data have been corrected for the surface area increase described for the curve of Figure 4.

The oxidation rates for both alloys at 500 and 600° C, and at 700° C as well as for the binary, are obviously out of line with those observed at higher temperatures. It is believed that this effect is related to the phase transformations which occur in this temperature range. As noted previously, the equilibrium structure of both alloys below about 650° C is a two-phase system consisting of an α -uranium phase plus a bcc niobium-rich phase. Within the time required to bring the specimen furnace to temperature (about 2 hrs) a considerable fraction of the alloy is transformed, yielding a feathery "pearlitic" structure similar

Figure 4. OXIDATION RATE CURVE FOR THE URANIUM-NIOBIUM-ZIRCONIUM ALLOY AT 800° C AND IN OXYGEN AT 0.05 TORR.

to that shown in Figure 7. The dark areas of Figure 7 represent transformed regions in the specimen. Note the pearlite-like structure in these regions. The dark color of the uranium-rich phase (α phase) results from the layer of superficial oxide which forms readily at room temperature. The α phase has much less resistance to oxidation than the original alloy.⁽⁶⁾ This fact undoubtedly accounts for the relatively high rates of oxidation observed for both alloys at 500 and 600° C.

The equilibrium form for the binary alloy at 700° C is also a two-phase system.⁽¹⁾ Both phases are bcc, one being uranium rich and the other niobium rich. Again, it is assumed that it is this phase transformation which alters the oxidation characteristics of the alloy in comparison to its behavior at higher temperatures.

Considering only those data taken above the transformation temperatures for the two alloys, inspection of Figures 5 and 6 shows immediately that the oxidation-rate curves are only approximately linear even on a log-log plot. Nonetheless, it is possible to fit the data reasonably well to a rate equation of the form $x = kt^{(1/n)}$, where x is the quantity of oxygen consumed per square centimeter

Figure 5. TYPICAL OXIDATION-RATE CURVES FOR THE URANIUM-NIOBIUM-ZIRCONIUM ALLOY IN OXYGEN AT 0.05 TORR AND IN THE TEMPERATURE RANGE FROM 500 TO 1,000° C.

of specimen surface in time, t ; n and k are constants. In the temperature ranges from 800 to 1,000° C and 700 to 1,000° C for the binary and ternary alloys, respectively, values of n between 1.6 and 1.8 were obtained. Adopting an average n value of 1.7, rate constants were computed for oxidation in these temperature ranges, thus making possible the calculation of an activation energy for the oxidation process. Values of about 15 kcal/mol were obtained for both alloys.

Given the complexity of the oxidation process for these alloys and the assumptions used in obtaining the rate constants, the value cited for the activation energy should be considered only an approximation. It is clear, however, that the activation energy is remarkably small. This fact suggests the importance of short-circuit diffusion modes in material transport processes across the oxide; and, as will be seen later, the morphology of the oxide strongly supports such an idea.

HOT-STAGE MICROSCOPY

A specimen of the ternary alloy was oxidized at 800° C in air at a pressure of 0.5 torr on the stage of a Reichert hot-stage microscope, Model Me F. The specimen, shown in cross section in Figure 3, was a 3/8-inch-diameter by 1/2-inch-high cylinder. A mechanical vacuum pump was attached to the oxidation

chamber, and the pressure in the chamber was regulated through the adjustment of a variable leak valve.

Evidence of stress generation during oxidation was very apparent. Severe roughening of the specimen surface was observed. After 20 minutes of oxidation, cracks could be seen to propagate through the oxide, and these cracks widened and deepened as the oxidation proceeded.

These observations are significant, chiefly for what they imply concerning the distribution of stresses in the oxide. The net stress in the oxide is compressive; yet, within a short time after the beginning of oxidation, the oxide at the gas/oxide interface comes under a sufficiently large tensile stress to cause cracking to occur. Evidently, only a fraction of the oxide is actually under compression, and any estimates of the magnitude of that stress based on an average stress in the oxide will be conservative.

