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CORROSION MECHANISM OF
ZIRCONIUM AND ITS ALLOYS:

32
III. SOLUTE DISTRIBUTION BETWEEN
CORROSION FILMS AND
ZIRCONIUM ALLOY SUBSTRATES

D.L. DOUGLASS

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CORROSION MECHANISM OF ZIRCONIUM AND ITS ALLOYS:
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D. L. Douglass

ABSTRACT

Analyses of stripped corrosion films were performed by wet chemical methods, activation, and microprobe analysis. It was found that the amount of tin, niobium, and chromium in post-transition oxide films was directly proportional to the amount in the alloy. There was no measureable difference in film composition of a given alloy as a function of film thickness, and the combination of alloying elements in ternary alloys had no effect on the amount of a given element in the corrosion film.

Analyses of a pre-transition film in a Zr-1Cr binary alloy were made by using a tracer, Cr^{51} . No concentration differences in chromium were found in corrosion films formed in 400°C steam over a range of thickness from 7000 to 18,000 $\text{\AA}$. It was concluded that this alloy did not exhibit concentration changes in the substrate adjacent to the oxide film as found by Wagner for Ni-Pt alloys, and that diffusion of chromium in the metal was unimportant for this particular case.

The beneficial effect of chromium and harmful effect of both tin and niobium on post-transition corrosion rates can be associated with the amount of solute in the film, although no suitable mechanism for these effects can be found at present.

INTRODUCTION

The development of oxidation-resistant alloys has been empirical for the most part because there are no basic theories which would permit development from a fundamental approach. The Wagner-Hauffe rules ⁽¹⁻³⁾ have provided a starting point for metals which form semi-conducting oxide films. The effect of alloying additions in the metal has been analyzed with respect to the anticipated defect structure of the oxide after incorporating the alloying elements into the oxide. It is then possible to analyze the rate-controlling diffusion steps through the oxide for films of various compositions. Much of the analysis of oxidation of alloys has been done in terms of this theory, but no meaningful results can be obtained unless both the actual film composition and the diffusion rates of the proper species are known. There are no cases, to the knowledge of the author, in which both of these factors are known.

Until recently, there has been no way of determining film compositions in situ. It has been necessary to physically or chemically remove the film and subsequently analyze for each constituent. This technique has been successfully used with stainless steel, ^(4,5) although in these instances the diffusion rates of the rate-controlling species have not been determined. The advent of the electron microprobe analyzer has opened up new avenues of approach to this problem provided suitable oxide standards are available.

The development of zirconium alloys has been restricted for the above reasons. No suitable means of film removal have been available, and no data exist in the literature on microprobe analyses of oxide films. The results of microprobe analyses of corrosion films and of the analysis of stripped films of the same alloys by both wet chemical and by neutron activation techniques are reported here.

Another important question which must be considered is how the film composition changes during the course of oxidation. Wagner ⁽⁶⁾ has shown that solid solutions of widely differing oxidation potentials undergo preferential

oxidation which will lead to compositional changes in both the oxide film and in the alloy substrate. The results on films of different thicknesses (corresponding to either different times at a given temperature or different temperatures for a given time) which correspond to different stages of the oxidation process are described.

EXPERIMENTAL PROCEDURES

ALLOY PREPARATION

A binary alloy of zirconium containing Cr^{51} was prepared by consumable arc melting on a water-cooled copper hearth. The button was turned over after each melt and remelted seven times to ensure homogeneity. The button was hot-rolled at 750°C , pickled, cold-rolled, and annealed for 24 hours at 565°C . Crystal bar zirconium and electrolytic chromium were used as melting stock. The isotope of chromium was prepared from the same lot of chromium by irradiation in the General Electric Test Reactor.

Ternary alloys were prepared by consumable arc melting of electrodes. Melting was repeated three times. The ingots were canned in mild steel and extruded at 850°C . The jacketing was removed, the surface cleaned, and the alloys were cold-rolled to strip with intermediate anneals at 650°C . The final strip was cut into corrosion coupons, pickled, and annealed 24 hours at 800°C , and furnace-cooled.

CORROSION TESTS

Duplicate, and in some cases triplicate, samples were tested in both 360°C water and 400°C steam in Type-347 stainless steel autoclaves. De-ionized water of pH 7 was used. The samples were removed intermittently, weighed, and retested for periods up to 112 days.

