ACCELERATED OXIDATION
OF ZIRCALOY-2 IN SUPERCRITICAL STEAM

by

B. COX

Chalk River Nuclear Laboratories
Chalk River, Ontario
April 1973

AECL-4448
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ABSTRACT

Although a few earlier examples of excessive oxidation of Zircaloy-2 in high temperature (>450 C) steam at high pressures (≥1500 psi) have been reported, evidence suggested that at higher steam pressures the effects could be more serious. We have shown that the oxidation rate of Zircaloy-2 rises rapidly as the steam pressure increases into the supercritical region.

The large pressure dependence of the oxidation rate is a function of heat treatment, which apparently displaces the oxidation rate versus pressure curve along the pressure axis. Thus the previous instances of catastrophic oxidation of Zircaloy-2 at high temperatures represent the appearance of highly pressure dependent oxidation following heat treatments which shift the curve into the range of normally employed test pressures (≤1500 psig). The onset of this phenomenon appears to be related to changes in the growth morphology of the oxide.

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Oxydation accélérée du Zircaloy-2 dans la vapeur surcritique

par

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Résumé

Bien que l'on ait signalé antérieurement peu de cas d'oxydation excessive du Zircaloy-2 dans de la vapeur à haute température (>450°C) et à haute pression (≥1500 psi), les faits ont démontré qu'aux pressions de vapeur plus élevées, les effets peuvent être plus graves. Nous avons constaté que le taux d'oxydation du Zircaloy-2 s'accroît rapidement à mesure qu'augmente la pression de vapeur dans la région surcritique.

La grande dépendance sur la pression du taux d'oxydation est en fonction du traitement thermique qui, apparemment, fait passer la courbe "taux d'oxydation-pression" le long de l'axe des pressions. Ainsi, les exemples antérieurs d'oxydation catastrophique du Zircaloy-2 aux hautes températures donnent l'apparence d'une oxydation dépendant beaucoup de la pression après certains traitements thermiques qui font passer la courbe dans le domaine des pressions d'essai normalement employées (≥1500 psig). Le début de ce phénomène semble être lié à des changements dans la morphologie de croissance de l'oxyde.

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1. INTRODUCTION

Although Zircaloy-2 has been extensively tested in high pressure steam at temperatures from 400-500 °C (1-5), and in low pressure steam at higher temperatures (6,7), it was generally observed that the post-transition oxidation rate was relatively insensitive to the steam pressure. The oxidation rate is a function predominantly of the temperature, although the oxidation resistance of Zircaloy-2 becomes relatively worse than that of alloys not containing tin at these temperatures. However, instances of catastrophic oxidation of Zircaloy-2 in high temperature high pressure steam have been observed (1,8-11), and have been explained as effects of poor heat treatment. Virtually all reported instances of failure were of material in the α-annealed conditions, with or without some residual cold-work, or material heat-treated in the α + β region.

Studies of unalloyed zirconium (12) have shown that, in steam, the effect of pressure on the oxidation rate leads to a complicated series of curves giving regions with an apparently negative temperature coefficient. The Zr-Cu-Mo and Zr-Cu-W alloys also gave evidence for pressure-dependent oxidation rates at the highest temperatures and pressures used (12), and the effects were also heat treatment dependent.

It was surmised that the same phenomenon might account for the instances of excessive oxidation of Zircaloy-2, and that at ~1500 psig, depending on heat-treatment, this alloy might be entering a region where oxidation rate increases rapidly with increasing steam pressure.

Since equipment capable of corrosion testing at temperatures above 500°C with simultaneous pressures greater than 1500 psig was not available at CRNL at the start of this project, two autoclaves capable of operating at up to 700°C and 5000 psig were purchased in 1965. These autoclaves have behaved poorly at the upper end of their temperature and pressure range. Deformation of the sealing faces during operation has necessitated remachining after almost every high temperature experiment (at pressures ≥2500 psi), and leak tightness has been difficult to ensure even with this precaution. Thus, the experiments have progressed very slowly
and it has proved impossible to complete the programme originally envisaged. During this period the extensive studies of Johnson(13) were published. Sufficient experiments and specimen examination have been performed to warrant the drawing of some conclusions, and some significant differences from the observations of Johnson are apparent. The work is therefore being reported in its current state, since further expenditure on the rehabilitation or replacement of the present equipment does not appear to be warranted.

