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Anodic oxidation of zircaloy-2

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The anodic polarization of zircaloy-2 in different electrolytic baths has been investigated in order to obtain thick oxide films with properties suitable for wear applications.

The operative conditions to obtain hard, thick, compact oxide films resistant to thermal shocks have been determined. The influence of the bath composition and temperature on the oxide growth is reported.

1. Introduction

The severe operating conditions in high temperature pressurized water reactors often cause unavoidable serious damage due to crevice corrosion, wear and spalling to intermittently moving parts. Many efforts have been made to overcome these difficulties by a proper material selection [1–4]. Watson [5], searching for new materials or coatings for metallic surfaces operating in water-lubricated mechanisms, observed that alloys such as zircaloy-2, supporting thick oxide layers, offer many advantages. The main problem was to find out proper conditions to avoid cracking and spalling of the oxide during the thermal oxidation. Watson observed that the most convenient way of forming homogeneous and compact oxide layers on zircaloy-2 was by air-blasting the surface of the alloy with hard abrasive grit of a given particle size, followed by oxidation in air at 650° C for 24 h or more.

It must be pointed out that zirconium oxide is soluble in the underlying metal matrix at temperatures $> 450^\circ$C, with consequent worsening of the mechanical properties of the alloy [6]. In order to avoid this, we have undertaken a study on the possibility of obtaining thick oxide films on zircaloy-2 by anodization in appropriate electrolytic baths.

A survey of the data reported in the literature indicated that the maximum thickness of anodic oxides in zircaloy-2, obtained in a great number of electrolytes by different authors, was in the range of 1–2 μm [6], well below the values which are obtained by thermal oxidation [5].

As regards zirconium metal, Rozenfeld [7] obtained relatively thick oxide films by anodization in 60% nitric acid at room temperature, but the adherence and compactness of the films were generally poor: 15 μm films cracked spontaneously. Similar results were reported by Misch [8].

In a previous work we obtained thick oxide films on aluminum by anodization in mixtures of fused alkali nitrates [9–12]. These oxides exhibited mechanical properties and corrosion resistance in different environments comparable to or higher than those of oxides prepared in conventional electrolytic baths. Fused nitrate baths have also been used to study the growth kinetics of oxide films, without any current applied, on zirconium alloys [13–16] since this environment was considered the most suitable to simulate thermal oxidation conditions. Furthermore, according to Hardy-Grena [17], the resistance to hydrogen embrittlement of certain zirconium alloys would improve after prolonged contact with fused nitrates, without applied current.

Taking into account all the previous observations, we have undertaken a study to prepare thick oxide films on zircaloy-2 in different fused mixtures and concentrated nitric acid, at various temperatures.

2. Experimental

The samples to be anodized (10 mm diameter x 10 mm length) were cut from a zircaloy-2 rod (CEFILAC) the composition of which is reported in Table 1. The sample surfaces were degreased in trichloroethylene, ground with 240 and 400 grit

Table 1. Chemical composition of the Zy-2 rod

Element	ppm	*Element*	%
H	5	O	0·12
N	36	Cr	0·10
Ca	< 30	Fe	0·16
Mg	< 20	Ni	0·06
Cl	< 20	Sn	1·2
Hf	< 84		

Table 2. Preparations of the Zy-2 sample surfaces before anodization and corresponding roughness values

Surface preparation	*Roughness* (μm)
Polishing with 240, 400 SiC papers	0·25
Polishing with 240, 320, 400, 600 SiC papers	0·25
Polishing with SiC papers and diamond pastes	0·2
Polishing with SiC papers and pickling in HF-HNO$_3$	0·2
Machining	1
Machining	2
Machining	3

SiC papers, rinsed in soap water, washed with water and alcohol, weighed and mounted in a Stern–Makrides teflon compression gasket assembly [18]. The investigation on the possible influence of surface roughness on the anodic oxide growth was performed by varying the previous procedure, as indicated in Table 2.

NaNO$_3$ (45 mol %)-KNO$_3$ and KNO$_3$ (44·2 mol %)-NaNO$_2$ (48·9 mol %)-NaNO$_3$ mixtures were used for tests conducted at high (250–280° C) and moderately high (150–200° C) temperatures. The pure salt [Ca(NO$_3$)$_2$·4H$_2$O] was used for operation at lower temperatures (70–100° C). Aqueous solutions were prepared from reagent grade chemicals (ERBA RP) and Analar water.