FILM STRIPPING

Corrosion samples were abraded on the edges to expose the substrate metal and then subjected to metal dissolution in ethyl acetate-10% bromine solutions at 74°C. The substrate was completely dissolved within 1 to 2 hours, leaving the oxide films intact. The films were washed, rinsed, dried, and analyzed by either wet chemical methods, or irradiated and analyzed by neutron activation methods. Duplicate samples were run for each analysis; NBS standards were used as independent checks. The accuracy is given as $\pm 10\%$ of the amount reported.

ELECTRON MICROPROBE ANALYSIS

Some representative alloys were prepared for metallographic examination, the corrosion coupons were mounted perpendicular to the plane of section with the exception of two samples which were mounted as taper sections. The samples were ground through 6-micron diamond dust and attack-polished with dilute HF solution with Linde A abrasive. No etch was used. The mounts were thinned to the maximum value handled by the probe and then vapor-coated with aluminum in a coating unit used for electron microscopy shadowing.

Microprobe traverses were performed on an ARL microprobe at both the ARL laboratories in Glendale, California and at NMPO (General Electric) in Cincinnati, Ohio. Continuous traverses were made at the rate of 8 microns/minute with a multiplexing device to determine and record data from three elements in rapid succession. Suitable standards were not available, therefore, no corrections were made to the data for either fluorescence or absorption. Data will be presented in a comparative fashion; all the samples were run under identical settings.

RESULTS

CORROSION TESTS

The corrosion behavior of all alloys studied is shown on double logarithmic plots of weight gain versus time in Figures 1, 2, and 3. Linear plots of the individual samples of two Zr-Nb-Sn alloys are shown in Figures 4 and 5. There should not be too much significance placed on the log-log plots for the reasons suggested by Cox,⁽⁷⁾ but it is apparent that all the ternary alloys were in the post-transition period of the corrosion process. From the mechanistic point of view this means that either the reactants had direct access to each other (the film was no longer a physical barrier) or that the film possessed an effective thickness for diffusion which remained constant.

If the corrosion kinetics, which indicated that the reaction was linear, were indicative of a constant diffusion thickness in the oxide film we might expect to see concentration changes as a function of film thickness for the reasons suggested by Wagner.⁽⁶⁾ On the other hand, if the reaction were zero order for which case the reactants would be directly accessible to each other, we would not expect to observe changes in composition with thickness. Therefore, it was decided to study an alloy which was known to corrode by some process involving diffusion. However, the thickness of films over the range of interest is so small that it would be very difficult to obtain enough mass for accurate analyses. This problem was circumvented by using a radioactive tracer, Cr^{51} , which was added to a Zr-1 Cr alloy. The corrosion kinetics for this alloy (Figure 3) indicate that a quartic rate law was followed in which $\Delta W = kt^{1/4}$. A test plot of ΔW^4 versus time gave a nearly linear relationship. There is no accepted mechanism for a gas-solid reaction which follows the above time law, although it is generally agreed that the reaction product forms a protective barrier and that some diffusion process is involved.

Figure 1. CORROSION BEHAVIOR OF Zr-Sn-Nb ALLOYS

Figure 2. CORROSION BEHAVIOR OF Zr-Cr-Sn AND Zr-Cr-Nb ALLOYS

Figure 3. CORROSION BEHAVIOR OF Zr-1 Cr ALLOY IN 400°C STEAM

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FILM COMPOSITIONS

A summary of corrosion conditions, alloy compositions, film thickness, and the film compositions, which have been converted to atomic percentages, are listed in Table 1. The film compositions were calculated by assuming that the cations substituted for zirconium in the film and that the total cation content was equal to the amount present in stoichiometric zirconia. Any departures from stoichiometry with respect to anions would give a negligible change in the stated film compositions.

The film compositions are plotted against the alloy compositions in Figure 6 and show a linear relationship. The amount of solute in the film is directly proportional to the amount in the alloy regardless of which elements were combined in the alloy. For example, the chromium could be combined with tin or with niobium, and the proportionality still existed.