Figure 6. TYPICAL OXIDATION-RATE CURVES FOR THE URANIUM-NIOBIUM ALLOY IN OXYGEN AT 0.05 TORR AND IN THE TEMPERATURE RANGE FROM 500 TO 1,000°C.

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Figure 7. CROSS SECTION THROUGH A URANIUM-NIOBIUM ALLOY SPECIMEN THAT HAD BEEN ANNEALED FOR FOUR HOURS AT 500° C. (1,000X)

OXIDE MORPHOLOGY

The morphology of the oxide formed on both alloys is quite complex, and a variety of techniques were used to characterize it. Figures 8 and 9 show cross sections through the oxide on the ternary and binary alloys, respectively. Both specimens were oxidized at 800° C in oxygen at 0.05 torr—the former for six hours and the latter for 14 hours. Note that the scale on the ternary alloy consists of two layers. The outer portion is relatively homogeneous and heavily cracked; the inner layer, on the other hand, is comparatively compact. The few cracks in it may well have formed on cooling. This inner layer contains two phases, a gray phase which is the uranium dioxide and "stringers" of a metal-like phase whose probable identity will be discussed later. This structure is illustrated in Figure 10. Although a binary alloy specimen (oxidized for 90 min at 1,100° C in oxygen at 0.05 torr) is shown in Figure 10, the morphology of its oxide is very similar to that for the ternary near the oxide/metal interface.

The oxide on the binary differs from that on the ternary alloy in that it is compact and almost crack free. However, it exhibits the same two-phase array

of oxide and metal-like stringers (Figure 9). This structure is best defined near the oxide/metal interface, but extends almost all the way to the outer surface of the oxide (see Figure 10). The stringers do tend to become more broken up and irregular as the gas/oxide interface is approached, and frequently a narrow band free of stringers may be observed at the oxide/gas interface. Oxidation at the lower temperatures resulted in stringers which were shorter, narrower, and less regular than those shown in Figure 10; however, this basic structure was always present. The unoxidized portion of the binary specimen (Figure 9) was partially transformed on cooling from the oxidation temperature. The dark patches seen in the metal result from superficial oxide formation on these transformed regions after the specimen was cross sectioned.

Still another view of a cross section through the oxide/metal interface of a ternary specimen is presented in Figure 11. The photograph is an electron micrograph made from a carbon replica of a lightly etched metallographic specimen. Again, the two separate phases are readily discernible, and the general columnar structure of the oxide is evident.

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Figure 8. CROSS SECTION THROUGH THE OXIDE FORMED ON A URANIUM-NIOBIUM-ZIRCONIUM ALLOY SPECIMEN IN SIX HOURS AT 800° C AND IN 0.05 TORR OXYGEN. (200X)

Y-105364

Figure 9. CROSS SECTION THROUGH THE OXIDE FORMED ON A URANIUM-NIOBIUM ALLOY SPECIMEN IN 14 HOURS AT 800° C AND IN 0.05 TORR OXYGEN. (425X)

Finally, a view of the underside of the oxide found on a binary specimen is given in Figure 12. This sample was obtained by quenching into mercury a specimen oxidized at 800° C. The mercury induced very severe intergranular cracking in the specimen; and, on one fracture cross section, a metal grain at the oxide/metal interface popped out, revealing the underside of the oxide.

For at least two reasons it is felt that the oxide was not significantly attacked by the mercury: (1) the reaction interface defined by the bottom of the oxide "fingers" was extremely uniform for this specimen; and, even at the high magnifications of the electron microscope, the line of this reaction front did not appear to have been disturbed in the region shown in Figure 12; (2) the amplitude and spacing of the roughnesses shown in Figure 12 match those which might be deduced from the cross-sectional view of the oxide seen in Figure 11. The dark, rounded regions in the photograph are, however, holes in the oxide. These rounded regions are associated with the positions of the metal-like stringers in the oxide and, thus, it is concluded that the parting of the oxide and metal was a result of an attack by the mercury on the metallic components at the oxide/metal interface.