The cell was a cylindrical pyrex vessel, with a teflon cover, through which electrodes, gas inlet and outlet and thermometer (or thermocouple) could be introduced. The cathode was a large platinum gauze concentric to the anode. A large platinum sheet was used as the reference electrode. The electrolyte was vigorously stirred by a flow of dry nitrogen. The high temperature tests were performed in a furnace assembly similar to that described elsewhere [9]. The temperature was regulated to within ± 1° C. Constant current anodizations were performed by a potentiostat-galvanostat 146LC (GAI-Roma). Voltage-time curves were recorded by an HP7100BM strip chart recorder connected to a Keithley 610C electrometer. Oxide film thicknesses higher than 2 μm were measured by an optical microscope (Reichert model: Metavert). Microhardness measurements were performed by a Durimet (Leitz). X-ray analyses (CuK$_\alpha$) were performed by a Phillips RX diffractometer.

3. Results and discussion

3.1. *Anodization in fused salts*

Black oxide layers, 15–30 μm thick, brittle and incoherent, were obtained by anodizing zircaloy-2 samples at constant current in the fused mixtures

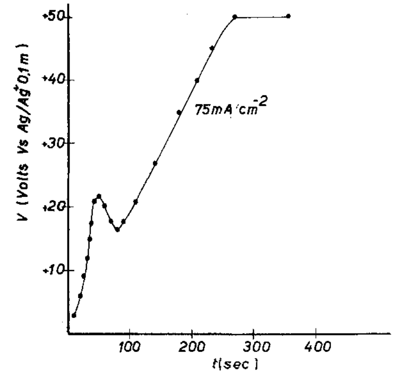

Fig. 1. Anodic polarization curve of Zy-2 in NaNO$_3$–KNO$_3$; $T = 260°$ C, $i = 75$ mA cm^{-2}.

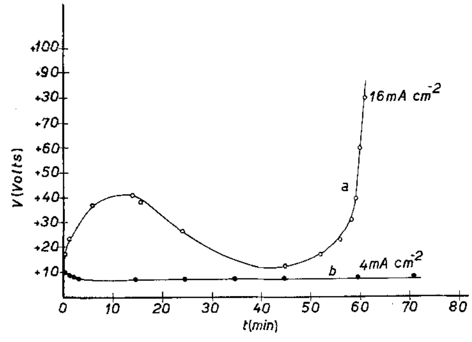

Fig. 2. Anodic polarization curve of Zy-2 in NaNO$_3$–NaNO$_2$–KNO$_3$; $T = 170°$ C (a) $i = 16$ mA cm^{-2} ; (b) $i = 4$ mA cm^{-2}.

$NaNO_3$–KNO_3 at 250–280° C, and $NaNO_3$–KNO_3–$NaNO_2$, at 160–200° C. The shape of the voltage-time curves was of the type reported in Figs. 1 and 2. It was observed that at the voltage peak the black oxide flaked off and the following voltage rise corresponded to the formation of a thin (< 1 μm) oxide film. At lower applied currents (Fig. 2b) the oxide yield was very low. X-ray diffraction data revealed the presence of monoclinic zirconia and traces of the tetragonal phase. The micrograph of the section of a sample anodized in a nitrate-nitrite fused mixture at 170° C is shown in Fig. 3. The oxide layers are clearly barely compact; microhardnesses as low as 100 VHN were measured.

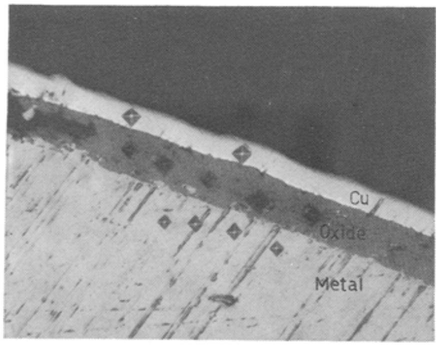

Fig. 3. Micrograph of the cross-section of a Zy-2 sample, anodized in $NaNO_3$–$NaNO_2$–KNO_3 at 170° C.

