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INTERNAL STRESS IN GROWING ZrO_2 FILMS

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Summary

The anodic and open-circuit stresses were studied during the potentiostatic anodic oxidation of zirconium. The anodic stress, *i.e.* the superposition of growth and electrostrictive stresses, was found to be compressive whereas the open-circuit stress was found to be tensile in the growing zirconium oxide. For a constant value of anodization time, the anodic stress was observed to decrease and the open-circuit stress to increase with increasing thickness of the growing zirconium oxide.

1. Introduction

When valve metals such as the tantalum, niobium, aluminium and zirconium are anodized to form barrier anodic oxides, the growth of these oxides is accompanied by the development of internal stress in the growing oxides. These stresses may be either tensile or compressive and may reach values high enough to break the growing oxides. Therefore, the origin and sequences of stress effects during the anodization of valve metals are subjects of considerable research interest.

The internal stress in the anodizing valve metals can be divided into three types: (1) the open-circuit stress which mainly depends on the surface morphology of the metal surface, (2) the growth stress which is due to the ionic migration during the anodic oxide growth and (3) the electrostrictive stress which is proportional to the square of the applied electric field during the anodization process.

Until now, the majority of investigators have measured the open-circuit stress in different anodic oxides of valve metals after galvanostatic oxide growth, *i.e.* when the applied current was kept constant and the voltage across the growing oxide increased with increasing anodization time.

Vermilyea [1] studied the stress in anodic oxides of tantalum, titanium, aluminium, zirconium and niobium by growing the oxide films at a constant current density in a borate bath. He observed tensile stress in all films at small thicknesses and the stress in zirconium oxide changed to compression with rising thickness. The same investigator explained his experimental results as follows. Under the influence of the applied electric field, protons migrate out of a hydrated oxide, leaving it in a state of tension. Increased water trapping at high electric fields would

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give greater tensile stresses. The stresses obtained with an anodizing voltage applied were always more compressive than those with the electric field off.

Bradhurst and Leach [2] found that in the early stages of aluminium anodization in a sulphuric acid solution, the open-circuit stress was tensile and later became compressive. When the aluminium was anodized in an ammonium citrate solution at low applied current densities, the same investigators [3] also observed that the stress in the anodic aluminium oxides was compressive while at higher applied current densities it became tensile.

Archibald and Leach [4] measured the open-circuit stress in anodic zirconium oxides grown galvanostatically in an ammonium borate solution and found higher values of compressive stress for anodic oxides grown on electropolished and mechanically polished zirconium than on chemically polished zirconium contaminated with fluorine. They also observed a transition from compressive to tensile stress at about 30 V for zirconium oxide doped with fluorine from either the anodization solution or the chemical polishing solution. This phenomenon was correlated with the dilution by oxygen of the fluorine left on the metal surface after the polishing treatment.

Archibald [5] anodized titanium galvanostatically in an ammonium borate solution containing fluoride ions and measured the open-circuit stress of the grown oxides. This investigator found that a rise in the fluoride ion concentration in the solution results in a rise in the magnitude of the measured tensile stress.

Using a very sensitive technique, Wuthrich [6] anodized aluminium galvanostatically in an ammonium borate solution and observed the open-circuit stress to be tensile and the growth stress to be always compressive.

All of the above investigations concerning the open-circuit or growth stresses were performed in anodic oxides grown galvanostatically.

Only one research investigation has been reported [7] for the internal stress in anodic oxides of titanium grown potentiostatically, *i.e.* when the applied voltage between the titanium metal and the standard calomel electrode (SCE) was kept constant and the electric current through the electrolytic cell changed with time during the anodization process. According to this investigation, the growth and the electrostrictive stresses were found to decrease and the open-circuit stress to increase with increasing thickness of the growing titanium oxide.

The purpose of the present work is to study the internal stress in anodic zirconium oxide films grown potentiostatically. The stress in zirconium oxide films is a very important experimental parameter since it is related to several properties of these films, *e.g.* surface morphology, mechanical behaviour, wear and corrosion resistance, and dielectric and electronic conduction.

2. Experimental details

The specimens used for stress measurements were cut from a zirconium foil of 99.99% purity. The main impurities were oxygen, carbon and iron.