MARKER EXPERIMENTS

It was discovered that when an oxidized specimen of either the binary or ternary alloy was annealed in vacuum at temperatures of 800 - 1,000° C and at a pressure of 1×10^{-7} torr, several changes in the oxide morphology occurred: the metallic stringers in the oxide tended to spheroidize; and, in some instances, large metallic particles developed near the oxide/metal interface. In addition, a layer of new, stringer-free oxide that was approximately two microns thick formed at the oxide/metal interface. These features can be seen in Figure 13(a). Note that the stringers in this case serve more or less as a marker. New oxide is formed below them at the oxide/metal interface.

When a specimen is subjected to alternate oxidation and annealing cycles, the new layer of oxide formed at the oxide/metal interface during the anneal itself acts as a "marker" (see Figure 14). Once again, new oxide is formed below the marker. Oxidation was accomplished at 900° C in oxygen at 0.05 torr while

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Figure 10. CROSS SECTION THROUGH THE OXIDE/METAL INTERFACE OF THE URANIUM-NIOBIUM ALLOY THAT WAS OXIDIZED FOR 90 MINUTES AT 1,100° C IN OXYGEN AT 0.05 TORR. (1,000X)

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Figure 11. DIRECT CARBON REPLICA (PRESHADOWED WITH CHROMIUM) OF A CROSS SECTION THROUGH THE OXIDE/METAL INTERFACE OF A LIGHTLY ETCHED SPECIMEN OF THE TERNARY ALLOY THAT WAS OXIDIZED FOR 2.5 HOURS AT 800° C IN OXYGEN AT 0.05 TORR. (35,000X)

the anneals were at the same temperature and at a pressure of 1×10^{-7} torr. The sequence followed was: oxidation for 40 minutes, anneal for 1,300 minutes, oxidation for 70 minutes, anneal for 1,400 minutes, and oxidation for 100 minutes.

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Figure 12. SCANNING-ELECTRON MICROGRAPH OF THE UNDERSIDE OF THE OXIDE FORMED ON A BINARY ALLOY SPECIMEN THAT WAS OXIDIZED FOR SIX HOURS AT 800° C IN OXYGEN AT 0.05 TORR. (10,000X)

(a) Optical Micrograph

(b) Niobium $L\alpha$ X-ray View of the Same Area (light areas are regions of high Nb concentration)

R-54103

Figure 13. CROSS SECTION THROUGH THE OXIDE/METAL INTERFACE OF A BINARY SPECIMEN THAT WAS OXIDIZED FOR SIX HOURS AT 900°C IN OXYGEN AT 0.05 TORR AND THEN ANNEALED AT 900°C FOR ONE WEEK AT A PRESSURE OF 1×10^{-7} TORR. (2,500X)

Figure 14. OXIDATION-RATE CURVE FOR THE URANIUM-NIOBIUM ALLOY SPECIMEN THAT WAS SUBJECTED TO ALTERNATE PERIODS OF OXIDATION AND VACUUM ANNEALS. (The Photographic Insert, at 500X, Shows the Specimen in Cross Section)

These observations indicate the occurrence of anion diffusion in the oxide and are consistent with the fact that anion diffusion rates in uranium dioxide exceed those for cations⁽¹⁰⁾ by several orders of magnitude. It might be concluded immediately that mass transport across the oxide occurs exclusively by anion diffusion except for the fact that niobium pentoxide (Nb_2O_5) is observed at the gas/oxide interface of the binary specimens (see next section), implying the outward diffusion of niobium. Furthermore, the thickness of the outer, two-phase layer of the oxide (Figure 14) increased slightly during the subsequent oxidation cycles to which the specimen was subjected; that is, additional new oxide was formed above the marker. Given the differences in the anion and cation diffusion coefficients in uranium dioxide, however, it seems more reasonable to interpret this latter result not as evidence for significant diffusion of uranium in the oxide but rather in terms of a continued oxidation of the stringers embedded within

the oxide scale. Thus, except for the relatively small amount of niobium which diffuses outward, it is concluded that the large majority of mass transport across the oxide occurs via anion diffusion.