Similar results were obtained by anodizing zircaloy-2 samples in fused tetrahydrate calcium nitrate, at temperatures in the range 70–100°C. The voltage-time curves were of the type reported in Fig. 4.

Suitable conditions to obtain thick, hard and compact oxide layers were not found by operating over a wide range of temperatures, electrolytic bath compositions and at different values of applied current or voltage.

3.2. *Anodization in concentrated nitric acid*

Preliminary tests indicated that anodizing zircaloy-2 samples in 65% nitric acid gave rise to the formation of black oxide layers, which were relatively thick, hard and compact, unlike the films obtained on pure zirconium metal [7, 8]. Therefore a systematic investigation at different temperatures and applied currents was undertaken, to establish the most suitable conditions for oxide film thickening. The results obtained are reported in Table 3 and Figs. 5–8. The following observations can be made.

Operating at 0° C and at applied currents higher than 1·8 mA cm^{-2}, all the voltage-time curves exhibited a voltage plateau, the height and length of which depended upon the value of the applied current; then the voltage increased rapidly up to values higher than + 100 V (Fig. 5). The voltage plateau was associated with the growth of the thick film. The following sharp voltage increase corresponded to the breakaway of the thick black oxide. In this case the sample surface was found to be covered by a thin barrier-type film (< 1 μm).

Micrographs of the section of a zircaloy-2 specimen anodized at 0° C are reported in Fig. 9. The oxide hardness ranged between 650 and 800 VHN, depending upon the anodization conditions.

The potential-time curves, corresponding to anodizations performed at 0° C on specimens with

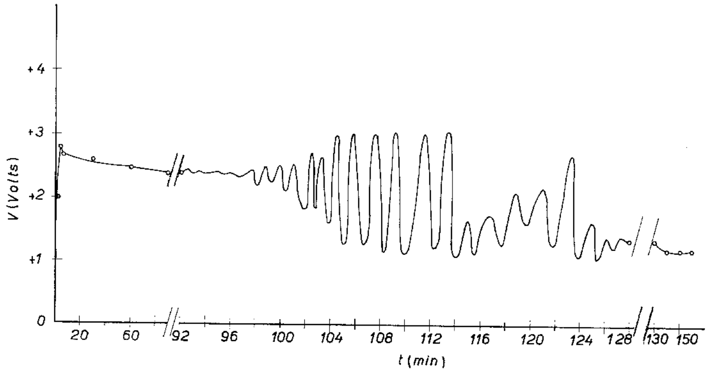

Fig. 4. Anodic polarization curve of Zy-2 in $Ca(NO_3)_2 \cdot 4H_2O$; $T = 70°$ C, $i = 2{\cdot}1$ mA cm^{-2}.

Table 3. Anodization characteristics of Zy-2 samples in 65% HNO_3

Test no.	*Temperature* (°C)	*Applied current* ($mA\,cm^{-2}$)	*Time* (min)	*Passed charge* ($C\,cm^{-2}$)	*Optical thickness* (μm)	Δp (mg)	$\frac{\Delta p_{\text{theor.}}}{\Delta p_{\text{exper.}}}$
C-46	−6	2·10	169	21·2	*	–	–
C-31	0	4·17	104	26·0	*	–	–
C- 2	0	3·14	124	23·4	15·0	–	–
C-41	0	3·14	94	17·7	8·5	–	–
C-23	0	2·65	132	21·0	18·0	–	–
C- 3	0	2·10	289	36·2	30·0	6·10	2·95
C-36	0	2·10	232	29·1	–	4·50	3·10
C-33	0	1·74	159	16·6	12·0	2·30	3·48
C-34	0	1·74	413	43·1	30·0	7·30	2·88
C-38	0	1·74	83	8·7	3·4	–	–
C-39	0	1·74	88	9·2	4·4	–	–
C- 5	0	1·57	331	31·2	22·0	4·95	3·03
C-51	0	1·57	555	52·3	32·0	–	–
C-54	0	1·57	550	52·0	30·0	8·10	3·10
C-30	25	2·10	131	16·4	15·0	–	–
C-43	50	2·10	286	35·9	26·0	–	–
C-44	60	2·10	114	14·3	12·0	–	–

* Sample anodized up to $V > 100$ volts.