The zirconium specimens were vacuum annealed at 778 K for 4 h. The zirconium specimens were then mechanically polished with emery paper of increasing fineness. After this treatment, the specimens were chemically etched in a fresh mixture of 40% HNO_3, 5% HF and 55% H_2O for 2 min. The specimens were then immersed in methanol, washed in doubly distilled water and dried. The final zirconium specimens had 0.12 mm thickness.

Before anodization the zirconium specimens used for anodization were lacquered on the back side, except for an area used for electrical contact, and on the front side. The specimens were 10 cm long. The dimensions of the specimens were selected so that the length:width ratio of the specimens was 20:1. Under these experimental conditions, bending of the anodizing zirconium specimens was assumed to be uniaxial rather than biaxial.

The anodization of zirconium specimens was performed in a standard three-electrode cell under potentiostatic conditions. The applied voltages were referred to a SCE. The current variation with time was also monitored. The electrolyte used for zirconium anodization was a 0.05 M Na_2SO_4 solution of pH 9 and 290 K. The thickness of the various anodic zirconium oxide films was calculated with the aid of an impedance technique, assuming that the dielectric constant of the zirconium oxide was equal to 24.5 [8].

In order to find the internal stress in growing anodic zirconium oxides potentiostatically, the specimens' deflections were measured with a travelling vernier microscope. After the specimen deflection had been measured in a particular anodizing condition, the internal stress was calculated from the following equation [9, 10]

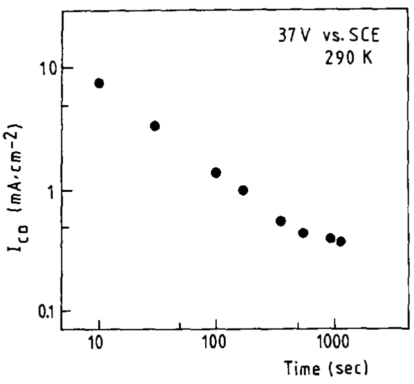
$$\sigma = \frac{1}{1-\nu}\frac{Eb^2f}{3l^2d} \tag{1}$$

where σ is the stress in the zirconium oxide, ν is the Poisson's ratio of the zirconium (0.33), E is the Young's modulus of the zirconium (94.35 GN m^{-2}), b is the specimen thickness (0.12×10^{-3} m), l is the specimen length (0.1 m), f is the specimen deflection and d is the zirconium oxide thickness.

The data presented in this work are the average values of four independent experiments. In this study, we use the term "anodic stress" which is defined as the observed stress during the growth of zirconium oxide and includes growth and electrostrictive stresses.

3. Results and discussion

Figure 1 shows the anodic current density as a function of time during the potentiostatic anodization of zirconium at an applied voltage of 37 V *vs.* SCE and a temperature of 290 K. In the region 0–200 s of anodizing time, we observed a fast decrease in anodic current density which was due to the rapid thickening of anodic zirconium oxide. For higher values of the anodizing time, we observed a slower decrease in the anodic current density which must have been due to the slower thickening of the anodic zirconium oxide.



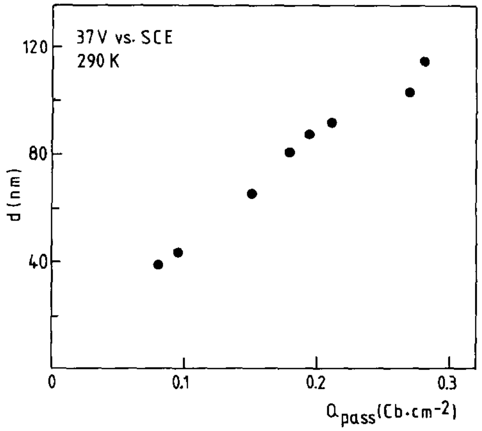


Fig. 1. The anodic current density as a function of time during the potentiostatic anodization of zirconium in the sulphate electrolyte at pH 9.

Fig. 2. The increase of zirconium oxide thickness as a function of the passed charge during the potentiostatic anodization of zirconium in the sulphate electrolyte at pH 9.

With the aid of Fig. 1, the passed charge could be calculated as a function of anodizing time. Figure 2 shows the measured oxide thickness as a function of the charge passed during the anodization process. Figure 3 shows the zirconium oxide thickness as a function of anodizing time.