The question of the ultimate origin of the oxygen required to form the thin "marker" layer of oxide during annealing is an interesting one. The specimen will getter any residual oxygen in the system, but it is estimated that the total of new oxide formed in this way would be small. A more likely source of oxygen appears to be the existing oxide scale itself. At the oxygen pressure at which the specimen was originally oxidized (0.05 torr) and in the temperature range encompassed by this study, the equilibrium oxide of uranium is the octoxide (U_3O_8).⁽⁷⁾ At the annealing pressure, however, the equilibrium oxide is a slightly hyperstoichiometric form of the dioxide. (For example, at 900° C, the equilibrium oxide is $\text{UO}_{2.018}$.)⁽⁸⁾ Of course, it is not expected that, during the oxidation stage, the entire oxide scale would be in equilibrium with the surrounding gas. Various analytical techniques, for example, failed to reveal the presence of detectable quantities of either the octoxide or monoxide in the oxide scale; however, it seems highly probable that the outer layers of the oxide were hyperstoichiometric, perhaps with oxygen excesses as high as 5 to 10 percent. Near the oxide/metal interface, on the other hand, the effective oxygen pressure is so low that the oxide must be essentially stoichiometric. Thus, a very large oxygen gradient is visualized as existing across the oxide scale during oxidation. The anneal has the effect of leveling out this gradient—some of the excess oxygen being used up in the formation of new oxide at the oxide/metal interface.

It is of interest to note that these interruptions in the oxidation process did not produce significant changes in the rate of oxidation when oxidation was resumed. At first glance it might seem that this result is inconsistent with the argument that the effect of the vacuum anneal is that of leveling out the oxygen gradient in the oxide scale and reducing the extent of hyperstoichiometry of the uranium dioxide. It is well known that the self-diffusion coefficients for both uranium and oxygen in uranium dioxide depend strongly on the composition of the oxide,⁽⁹⁾ but it is the chemical diffusion coefficient which should govern diffusion during oxidation; and, in uranium dioxide, it is relatively insensitive to oxide stoichiometry.⁽¹⁰⁾

IDENTITY OF THE OXIDE PHASES

X-ray patterns, both powder patterns and diffractometer traces, of the oxide scale on the two alloys showed the matrix to be predominantly uranium dioxide. It was impossible to detect either the octoxide or monoxide. Electron micro-

probe studies revealed the presence of zirconium in the uranium dioxide matrix of the scale on the ternary, a result which is consistent with the fairly high level of solubility of zirconium dioxide in uranium dioxide⁽¹¹⁾; however, for neither alloy could niobium be detected (detection limit, ~ 0.5 wt %) in the oxide matrix by this method. Furthermore, discrete particles of the oxides of either niobium or zirconium were never observed except during the oxidation of the binary alloy at 900 and 1,000° C. At those temperatures, whiskers of niobium pentoxide (identified by reflection electron diffraction) formed on the outer surface of the oxide, as seen in Figure 15.

Because the diameter of the metal-like stringers in the oxide was considerably less than one micron, it was difficult to establish their identity unambiguously with an electron microprobe. The electron beam of the microprobe excites fluorescence from a hemispherical region of the sample roughly three microns in diameter. Thus, even when the beam was positioned directly on a stringer, there was considerable overlap into the surrounding oxide matrix.