TABLE 1. CORROSION FILM COMPOSITIONS

Alloy Composition, at.%			Corrosion Conditions					Film Compositions, at.%			
Cr	Nb	Sn	Temperature, °C	Medium	Exposure, Days	ΔW , mg/dm ²	Film, μ	Sn Neutron Activation	Cr (Chemical Analysis)	Neutron Activation	Nb (Chemical Analysis)
0.91	--	1.94	360	water	112	56.7	3.8	0.71 0.57	0.40	0.25 0.25	--
0.91	--	1.94	400	steam	105	3620	240	0.75 0.63	0.40	0.37 0.39	--
3.92	--	2.12	360	water	100	183	12	0.69	1.56	1.42	--
3.92	--	2.12	400	steam	100	680	45	0.91 0.80	1.60	1.43	--
1.91	2.40	--	360	water	112	128	8.5	--	0.70	0.69	1.01
1.91	2.40	--	400	steam	105	328	22	--	0.72	0.71	0.81
--	0.67	1.94	360	water	98	67.6	4.5	0.51	--	--	0.27
--	0.67	1.94	400	steam	98	302	20	0.47	--	--	0.28
--	1.92	1.94	360	water	112	108	7.2	0.81	--	--	0.70
--	1.92	1.94	400	steam	105	410	27	0.53	--	--	0.58
--	1.97	2.98	360	water	100	138	9.1	0.90 1.10	--	--	0.80 0.81
--	1.97	2.98	400	steam	100	549	36	0.97 1.21	--	--	0.87 0.87
Zr-2*	--	1.23	360	water	112	36.8	2.5	0.37	0.08	--	--
Zr-2*		1.23	400	steam	105	126	8.3	0.25	0.08	--	--

* Zircaloy-2

Figure 4. LINEAR PLOT OF CORROSION BEHAVIOR OF Zr-2Sn-2Nb ALLOYS

Figure 5. LINEAR PLOT OF CORROSION BEHAVIOR OF Zr-3 Sn-2 Nb ALLOYS

FIGURE 6. RELATIONSHIP BETWEEN POST-TRANSITION CORROSION FILM COMPOSITIONS AND ALLOY COMPOSITIONS

The results for the tin analyses (Figure 6) were obtained by neutron activation, and considerable scatter existed. A scatter band was thus drawn rather than a single line. The data for niobium were obtained by chemical analyses because the energies of activated niobium were too close to those of zirconium to permit a determination of the niobium by neutron activation. To use this method of analysis for niobium it would be necessary to separate niobium from zirconium chemically before the counting was performed. The chromium results were obtained by both chemical and neutron activation analyses, and the agreement was excellent (Figure 6).

Chemical analyses for tin proved to be erratic and subject to certain errors which were difficult to eliminate. Reproducibility could not be obtained in the chemical analyses, but it was found that neutron activation gave reproducible results, therefore, only the neutron activation data are presented.

Microprobe traverses were made on two Zr-Nb-Sn alloys for two film thicknesses (Figures 7 and 8). The concentrations are given in terms of relative amounts because there were no suitable standards with which fluorescence and absorption corrections could be made. To enable comparisons to be made from one sample to another identical settings on the probe were used. The small concentration of alloying elements necessitated a high sensitivity on the instrument which resulted in a noticeable increase in background. Background levels were established for both metal and oxide by using pure zirconium and pure ZrO_2 , respectively. The electron beam was held on a given area for several minutes to give a band which includes the statistical variations. It is then possible to note slight increases in concentrations above the background bands. These bands are shown also in Figures 7 and 8 as cross-hatched areas.

Figure 7. Zr-2Sn-2Nb MICROPROBE TRAVERSES OF CORROSION SAMPLES

Figure 8. Zr-3Sn-2Nb MICROPROBE TRAVERSES OF CORROSION SAMPLES

The niobium traverses in both oxide and metal gave values which were either partially or wholly within the background band. The niobium K- α , line was used, the wavelength of $0.746 \text{ \AA}$ being very close to $0.786 \text{ \AA}$ for the zirconium K- α , line. Although these lines are far enough apart for detection, the intensity of the white radiation from the major constituent, zirconium, is about the same intensity of the niobium K- α radiation, and the detection of small differences in niobium concentration in a zirconium matrix, therefore, is almost impossible.