2. EXPERIMENTAL

The material used was selected from two batches of Zircaloy-2 (Ac and Bh) which have been extensively used for previous studies. The specimens were initially in the form of cold-rolled and annealed sheet, and analyses are given in Table 1. For comparison purposes some specimens were quenched from the β-phase before testing. Specimens were pickled in mixed nitric/hydrofluoric acids before exposure.

Specimens were exposed to steam from degassed, demineralised water at temperatures of 350, 400, 500 and 600°C and pressures of 15 psia, 500 psig, 1500 psig, 3000 psig and 5000 psig. The last two pressures were attainable only above the critical temperature of water (374°C) and the maximum pressure at 350°C was therefore SVP (~2700 psig).

Specimens were examined by weight change, optical and electron microscopy, and mercury porosimetry(14).

A few experiments were performed on several batches of Zr-0.5% Cu-0.5% Mo whose analyses are given in Table 2.

3. RESULTS

Pre-transition oxidation curves at 350°C are shown in Figure 1 as a function of pressure. Post-transition data at higher temperatures are given in Figures 2-6; all points are means of four specimens. The results at various temperatures for the α-annealed, batch Ac specimens (the most complete data) are compared in Figure 7. Results for the several batches of Zr-0.5% Cu-0.5% Mo at 400°C are given in Figure 8.
Visual observations showed that enhanced oxidation of Zircaloy-2 tended to start at one end of the specimen and spread over the surface; this is shown, in section, in Figure 9. No instances of very localised pustules have been seen, although at the lower pressures the patches of oxide breakdown tend to be initially small, but these were not visually similar to those reported in Johnson's work. At higher magnifications, in the optical microscope, it was observed that the oxide layer on the "normal" end of a specimen appeared to continue as a shell or layer over the thick oxide responsible for the enhanced weight gain (Figure 10). The thick inner oxide gave the impression of being columnar when viewed in polarised light (Figure 10). Electron microscope examination of the thick oxide (Figures 11-12) did not confirm the columnar nature of the thick oxide, but showed it to contain some large isolated crystallites, unlike the alternate layers of large and small crystallites observed in normal post-transition oxide films on Zircaloy-2. Examination of the oxide/metal interface (Figure 13) showed some characteristic differences from previous observations on Zircaloy-2. Thus, the hemispherical features commonly seen on the oxide/metal interface were larger and more prominent in this instance than is normally the case for Zircaloy-2, and were closer to the features previously observed with zirconium. The hemispherical features were often separated by deep voids (Figure 14), presumably filled (initially) with unoxidised metal.

Although the oxide was extensively cracked, there was no evidence for any localised oxidation beneath prominent cracks seen in the metallographic sections. Examination of the oxide-metal interface on the scanning electron microscope (Figure 15) showed examples of cracks emerging at the interface without causing any local modification of the topography. This evidence suggests that the cracks formed after oxidation, either during the cooling of the specimen or during subsequent specimen preparation. The alternative possibility, that the oxide is so porous that the introduction of large cracks causes no local change in oxidation rate, seems less probable.

Mercury porosimeter studies of a series of specimens oxidised to approximately equal weight gains at a range of pressures are shown in Figure 16. Curves at the same pressure but for a range of weight gains are compared for oxides formed
at 500 psig (Figure 17). Unfortunately insufficient data are available at higher pressures to permit such a comparison at the highest pressures used in this study. Electron microscope replicas of fractured oxide sections did show evidence for pores of ~200Å diameter (Figure 18) in regions where a reasonably smooth fracture surface permitted such features to be readily seen. The reasons for ascribing this type of contrast to pores are shown diagrammatically in Figure 19.

Hydrogen uptake has not been measured routinely in this study, but metallographic evidence of hydride distributions has been obtained. The localisation of hydride to that end of a specimen which was oxidising most rapidly is seen in Figure 20. This emphasises the magnitude of the oxidation and hydrogen uptake rates, since to achieve this hydrogen distribution the rate of hydrogen uptake must exceed the rate at which the hydrogen can diffuse away through the metal. Considering the high diffusion coefficient for hydrogen at 600°C, this therefore represents a very high rate of uptake.