In an effort to resolve this problem, an examination was made of not only "as-oxidized" specimens but also specimens used in the marker experiments described earlier. The coarsened stringers of these specimens were in some instances large enough to encompass the entire volume excited by the microprobe and were obviously rich in niobium, as indicated in Figure 13(b). This photograph shows the same area of the specimen as in Figure 13(a). It is a display of the niobium L α X rays obtained from the microprobe. The light areas represent regions of high niobium concentration, and the correspondence between these regions and the metallic particles seen in Figure 13(a) is evident.

For some of the larger particles in the oxide, the microprobe results indicated niobium concentrations as high as 70 atom percent (balance U). The smaller particles frequently yielded apparently smaller niobium concentrations (30 - 40 at %); however, in all such cases there was an overlap of the microprobe beam into the surrounding uranium dioxide matrix. Such an overlap would, of course, lead to low values for the niobium concentration; consequently, it is believed that the compositions of both the large and small particles are approximately the same.

It is also significant that the total of the concentrations of uranium and niobium in the larger particles so closely approximated 100 percent. For example, for a specimen of the binary alloy, the totals (in wt %) obtained from three such particles were 97, 99, and 101.5 percent. Thus, it can be concluded that the metallic phase in the oxide scale on the annealed samples is thus a niobium-rich uranium alloy which contains relatively little oxygen.

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Figure 15. SCANNING ELECTRON MICROGRAPH OF NIOBIUM PENTOXIDE WHISKERS FORMED AT THE OXIDE/GAS INTERFACE OF A URANIUM-NIOBIUM ALLOY SPECIMEN DURING OXIDATION AT 1,000° C IN OXYGEN AT 0.05 TORR. (10,000X)

For the reasons already given, the same degree of certainty cannot be expressed concerning the composition of this phase before annealing. However, the following results for unannealed specimens suggest that the stringer composition is basically the same before annealing as after:

1. Electron microprobe analyses of the oxide made at two-micron intervals along a trace parallel to the oxide/metal interface revealed regions of high niobium content with a spacing which agreed qualitatively with the average spacings of the stringers in the oxide, as determined optically.
2. At 1,100°K, the standard free energies of formation of uranium dioxide, zirconium dioxide, and niobium monoxide are, respectively: - 107, - 106, and - 85 kcal/gram/atom oxygen.⁽¹²⁾ Hence, it is thermodynamically possible for elemental niobium to coexist in a uranium dioxide-uranium-oxygen environment such as would exist in a compact uranium dioxide scale, and the argument that the metallic stringers in the oxide scale are rich in elemental niobium is thermodynamically consistent. A similar consistency is evident in the fact that the stringers in the uncracked oxide on the binary alloy tend to disappear near the oxide/gas interface where the partial pressure of oxygen in the oxide would be expected to be highest. Likewise, on the basis of these thermodynamic arguments, it would be expected that the stringers would disappear completely from the cracked, outer layer of the ternary oxide, as observed. Extensive cracking of the outer layer of oxide has the effect of isolating that portion of the oxide from the source of unoxidized uranium atoms, thus permitting a buildup of oxygen pressure to the point where oxidation of the niobium becomes possible.
3. The observations of niobium pentoxide whiskers at the oxide/gas interface of the binary specimens was unexpected. Niobium is not only a more noble metal than uranium, but is also a comparatively minor constituent of the alloy. Yet the presence of the pentoxide can be understood in terms of the existence of free niobium as a separate phase in the oxide scale and its subsequent diffusion (probably along easy diffusion paths associated with the stringers) to the oxide/gas interface.

These observations show that the stringers in the oxide scale on the "as-oxidized" specimens are enriched in niobium, which is in a lower oxidation state than +5. That the stringers are actually metallic; that is, that they are a niobium-uranium alloy, is still not completely proven. However, given the very large free energy of formation of uranium dioxide and the compactness of the oxide scale near the oxide/metal interface, it seems probable that the stringers are, in fact, metallic, at least near the oxide/metal interface.