The tin traverses were made with the L- α , line of tin of wavelength $3.600 \text{ \AA}$. This value is in the low-intensity portion of the continuous white radiation of zirconium, and the peak-to-background ratio was sufficiently high for detecting tin variations. The variation of the tin content of the alloy is seen to vary rather widely over small distances and may be attributed to the difference in tin content between the two phases within the alloy substrate. It was not possible to correlate the variations in microstructure because the beam diameter of 2 microns was slightly larger than the size of the second-phase particles. The beam overlapped the particles and gave a semi-integrated value of matrix and second phase.

The difference between 2 and 3 at. % tin in the two alloys was readily detected for identical traverse conditions. The 2 at. % tin gave a value of 47 to 48 ± 5 units, whereas the 3 at. % tin gave a value of about 56 ± 5 units. The tin content of the 3 at. % alloy film was higher than that of the 2 at. % alloy film which agrees with the results obtained by neutron activation. The tin content did not vary between films of different thicknesses which were formed at the two different corrosion temperatures.

Long time scans of the film formed at 400°C on the Zr-2Sn-1Cr alloy indicated that the chromium concentrations were higher in some portions of the film compared to other parts, but it was not possible to determine the extent of the differences. It can thus be concluded that the films were not entirely homogeneous.

The metallographic appearance of the corrosion films which were examined with the microprobe is seen in Figure 9. The films generally appear to be free of substructure and to have a uniform thickness. There was no evidence of selective penetration of the alloy during oxidation.

It was also of interest to examine the surface of the oxide films to establish the existence of cracks or second-phase particles. Electron micrographs of surface replicas made directly from the corrosion sample surface are shown in Figure 10. Cracks may be seen at some grain boundaries and in some cases at the site of the second-phase particles in the alloys. The oxide films are generally replicas of the metal surface, and the apparent presence of the second-phase particles in the oxides is due to different thicknesses of the oxide which were caused by differences in oxidation rate between the metal matrix and the second phase.⁽⁸⁾

All of the results so far have pertained to post-transition corrosion films, which as stated earlier should not show any difference in composition as a function of thickness if the reaction occurred by a zero order (linear reaction) process. The only pre-transition alloy studied was the Zr-1Cr alloy which contained Cr⁵¹. This was found to have a constant composition as indicated by a constant amount of tracer in the films. The stripped films varied in thickness from about 7000 Å to about 18,000 Å, and the tracer concentration was that which gave about 1.25×10^6 counts/min/g of oxide. There was no evidence that enrichment or depletion of the pre-transition corrosion film had occurred.

DISCUSSION

The results of three types of analyses, chemical, neutron activation, and microprobe, show that the concentration of the alloying constituents in the corrosion film is dependent upon the amount present in the alloy. It makes little difference whether a given element is in combination with a second or third element in the alloy; the proportionality still holds. There seems to

112 Days 360°C

500X

105 Days 400°C

500X

Zr-2Nb-2Sn

100 Days 360°C

500X

100 Days 400°C

500X

Zr-2Nb-3Sn

112 Days 360°C

500X

Taper Section, 45°

105 Days 400°C

150X

Zr-2Sn-1Cr,

Figure 9. CORROSION FILMS OF SOME TERNARY ZIRCONIUM ALLOYS

98 Days 360°C

2000X

98 Days 400°C

2000X

Zr-1Nb-2Sn

100 Days 360°C

2000X

100 Days 400°C

2000X

Zr-2Nb-3Sn

112 Days 360°C

2000X

Zr-2Sn-1Cr

Figure 10. ELECTRON MICROGRAPHS OF OXIDE FILM SURFACES

be no measureable change in concentration with film thickness for both pre-transition or post-transition corrosion films. It appears that corrosion proceeds by a uniform advancement of the oxide film which consumes the metal substrate without causing any concentration changes in either metal or oxide.

These results clearly show that the classical type of diffusion in the metal substrate observed by Wagner in Ni-Pt alloys does not play a role in zirconium alloy corrosion under the conditions used in this study. This conclusion is not too surprising in view of (a) the low solubility of alloying elements in alpha zirconium, and (b) the extremely high affinity of zirconium for oxygen compared to that of the additions.

The low solubility of the alloying additions in zirconium results in the formation of intermetallic compounds in which the local concentration of additions is high. The alloy-poor matrix is oxidized by a reaction which occurs at the oxide-metal interface which advances uniformly into the metal. The small intermetallic particles are occluded by the oxidized matrix and are either oxidized and dissolved or dissolved directly into the oxide layer. The inhomogeneities which were observed in the probe analyses are indicative of the fact that the alloy-rich regions corresponding to the particles have not completely diffused throughout the oxide to give a homogeneous solution. No evidence of any other oxide phase has been detected by x-ray diffraction; therefore, it is logical to conclude that in the absence of other equilibrium oxide phases composition variations will become less if sufficient time for homogenization is provided.

