MASTER

HIGH TEMPERATURE OXIDATION OF URANIUM ALLOYS*

by

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ABSTRACT

The oxidation characteristics of U-16.6 at.% Nb-5.6 at.% Zr, U-21 at.% Nb, U-15 at.% Zr, and U-18 at.% Mo in the temperature range 700 to 1100°C are discussed. Stresses as large as 10^6 psi develop in the oxide scales on these alloys as oxidation proceeds, and these stresses lead to large increases in the lateral dimensions of the specimens. The morphology of the oxide scales is described, and a mechanism of stress generation is suggested. Several stress relief processes, including the plastic deformation of both oxide and metal, are discussed.

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INTRODUCTION

A problem in oxidation research currently receiving considerable attention is that of the influence of stress on the oxidation process and of the role of the mechanical properties of both oxide and metal in oxidation mechanisms. Very substantial stresses are generated during the oxidation of most metals, and a variety of stress-relief mechanisms can operate in the oxide and the parent metal as well. The identification of these processes and an assessment of their relative importance now appears essential to a complete understanding of oxidation phenomena. This paper, which describes the oxidation properties of a series of uranium alloys, represents a further contribution to experimental data in this area.

Uranium and its alloys are well suited to a study of this sort. During oxidation, material transport across the oxide scale occurs almost exclusively via anion diffusion (1). Thus one of the most effective stress generating mechanisms, the formation of new oxide at a confined interface, is operative in these alloys. Furthermore, stress relief occurs in a variety of ways in both the oxide and the alloys themselves, and, in some cases at least, through the proper choice of experimental conditions it is possible to sort out the various mechanisms involved.

EXPERIMENTAL PROCEDURES

Alloys studied included the ternary alloy U-16.6 at.% Nb-5.6 at.% Zr and the binary alloys U-21 at.% Nb, U-15 at.% Zr, and U-18 at.% Mo. In addition a limited amount of work was done on pure uranium. Test speci-

mens were generally in the form of coupons $1 \times 2 \times 0.05$ cm. Prior to oxidation they were mechanically polished and then electropolished in a 6 vol. % solution of HClO_4 in methanol at dry-ice temperatures. Oxidation temperatures ranged from 700 to 1100°C , and the specimens were always held in vacuum at the oxidation temperature long enough to ensure the complete transformation of the alloy to its equilibrium bcc-gamma structure before oxidation was initiated. Thus during oxidation all specimens were single phase. Specimens were oxidized in purified, flowing oxygen at a pressure of 0.05 torr unless otherwise specified. This rather low oxygen pressure was selected to prevent excessive self-heating of the samples during oxidation.

SURFACE AREA INCREASE

A remarkable feature of the oxidation of these alloys is the large increase in the lateral dimensions of the specimens that occurs during oxidation. Figure 1 shows two originally identical specimens of the ternary alloy. The bottom specimen is unoxidized, while the specimen at the top was oxidized for 3 hr at 800°C . The increase in area during oxidation is obvious even though only about 15% of the alloy was converted to oxide. An additional three hours of oxidation produced a doubling of the specimen area (1).

The other alloys and U itself also undergo an area increase during oxidation. As shown in Fig. 2, however, the magnitude of the increase is smaller than that for the ternary alloy, ranging from $\sim 5\%$ for pure U to 11% for the U-18 at.% Mo for oxidation times producing equal thick-

nesses of oxide.

This phenomenon, while unusual, is not unique to U and its alloys. It has been reported for Zr and its alloys (2, 3, 4) and to a lesser degree for Ni (5) and Ta(6).

OXIDE MORPHOLOGY

A characteristic feature of the oxide formed on these alloys is the presence of two phases in the scales. Figure 3 shows a typical result for U-21 at.% Nb; the gray regions are UO_2 , while the metallic stringers are an unoxidized Nb-rich phase containing U. Note that at the oxide-metal interface the oxide and metal stringers are closely interspersed with the result that the oxide is securely "pegged" to the metal substrate. As a consequence, any stresses developed in the oxide can be transmitted very efficiently to the substrate alloy.

The morphology of the oxide on the ternary alloy and on U-18 at.% Mo is also very similar to that shown in Fig. 3. The scale on the ternary differs in that it exhibits many vertical cracks near the oxide-gas interface and in that in the vicinity of these cracks the metal stringers in the scale are completely oxidized. The stringers in the scale on U-18 at.% Mo were smaller and slightly less well aligned than for U-21 at.% Nb; however, the differences among the three alloys are a matter of degree rather than kind.

A metallic phase was also present in the scale on the U-15 at.% Zr alloy (see Fig. 4). However, the metallic particles, which are probably Zr containing substantial amounts of dissolved oxygen, tended to be con-

centrated near the oxide-metal interface.

The basis for these morphologies is to be found in the differences in the standard free energies of formation of the various oxides involved. The values of ΔF^0 for UO_2 , ZrO_2 , NbO , and MoO_2 are -107, -103, -85, and -47 kcal/g-atom O, respectively. Evidently, the oxygen potential in the compact UO_2 scales is too low to permit the oxidation of Nb or Mo. Consequently, these metals are rejected at the oxidation front (the oxide-metal interface) where they agglomerate. The elongated shape of these metallic particles is no doubt dictated by the character of the stress fields existing in the oxide (see below).