It is permissible to speculate that the stringers originate as a result of the preferential oxidation of uranium at the oxide/metal interface with the consequent rejection of a niobium-rich niobium-uranium phase. Evidently, the rate of diffusion of the niobium back into the alloy is smaller than the rate of advance of the oxidation front, and the niobium-uranium particles are thus caught up in the oxide scale. The elongated form of the particles may be a result of the large lateral stresses which develop in the oxide (see next section). Alternately, the diffusion of niobium atoms to the oxide/gas interface (where complete oxidation is possible) might also tend to elongate the particles.

MECHANISM OF STRESS GENERATION

It is believed that the mechanism of stress generation during oxidation is essentially the same for both alloys and similar to that proposed for the oxidation of niobium.⁽¹³⁾ A number of studies of diffusion in uranium dioxide have been made,^(9, 10) and all lead to the conclusion that the rate of anion diffusion greatly exceeds that of cation diffusion in uranium dioxide. Thus, material transport across the oxide layer on the alloy specimens must have been primarily by way of anion diffusion; although, as indicated previously, some outward diffusion of niobium also seems to occur. Most of the new oxide, however, must be formed at the oxide/metal interface.

The oxide-to-metal volume ratio for uranium dioxide and uranium is almost 1.7:1; thus, when any volume element of metal is converted to oxide, the resulting volume increase must produce a very large compressive stress in the oxide since the new oxide is being formed at a constrained interface. Furthermore, given the morphology of the oxide, this new oxide is formed at or near the bottom of "fingers" of oxide which are interspersed with metal stringers at the oxide/metal interface.

If only the conversion to oxide of a small, localized volume of metal is considered, it is found that the stress system arising from the accompanying volume expansion is approximately spherically symmetrical. Macroscopically, however, the growth of a film of uniform thickness results in an essentially uniform, biaxial stress. The correctness of this statement becomes evident when it is realized that there is no resistance to the expansion of the oxide in the direction normal to the specimen surface. That component of stress must, therefore, be zero. The forces of cohesion between the oxide and metal, on the other hand, permit the buildup of stresses in a plane parallel to the surface of the metal, creating a biaxial stress system. The belief is held that it is this condition which leads to the very large increases in surface area noted during oxidation.

MAGNITUDE OF THE STRESS DEVELOPED IN THE OXIDE

Using the so-called "flexure" technique, an attempt was made to estimate the magnitude of the stresses generated during oxidation. This method, which has been described elsewhere,⁽¹⁴⁾ entails the use of a strip specimen (1 x 4 x 0.05 cm), one side of which is protected from oxidation by a thin aluminum-gold layer. When the reverse side of the specimen is oxidized, the specimen bends as a result of the stresses generated in the oxide. Measurements of the radius of curvature of the specimen makes it possible to compute the maximum bending stress to which the specimen is subjected.

Estimates of the actual stress existing in the system (ie, the stress which would have to be developed in either the oxide or the surface layers of the metal in order to produce the observed degree of flexure) depend entirely on the model that is postulated for stress generation. Since the level of oxygen solubility in uranium is apparently quite low,⁽¹⁵⁾ it is held that the major stress-generating mechanism is that outlined previously, and it is assumed that all the observed bending of the specimen results from compressive stresses developed in the oxide. On this basis, it is possible to use the flexure data to calculate the average stress in the oxide. The appropriate equation is:⁽¹⁶⁾

$$\sigma_F = \frac{1}{3} \sigma_s \frac{h}{w}, \quad (1)$$

where:

σ_F represents the average stress in the oxide,

σ_s the maximum bending stress in the metal, and

h and w the thicknesses of the metal specimen and oxide layer, respectively.

The value of σ_s is obtained directly from the flexure data using the equation:

$$\sigma_s = \pm \frac{Eh}{2\rho_x},$$

where:

E represents Young's modulus,

h the specimen thickness, and

ρ_x the radius of curvature of the specimen in its long dimension.