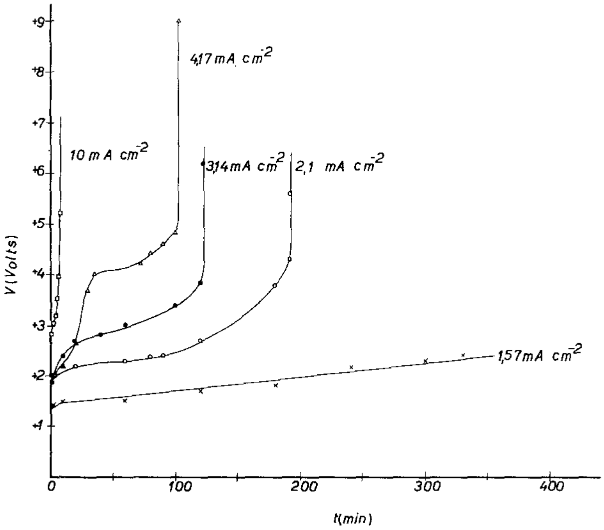

Fig. 5. Anodic polarization curves of Zy-2 in 65% HNO_3, $T = 0°$ C.

different surface finishes, are reported in Fig. 6. The different procedures followed for the surface preparation are described in Table 2. The comparison between the potential-time curves reported in Figs. 5 and 6 indicates that the different surface treatments do not have a marked influence on the oxide growth. This was confirmed also by the microscopic examination of the samples: the adherence of the oxide to the parent metal and its following growth are similar in all the cases investigated.

The results of tests performed at different temperatures, at the same applied current, are reported in Figs. 7 and 8. It can be seen that upon increasing the temperature the voltage levels off at less noble values. Furthermore at 25° C the voltage starts to increase after a much shorter time interval than at 0 and −6° C. In the range 50–70° C the

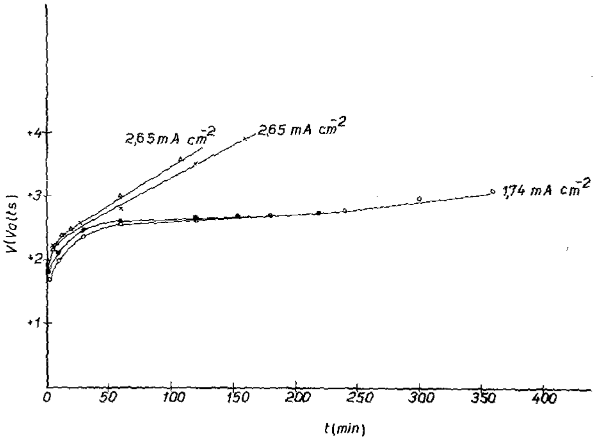

Fig. 6. Anodic polarization curves of Zy-2 samples with different surface finishes, in 65% HNO_3, $T = 0°$ C. ΔΔ machined, roughness = 1 μm; ×× machined, roughness = 3 μm; ○○ polished (diamond pastes), roughness = 0·2 μm; ●● pickled (HF-HNO_3), roughness = 0·2 μm.

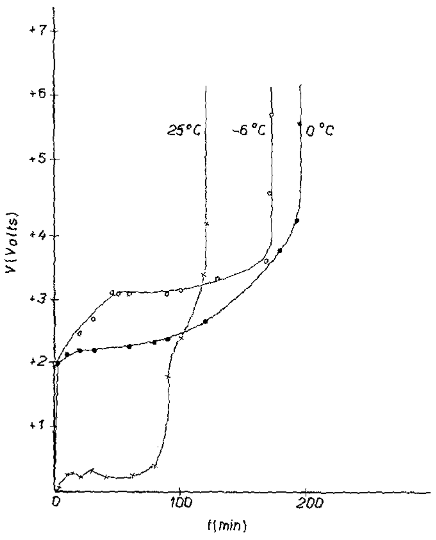

Fig. 7. Anodic polarization curves of Zy-2 in 65% HNO_3 at different temperatures; $i = 2{\cdot}1$ mA cm^{-2}.

shape of the potential-time curves resembles that obtained in fused calcium nitrate tetrahydrate, at the same value of applied current. Nevertheless some differences are evident on comparing the plots of Figs. 4 and 8. In nitric acid no voltage peak is observed and the voltage levels off at values markedly lower than in calcium nitrate; although for a given time interval the curve approximates a sinusoid, the voltage increases continuously. Visual and microscopic observation of the sample after anodization showed that the oxide layers appeared less incoherent and more adherent to the parent metal than the films obtained in calcium nitrate.