The case of the U-Zr alloy is especially interesting because the free energy of formation of UO_2 is only 4 kcal/g-atom more negative than that for ZrO_2 . In fact, at the extremely low oxygen pressures existing within the oxide scale, the small additional free-energy decrease associated with the solution of oxygen in Zr causes Zr(O) to be slightly more stable than UO_2 itself (7). These relationships manifest themselves in the distribution of Zr in the oxide and the metal. Figure 5 shows a microprobe trace perpendicular to the specimen surface for a specimen oxidized 50 min. at 800°C . Beginning in the metal about 20μ below the oxide-metal interface, the concentration of Zr began to decrease, dropping virtually to zero at a point just below the interface. A maximum in Zr concentration occurred at the interface itself, and, except for local fluctuations, the Zr concentration in the oxide was constant and on the average slightly higher than in the alloy itself. The Zr maximum at the interface is real; it was reproducible, and a narrow band of metal-like material, dif-

ferent from the substrate, was always visible at the interface in an optical microscope (see Fig. 4).

We have interpreted these results as follows: in the initial stages of oxidation, because of the relative free energies of formation of their oxides, U is oxidized preferentially and Zr rejected at the oxide-metal interface. At the oxygen potential existing at this interface, however, $Zr(O)$ is even more stable than UO_2 . Thus oxygen will continue to diffuse through the covering layer of UO_2 to produce a solid solution with the Zr at the interface. The possibility of forming $Zr(O)$ provides the driving force for the diffusion of Zr from the alloy to the oxide-metal interface. Finally, the oxygen potential at the UO_2 - $Zr(O)$ interface increases to the point where the Zr can be fully oxidized. The continued enhancement of the Zr concentration at the oxide-metal interface thus leads, by the mechanism outlined above, to a Zr concentration in the scale greater than that in the alloy itself.

MECHANISM OF STRESS GENERATION

The bulk of the oxide formed on all these alloys is UO_2 , and it is well established (8, 9) that the rate of oxygen diffusion in UO_2 exceeds that of U diffusion by several orders of magnitude at the temperatures of this study. Thus transport across the oxide scale occurs primarily via anion diffusion, and new oxide is formed at the oxide-metal interface, a fact we have also demonstrated in marker experiments (1). There is a volume increase amounting to a factor of 1.7 associated with the conversion of U to UO_2 , and we believe that it is the process of accom-

modating this volume increase which is the principle stress-generating mechanism for these alloys. As noted above, the morphology of the oxide scales is such that the scales are very securely "pegged" to the substrate metal, thus permitting the efficient transmission to the substrate of any stress which develops in the oxide.

The stresses generated by this mechanism can be very large. We have already reported the results of a series of flexure tests with the ternary alloy which indicated the existence of stresses on the order of 10^6 psi in the oxide (1, 10). Similar stress levels are to be expected in the oxide scale on the other alloys as well.

STRESS RELIEF MECHANISMS

At first thought the suggestion that an oxide scale could sustain stresses of 10^6 psi appears unrealistic. Two things should be borne in mind, however. First, given the mode of stress generation, the stress at the oxide-metal interface, where the stress is highest, must be highly compressive, and given the morphology of the oxide, the stress system must be almost hydrostatic in nature. On a localized scale conditions may exist which are roughly analogous to those in an extrusion process.

Secondly, stress-relief processes are constantly operating in both oxide and metal during oxidation, and the stress level we measure represents a "steady-state" condition. We find, for example, that stopping the stress-generating process, i.e., stopping the oxidation process, leads to a prompt reduction in the stress level in the oxide. Further-

more, the stress in the oxide is a sensitive function of oxidation rate (1). Evidently, the magnitude of the stress existing at any moment in the oxide represents a balance between the rates of stress generation and relief. Further consideration of stress-relief mechanisms is, therefore, in order.

Stress Relief in the Oxide.- Evidence of stress relief in the oxide may be found in the behavior of the outer layers of oxide formed on these alloys. The lateral dimensions of the first layers of oxide formed are, of course, determined by the initial dimensions of the specimen. Because of the predominance of anion diffusion in the oxidation process, these initial layers remain at the oxide-gas interface as oxidation proceeds, and their dimensions are fixed. If, however, additional oxidation produces an increase in the area of the substrate alloy, these outer layers must come under tension and must eventually either crack or undergo plastic deformation.

Figure 6 shows cross-sections through three U-18 at.% Mo specimens oxidized at 700, 800, and 900°C, respectively. The linear strain experienced by all three specimens during oxidation was $\sim 8\%$. The oxide on the 700°C specimen exhibited many vertical cracks, reflecting the tensile stress present in the outer layers of the oxide. The cracks in the 800°C specimen were much smaller, while at 900°C the outer layer of oxide sustained the full 8% strain without cracking at all.