4. DISCUSSION

Johnson has made a more extensive study of the variables affecting the accelerated corrosion than those reported here. Thus the effect of nitrogen, indents in the specimen, surface contamination with aluminum and iron, and various surface preparations (including prefilming at 360°C) were studied by Johnson, but have not been studied here.

The general responses to temperature, pressure and heat treatment are in agreement in both studies, although the accelerated oxidation rates observed by Johnson are often much higher than those recorded here. However, both studies are in agreement in observing no effect at 400°C. At 450°C Johnson reports small (but significant) increases in oxidation of one batch of material, and at 475°C and above, all batches showed severe nodular attack.

In fact the nodular nature of the attack observed by Johnson and the penetrating internal oxidation accompanying it are the biggest differences between his work and that reported here. In our studies the accelerated oxidation usually occurred fairly uniformly over a large fraction of the specimen
surface. Examination of the metal/oxide interface in these regions showed no evidence for even incipient penetrating attack, and a topography differing only in degree, and not in kind from those features commonly seen on the inner interfaces of thick oxide films on zirconium alloys\(^\text{(16,17)}\). In detail the topographic features observed here (Figure 13) were more like those seen in previous studies of the metal/oxide interface on unalloyed zirconium than those of thick oxides on Zircaloy-2. This would support the previous contention\(^\text{(16,17)}\) that the hemispherical features, so prominent on the interfaces of thick oxides on zirconium, represented the inner ends of the large columnar crystallites which are usual in thick films on this metal, but are not normally seen in thick oxide films on Zircaloy-2\(^\text{(15)}\). However, apart from the appearance of these films in polarised light, no evidence was found for columnar oxide crystallites in these oxides, although isolated large crystallites of oxide were present to judge from the fractured oxide (Figure 12). Thus, the prominent hemispherical features at the metal/oxide interface of oxides formed in high pressure steam could not be related directly to the presence of columnar oxide crystallites.

The absence of any evidence for nodular and penetrating oxidation in this study, and the observation of just this type of attack during the oxidation of specimens contaminated with traces of nitrate the chloride salts\(^\text{(18,19)}\), raises the question of whether such contamination could have been (at least partially) the cause of some of the features observed by Johnson\(^\text{(13)}\). Our experience showed that at low temperatures in steam (i.e. near to the saturation point) it was relatively easy for this contamination to be washed off and for the severe localised attack to be thereby prevented\(^\text{(18)}\). At higher temperatures where the steam conditions are far from saturated it would be more likely for such attack to occur, although this would obviously be a function of the method of autoclave start-up, which would influence the probability of any contamination being washed from the specimens.

While it is clear that no conclusions can be reached on the question of the possible involvement of contamination in Johnson's observations, the absence of any nodular and penetrating attack in the studies here (which extend to higher pressures and temperatures than those of Johnson), and the very small amounts of contamination necessary to cause the penetrating attack (and its often nodular nature), must leave a question
mark over the results reported by Johnson.

In the studies reported here the primary differences between the oxide formed during normal and accelerated oxidation were those seen in the electron microscope and porosimeter studies. Thus, the latter suggest that porosity develops in the oxide film formed on Zircaloy-2 much more rapidly (at equivalent oxide thicknesses) in high pressure than in low pressure steam. Electron microscope studies\(^{(15)}\) have shown that, at low pressures, the sudden growth of large oxide crystallites (which seems to accompany the transition in the oxidation kinetics and the appearance of porosity) does not continue so as to produce long columnar crystallites in the oxide, but that a layer of small crystallites renucleates at the oxide/metal interface. This cycle of growth of large crystallites and renucleation of small ones then repeats\(^{(15)}\). In high pressure steam, only isolated large crystallites of oxide could be identified, although in polarised light the oxides had a clearly columnar aspect. Pores were more readily visible on replicas of these films than has normally been the case with oxide films on Zircaloy-2\(^{(20)}\). Their size (200-300Å dia) was generally larger than the smallest pores observed previously in post transition thermal oxides\(^{(20)}\), in agreement both with the present porosimeter results and their more ready visibility.