Assuming that the ohmic drop in the electrolyte is negligible as compared to the resistance of the growing oxide film, the voltage variations, in galvanostatic operation, are a measure of the electrical resistance of the film. By interruption of the anodization before the sharp voltage increase and

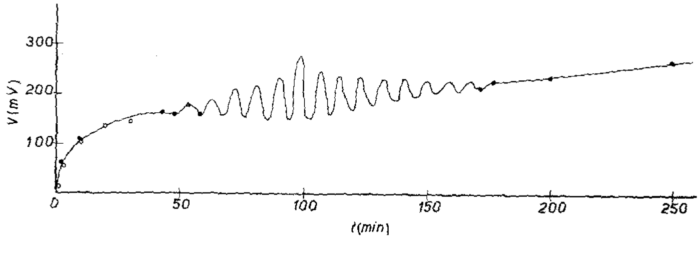

Fig. 8. Anodic polarization curves of Zy-2 in 65% HNO_3, $i = 2{\cdot}1$ mA cm^{-2}. ○○ $T = 70°$ C; ●● $T = 50°$ C.

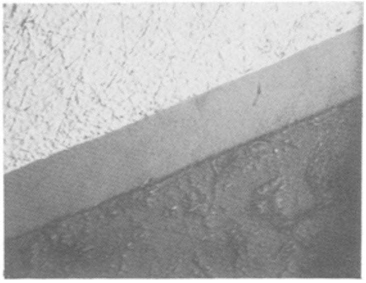

Fig. 9. Micrograph of the corss-section of a Zy-2 sample anodized in 65% HNO_3 ; $T = 0°$ C, $i = 1{\cdot}57$ mA cm^{-2}.

measuring the oxide thickness, it was found that the resistivity of the film formed in 65% nitric acid varied approximately from $2{\cdot}5 \times 10^5$ Ω-cm at 50–70° C to $5{\cdot}0 \times 10^5$ and $2{\cdot}5 \times 10^6$ Ω-cm at 25 and 0° C respectively.

A linear relationship was found between the weight gain of the samples anodized at 0° C and at different applied currents and the charge passed (Fig. 10). Nevertheless, the weight gain was only one third of the theoretical value for oxide formation (Table 3). The charge passed was directly proportional to the oxide thickness (Fig. 11). This was also so at different temperatures (Fig. 12).

Nevertheless it was observed that the optical thickness of the oxide coatings was greater than the values calculated on the basis of the weight gains and using the density value of the stoichiometric oxide ZrO_2 ($d = 5{\cdot}68$ g cm^{-3}). This would indicate a certain degree of porosity of the films. Furthermore, where the oxide thicknesses are in the order of 30–35 μm, the proportionality between charge passed and weight gain does not seem to be still valid, as indicated by comparing the tests C-3, C-34, C-51, C-54 (Table 3).

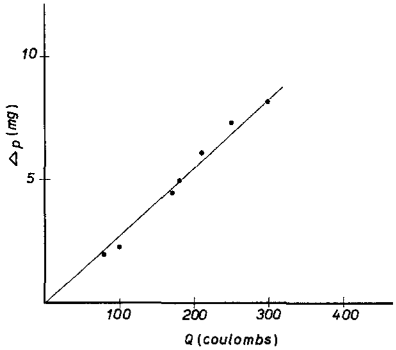

Fig. 10. Weight gain versus charge passed of Zy-2 samples anodized in 65% HNO_3; $T = 0°$ C.