The high affinity of zirconium for oxygen results in the oxidation of the alloy at a rate which is significantly greater than the diffusion rates of the additions in zirconium, and thus there is no opportunity for concentration gradients to build up in the substrate near the interface.

It has been observed in other investigations that the effect of tin on the steam corrosion rate of zirconium-tin alloys was to increase the rate with increasing tin content.⁽⁹⁻¹³⁾ In view of the experimental observations noted in this investigation, that the tin content of the film increases with tin content of the alloy, it appears that the harmful effect of tin on the corrosion rate is associated with the tin content of the film.

The reason for the above-mentioned behavior is not clear. Porte, et al.,⁽¹²⁾ have studied the oxidation of three tin-containing alloys in 700°C oxygen and found that the alloys, which contained up to 3.6 at. % tin, oxidized according to the cubic rate law and that little difference existed between the rate constants of the various alloys. However, breakaway was observed for all three alloys, whereas no breakaway was observed within the same time interval of 1400 minutes for pure zirconium. The time for breakaway decreased with increasing tin content, and the post-breakaway oxidation rate was higher for the alloys with the highest tin content. Porte, et al., suggested that the breakaway phenomena is related to the ionic size of the alloying additions and that insoluble additives become separate agglomerates of additive metal oxide located in the zirconium dioxide film. The correlation with ionic size differences is poor, and the reason given⁽¹²⁾ for the film breakdown seems doubtful. They⁽¹²⁾ hypothesized that the lattice distortions in the film, which came from incorporating solutes with different basis radii, will result in cracking the highly stressed film. It would appear from measurements of oxide plasticity at 700°C that the film should be sufficiently ductile to accommodate the epitaxial strains.⁽¹⁴⁾ As pointed out, the embrittlement of the substrate by oxide dissolution may be the factor that determines if the oxide film cracks. It would then be logical to examine the effect of tin on either the embrittlement of the zirconium alloy by oxygen dissolution or on the effect of tin on oxygen diffusion in the metal.

Niobium generally decreases the oxidation resistance of zirconium in steam^(10,11,13,15) and in oxygen,⁽¹²⁾ although the exact influence is strongly affected by the heat treatment of the alloys which can markedly change the constitution.^(15,16) Only monoclinic zirconia was observed in the present work, but Zmeskal and Brey⁽¹⁷⁾ have observed both the monoclinic and orthorhombic oxide, $6\text{ZrO}_2 \cdot \text{Nb}_2\text{O}_5$, in oxide film of alloys containing as little as 2% Nb. Porte, et al., have observed an unknown oxide phase during oxidation of a Zr-1.8Nb alloy at 700°C. There is a correlation between the appearance of a second oxide phase and the decrease in oxidation resistance of Zr-Nb alloys in oxygen.

The steam corrosion behavior is not as obvious. Dalgaard⁽¹⁵⁾ has detected only the monoclinic form of zirconia in the oxide films formed during steam corrosion of Zr-2.5Nb. Klepfer,⁽¹⁰⁾ Weinstein,⁽¹¹⁾ Richter and Tverberg,⁽¹⁶⁾ and Douglass⁽¹⁸⁾ have all observed decreased corrosion resistance in steam with increasing niobium content, and no observations of a second oxide phase have been reported in any of these investigations. In all cases transitions have been found, and because the film analyses reported in this study were all made on post-transition corrosion films it remains to establish how an increase in the niobium content of the films is related to increases in the post-transition corrosion rates.

The lack of a suitable theory to explain transition phenomena during corrosion and oxidation of zirconium alloys precludes an explanation of the behavior of niobium and tin additions. Also, the beneficial effect of chromium cannot be explained in terms of any mechanism. In conclusion, we can only say that corrosion resistance is improved by incorporating chromium into the oxide film, whereas, corrosion resistance is decreased when the tin and niobium contents of the film increase. Fortunately, the direct proportionality between film composition and alloy composition enables the selection of alloying additions to be made more readily.

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