We concluded from these observations on U-Mo and from similar ones for the other alloys that deformation of the oxide by plastic flow is a very active process during oxidation, especially at higher temperatures.

Stress Relief in the Metal.- The area increase that these alloys specimens experience during oxidation is another form of stress dissipation. This process can begin when the total strain energy in the oxide reaches such a magnitude that creep or plastic flow in the metal specimen can be induced. As might be expected, this effect is sensitive to specimen geometry, but even on specimens with small surface-to-volume ratios, we have observed creep in the surface layers of the metal (1).

Another mechanism of stress relief in the metal is evident in the oxidation behavior of the U-Nb-Zr ternary at low pressures. Figure 7 shows a cross-section through such a specimen oxidized 16,000 min at 900°C in oxygen at 5×10^{-6} torr. It would appear that the oxide on this specimen had grown under almost stress-free conditions. The area increase of the specimen was virtually zero as compared to a 40% gain expected for oxidation at 0.05 torr. Notice the very irregular character of the oxide-metal interface in contrast to the extreme smoothness of the oxide-gas interface. Furthermore, the oxide columns developed well defined polyhedral faces at their bases. It is difficult to reconcile these features with the deformation to be expected as new oxide is formed at the bottoms of the oxide columns. Yet anion diffusion does occur under these circumstances, and the same stress-generating process should operate here as at higher oxygen pressures.

A possible explanation of these results is suggested by a consideration of the magnitude of the oxygen flux through the scale compared to that of the vacancy flux from the metal to the oxide-metal interface. The compressive stress at the oxide-metal interface associated with the formation of new oxide should make this interface an excellent sink for

vacancies, and an adequate flow of vacancies to the interface could serve to relieve this stress.

The oxygen flux, J_{Ox} , can be obtained directly from our oxidation rate measurements and is 3×10^{14} atoms/cm²/sec. The vacancy flux is given by $J_v = D_v dc/dx$, where D_v is the vacancy diffusion coefficient in the alloy and dc/dx represents the vacancy concentration gradient in the vicinity of the oxide-metal interface. Using the fact that $D_v = D_s/c_o$, where D_s is the self diffusion coefficient for U and c_o is the equilibrium vacancy concentration at some distance x_o from the interface, one obtains after integrating: $J_v = D_s/x_o$.

At 900°C, D_s is 1×10^{-8} cm²/sec (11), and x_o may be taken as $\sim 10^{-3}$ cm, the average radius of the grains in the alloy. If one further assumes that the volume of a vacancy in the alloy is the same as that of a U atom, one obtains for the vacancy flux a maximum value of $\sim 5 \times 10^{17}$ vacancies/cm²/sec. At 900°C and 5×10^{-6} torr oxygen it thus appears that J_v ^(readily match) ~~can exceed~~ J_{Ox} , and it is plausible to suggest that the flow of vacancies to the oxide-metal interface from various sources in the metal (grain boundaries, dislocation loops, etc.) constitutes a mechanism of stress relief during oxidation.

Under conditions where the oxygen flux is small, this stress-relief mechanism may be the only one operative. At higher oxygen pressures, as we have said, plastic deformation of both oxide and metal also occurs, but even then one might expect vacancy flow to the oxide-metal interface to account for an important fraction of the stress relief that takes place.

SUMMARY

The high temperature oxidation characteristics of several U alloys containing Nb, Zr, and Mo were studied. In all cases oxide formation involved the generation of large stresses in the oxide, and the magnitude of these stresses was estimated to be 10^6 psi. Oxidation of these alloys proceeds via anion diffusion, and the stresses arise because of the need to accommodate the volume expansion accompanying the oxidation of U. The existence of these stresses activates several stress-relief mechanisms including the plastic deformation of both oxide and metal and a flow of vacancies to the oxide-metal interface.

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FIGURE CAPTIONS

Fig. 1. U-16.6 at.% Nb-5.6 at.% Zr specimens. Unoxidized sample at bottom. Identical specimen at top was oxidized 3 hr at 800°C in O₂ at .05 torr.

Fig. 2. Percentage area increase experienced by several U alloys during oxidation at 800°C.

Fig. 3. Cross-section through U-21 at.% Nb oxidized 600 min at 900°C.

Fig. 4. Cross-section through U-15 at.% Zr oxidized 50 min at 900°C in oxygen at 0.05 torr.

Fig. 5. Microprobe trace along cross-section of U-15 at.% Zr specimen oxidized 50 min at 900°C in O₂ at 0.05 torr.

Fig. 6. Cross-section through U-18 at.% Mo specimens oxidized at 700, 800, and 900°C. Area increase in all cases: 16%.

Fig. 7. Cross-section through U-16.6 at.% Nb-5.6 at.% Zr oxidized 16,000 min at 900° in oxygen at 5×10^{-6} torr.

FIG. 1

Fig. 2

Fig. 3

Fig. 4.

Fig. 5

Y-112614

700°C

800°C

900°C

U-18 at.% Mo

FIG. 6

Fig. 7