It should be emphasized that these equations are valid only as long as the stresses in the metal remain in the elastic region. Given the plastic deformation which must accompany the large surface area increases observed for the specimens used in this study, it is obvious that caution must be exercised in the application of these equations to the present work. It is for this reason that those stress calculations based on data taken in the very early stages of oxidation, when the bending stress on the specimen will be small, are considered to be the most accurate.

The results of two typical flexure experiments are indicated in Figure 16. The quantity plotted as the ordinate is proportional to the radius of curvature of the oxidizing specimen. Consider first the curve that represents an oxygen

Figure 16. RESULTS OF FLEXURE EXPERIMENTS WITH TWO URANIUM-NIOBIUM-ZIRCONIUM ALLOY SPECIMENS.

pressure of 0.005 torr. These data were obtained from a flexure specimen of the ternary alloy exposed to oxygen at a pressure of 0.005 torr for two minutes at 700° C. The extent of flexing of the specimen is plotted as a function of time. After 30 seconds, an oxide film, approximately 2,500 Å thick, had formed on the specimen, and the average stress in the film, as calculated from Equation 1, was 855,000 psi!

It may be argued that the suggested stress model leads to absurdly high stress values, yet it must be kept in mind that only 30 seconds of oxidation were required to produce the observed specimen flexure. Evidently, whatever stress-generating mechanism may be proposed, the process must be confined to a very thin layer at or near the specimen surface. Hence, subject only to the condition that all the strain in the metal be elastic, the stress generated must be very large.

In the experiment just described, oxidation was effectively stopped after two minutes by evacuating the system to a pressure of 10^{-6} torr. The specimen then "straightened" to a significant degree. This behavior is believed to be indicative of the decay of the stress levels reached in the system during oxidation and that it results from a partial recovery of the elastic strain developed in the metal. Such behavior also underscores the transient nature of the stresses which arise in the oxide.

To understand these results, it is important to keep in mind that the stress in the oxide is, indeed, very high, probably on the order of one million psi, especially near the oxide/metal interface. Thus, it is to be expected that stress-relief mechanisms will be operating in the oxide. On the other hand, after the first 30 seconds of oxidation, the maximum bending stress in the metal (using an elastic modulus of 5×10^6 psi for the alloy) is still small—approximately 1,500 psi. This value increases rapidly; and, after two minutes of oxidation, a maximum bending stress of 6,000 psi is computed, based on the assumption that only elastic strain is present in the metal. Only limited quantitative data on the physical properties of uranium-niobium-zirconium alloy at 700° C are available; however, at that temperature, the alloy is quite soft, exhibiting properties similar to those of lead at room temperature. Thus, it seems reasonable to assume that the strain in the metal is still elastic after 30 seconds of oxidation; but that, after two minutes, the yield strength of the metal has been exceeded with the result that plastic deformation has also begun in portions of the metal. Therefore, both the flexure experiments and observations of the surface-area increase make it clear that early in the oxidation process both elastic and plastic strain occur in the metal while plastic flow must occur in the oxide virtually from the beginning of oxidation because of the tremendously high stresses present there.

It may be said, then, that two competing processes occur during oxidation. First, there is a stress-generating step associated with the formation of the new oxide. Simultaneously, stress relief occurs through creep and/or plastic flow in the oxide and metal.

These same terms make it possible to understand the "unflexing" of the specimen. Referring again to Figure 16, evacuation of the system effectively eliminates

the stress-generating step by virtually stopping the formation of new oxide. The stress-relief processes, namely creep in the oxide and in the metal, then continue momentarily unopposed. Thus, at the moment of cessation of stress generation, the creep rate in the oxide should be very high, with the result that the stress level in the oxide will quickly drop below that required to continue the flexure of the metal. Further reduction of the stress level in the oxide as a result of continued creep would permit the dissipation of the elastic component of the strain in the metal through an unbending of the specimen. Complete unbending would not be expected because of the plastic deformation which had already occurred in the metal and because of the residual stress in the oxide.