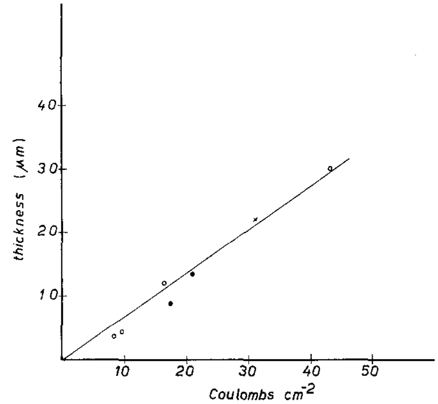

Fig. 11. Oxide thickness versus charge passed of Zy-2 samples anodized in 65% HNO_3, $T = 0°$ C. ○○ $i = 1{\cdot}74$ mA cm^{-2} ; ×× $i = 1{\cdot}57$ mA cm^{-2} ; ●● $i = 3{\cdot}14$ mA cm^{-2}.

The microscopic examination of the sections of various samples showed that the oxide coatings obtained at 50–70° C were less compact that those prepared at lower temperatures (Fig. 13a and b).

Several samples were submitted, after anodization, to repeated thermal cycles, between 20 and 350° C. This treatment did not affect at all the adherence and compactness of the oxide films.

In agreement with the observations of different authors [19, 20], X-ray diffraction analysis of the oxides prepared under different experimental conditions showed, in all the cases, the presence of monoclinic and amorphous zirconium oxide. The (1 1 1) peak of the tetragonal phase was also present, but tended to disappear when the film thickness increased [20].

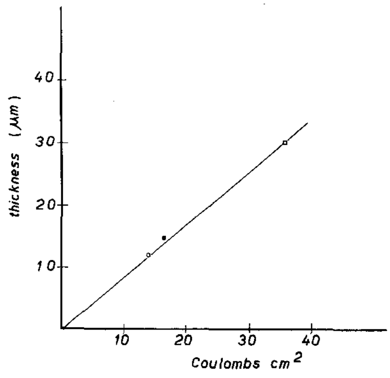

Fig. 12. Oxide thickness versus charge passed of Zy-2 samples anodized in 65% HNO_3, $T = 0°$ C, $i = 2{\cdot}1$ mA cm^{-2}. □□ $T = 0°$ C; ●● $T = 25°$ C; ○○ $T = 60°$ C.

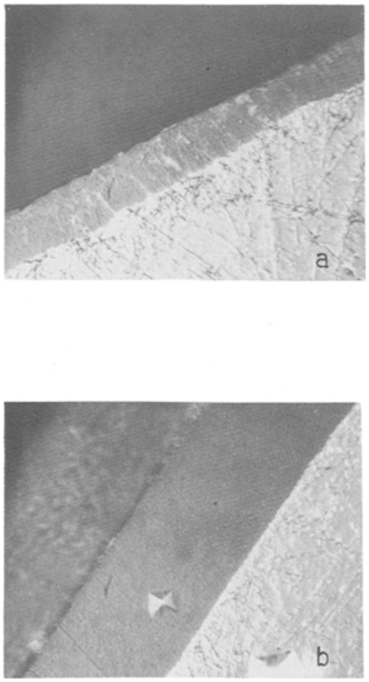

Fig. 13. Micrographs of the cross-section of Zy-2 samples anodized in 65% HNO_3, $i = 1{\cdot}57\,\mathrm{mA\,cm^{-2}}$. (a) $T = 60°\,C$; (b) $T = 0°\,C$.

4. Conclusions

The growth of thick oxide films on zircaloy-2 samples by anodization appears to depend upon the use of electrolytic baths containing high concentrations of nitrate ion. In fact Misch [8], anodizing pure zirconium metal in concentrated nitric acid, obtained thick oxide films, which cracked spontaneously, while in more diluted (15%) nitric acid only very thin and brittle films could be prepared.

The presence of water in the electrolytic bath is also important, as is evidenced by the results of the tests which were carried out in concentrated nitric acid, tetrahydrate calcium nitrate and fused alkali nitrates.

The results of the present work indicate that by anodizing zircaloy-2 in 65% nitric acid, at 0° C and at low applied current, it is possible to obtain an oxide film presenting such characteristics of compactness, hardness and thickness to make it probably suitable as wear resistant material.

Acknowledgements

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