The present studies give no clues as to the manner in which steam pressure might be expected to affect oxide nucleation. There is no evidence for solubility of ZrO\(_2\) in either low or high pressure steam which would point to an effect on crystal growth similar to that observed in hydrothermal growth of refractory oxide crystals. Measurements on small single crystals of ZrO\(_2\) have shown that the surface electrical conductivity is greatly enhanced in the presence of water\(^{(21)}\), and it is possible that variations in this property with steam pressure may be sufficient to alter the normal oxidation processes via an effect on the electric field in the oxide. However, growth of crystallites in a polycrystalline compact is usually controlled by the slowest diffusing species, zirconium in this instance, and there is little evidence about the factors affecting the diffusion of this species in zirconia\(^{(22)}\).
The localisation of hydrogen, absorbed during rapid oxidation, in the regions of the specimen oxidising most rapidly (Figure 18) shows that the rate of hydrogen uptake must be large compared with the rate of diffusion of hydrogen in the metal. It is possible that the local accumulation of hydrogen and the stresses resulting from this could be the cause of the specimen disintegration reported by some authors (1,8-11). Disintegration due to hydrogen absorption during normal oxidation in low pressure steam has been reported previously (23).

5. CONCLUSIONS

Despite difficulties with sealing the high temperature/high pressure autoclaves sufficient results have been obtained to demonstrate the effect of steam pressure on the oxidation of Zircaloy-2 in the α-annealed and β-quenched conditions. These results confirmed the earlier prediction of an oxidation rate rising steeply with increasing pressure at 500 and 600°C. The results are in general agreement with those of Johnson, but do not show severely localised penetrating oxidation. The behaviour is explained on the basis of the observed changes in oxide crystallite morphology induced by the high steam pressures.

ACKNOWLEDGEMENTS

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REFERENCES


15. B. Cox and A. Donner, J. Nucl. Mat., to be published.


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Figure 1  Effect of pressure on Zircaloy-2 oxidation at 350°C
Figure 2 Oxidation of Zircaloy-2 (α-annealed) in 400°C steam
Figure 3  Oxidation of Zircaloy-2 (α-annealed) in 500°C steam
Figure 4  Oxidation of α-annealed Zircaloy-2 (Ac and Sh) at 600°C and various pressures.
Figure 5  Oxidation of Zircaloy-2 (β-quenched) in 500°C steam
Figure 6  Oxidation of Zircaloy-2 ($\beta$-quenched) in 600°C steam
Figure 7  Arrhenius plot of the oxidation rates for α-annealed Zircaloy-2 (Ac)
Figure 8  Effect of pressure on oxidation of Zr-0.5% Cu-0.5% Mo at 400°C.
Figure 9  Section through β-quenched Zircaloy-2 specimen oxidised at 600°C/5000 psi

Figure 10  Polarised light micrograph of part of specimen from Figure 9
Figure 11  SEM view of section of thick oxide.
Figure 12  E.M. replicas of fractured thick oxide
Figure 13 SEM micrographs of oxide/metal interface at $600^\circ$C/$5000$ psi compared with those formed on zirconium and Zircaloy-2 at low pressure. (a) Zircaloy-2, $600^\circ$C/$5000$ psi, thickest oxide (b) same, thinnest oxide, (c) Zircaloy-2 $600^\circ$C, (d) Zirconium, $500^\circ$C, 1 atm. (X3000).
Figure 14

SEM micrograph of voids between hemispherical features on the oxide/metal interface
Figure 15

A crack emerging at the oxide/metal interface without disturbing the topography
Mercury porosimeter traces for specimens oxidised to approximately equal oxide thicknesses at a range of pressures.
Figure 17  Mercury porosimeter traces for specimens with a range of oxide thicknesses formed at a pressure of 500 psig.
Figure 18

Pores seen in fractured section of oxide film. (x40,000)
Diagrammatic representation of formation of the characteristic contrast features of a pore

1. ZrO₂ film with pores of different diameter
2. Plastic layer produced by adding ½ - 1% Formvar solution
3. Strip plastic film using sticky tape
4. N.B. Plastic spikes break off at different levels depending on pore diameter
5. Shadow with Au/Pd alloy at 30°
6. Coat uniformly with carbon
7. Dissolve plastic to leave shadowed carbon replica
8. View in transmission E.M.
9. Collapsed "spike"
10. Appearance of 3 features above ZrO₂ film with pores of different diameter

Figure 19
Figure 20

Hydride distribution in specimen oxidising rapidly at one end.