EFFECT OF OXYGEN PRESSURE ON FLEXURE

Both the rate of flexure and the extent of "unflexing" of a specimen in an experiment such as that just described are remarkably sensitive to oxygen pressure. The flexure curve in Figure 16 (marked with solid circles) was obtained, for example, by oxidizing a specimen at 0.002 torr oxygen pressure compared to the 0.005 torr pressure for the other sample. The effect on the flexure behavior is evident.

Given the observed differences in the flexure rates of the two specimens, an explanation may be suggested for the differences in the extent of unflexing when the system was evacuated. Unflexing with the partial recovery of the elastic strain present in the metal at the beginning of the vacuum anneal has already been identified. Furthermore, the creep rates for these alloys at the temperatures of the experiments are very high. Thus, the smaller the rate of flexure (strain rate), the longer will be the time required to achieve a given degree of flexure (strain); and, hence, the greater will be the time available for creep processes to dissipate the elastic strain in the metal. Therefore, a smaller degree of unflexing is expected from the specimen whose rate of flexure was smaller.

The great sensitivity of the flexure rate to oxygen pressure is more difficult to understand. At pressures in the neighborhood of 0.001 torr, it is impossible to envision that a 50 percent change in oxygen pressure could alter the oxidation process in any way other than producing a minor change in the rate of oxidation. In fact, it has been experimentally confirmed that, in this pressure range, a dependence of the oxidation rate on oxygen pressure does exist, but is small.⁽¹⁷⁾ Now, the flexure rate is related to the maximum bending stress exerted on the metal which, in turn, depends on the total strain energy in the oxide. In other words, both the magnitude of the average stress in the oxide and the oxide thickness are important in determining the flexure rate (see Equation 1).

A further complication arises when the stress distribution in the oxide scale is considered. In the estimates of oxide stress levels obtained through this study, an assumption has been made that the stress is uniform throughout the entire thickness of the oxide. While this approximation is reasonable when dealing with films which are, at most, a few thousand angstroms thick, it clearly fails relatively soon after oxidation begins because, as indicated earlier, of the development of a stress gradient in the oxide. The total strain energy in the oxide will, therefore, be determined by the magnitude of the maximum stress and the shape of this stress gradient.

If the contention is correct that small changes in oxygen pressure influence the oxidation process only to the extent of producing minor changes in the oxidation rate, it follows that the maximum stress achievable in the oxide or the shape of the stress gradient in the oxide, or both, are exceptionally sensitive functions of the oxidation rate. Perhaps when given the magnitude of the stress that is estimated to exist in the oxide and the extent of creep and plastic flow occurring in the oxide, such a result is not unreasonable.

CONCLUSIONS

The following conclusions can be stated as a result of this study:

1. Both the uranium-niobium-zirconium and uranium-niobium alloys undergo extraordinarily large dimensional changes during oxidation at temperatures above approximately 650° C.
2. From the oxidation-rate curves that were determined for both alloys at 100-degree intervals between 500 and 1,000° C and at an oxygen pressure of 0.05 torr, the activation energy for the process was found to be ~ 15 kcal/mole.
3. The morphology of the oxide formed on both alloys was basically similar and highly complex. A multiphased, columnar structure was observed, suggesting the possibility of extensive short-circuit diffusion through the oxide.
4. A mechanism for stress generation in the oxide was proposed, based on the details of the oxide morphology, the occurrence of anion diffusion, and the large oxide/metal volume ratio for uranium dioxide and the metal.
5. Stresses in the oxide on the order of one million psi were estimated on basis of flexure studies of the oxidizing specimens. Stresses of this magnitude are thought to account for the creep and/or plastic flow in both oxide and metal during oxidation.

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