The thickness of growing anodic oxide on zirconium is given theoretically by the following equation.

$$d(\text{theor}) = \frac{Q_p M}{x \rho F} \tag{2}$$

where Q_p is the charge passed, M is the molecular weight of zirconium oxide (123.22 g), z is the oxygen charge per zirconium molecule (4), ρ is the density of zirconium oxide (5.7 g cm^{-3}) and F is the Faraday constant (96 488 C).

Introducing the above values for the various parameters in eqn. (2) and the values of charge passed (Figs. 2 and 3) at various times of potentiostaic anodization of zirconium at 37 V *vs.* SCE, we find the expected values of the thickness of growing zirconium oxide (Table 1). In Table 1 we also include the measured oxide thicknesses and the calculated growth efficiency [$n = d(\text{exp})/d(\text{theor})$] at various times of zirconium anodization.

From the results given in Table 1, we can note that the growth efficiency of the potentiostatic anodization of zirconium is always lower than unity and decreases for anodizing times longer than 360 s. This is clear evidence that during the potentiostatic anodization of zirconium, a part of the passed charge is consumed for the growth of anodic oxide; another part, which is the smaller, is consumed for the creation of dissolution and electronic currents.

Figure 4 shows the zirconium specimen deflection during its potentiostatic anodization at an applied voltage of 37 V and a temperature of 290 K. After 18

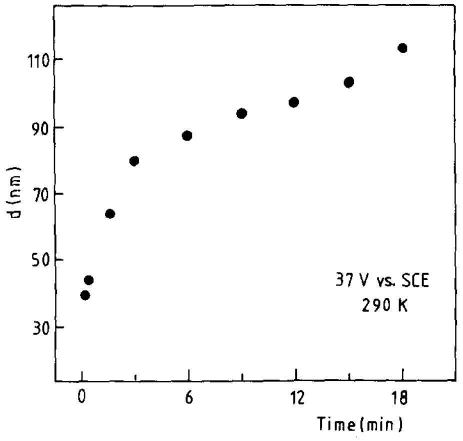


Fig. 3. Zirconium oxide thickness as a function of anodizing time.

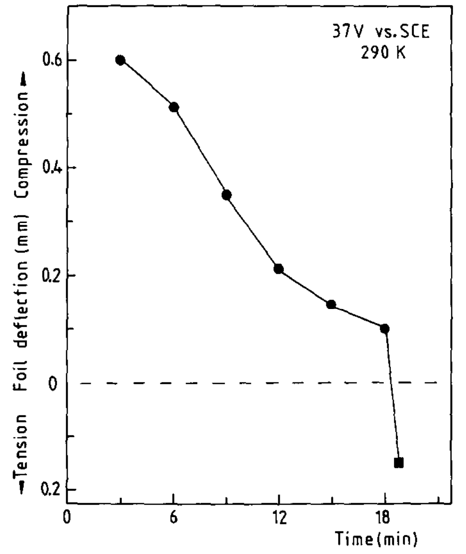
TABLE 1

Measured oxide thickness and calculated oxide thickness and growth efficiency during the potentiostatic anodization of zirconium at 37 V *vs.* SCE

t (s)	Q_p (C cm^{-3})	d(theor) (nm)	d(exp)	n
10	0.08	45	39	0.87
30	0.095	53	44	0.83
100	0.15	84	65	0.77
180	0.18	100	80	0.80
360	0.19	106	88	0.83
540	0.21	117	94	0.80
720	0.24	134	98	0.73
900	0.27	151	105	0.69
1080	0.28	157	114	0.72

min anodization time the power supply was disconnected from the anodizing circuit and the deflection of the zirconium specimen was also recorded during this open-circuit process (Fig. 4). By using eqn. (1) the stresses in the zirconium oxide during the growth, *i.e.* the anodic stress and the open-circuit stress, were obtained, see Fig. 5.

As we observed, the anodic stress in the growing zirconium oxide is compressive in sign and its magnitude decreases with increasing anodization time, *i.e.* zirconium oxide thickness. However, during the open-circuit time the compressive stress is changed to tensile stress. The observed anodic compressive stress during the zirconium oxide growth can be attributed to the superposition of growth and electrostrictive stresses. Unfortunately, the type of this superposition is unknown.



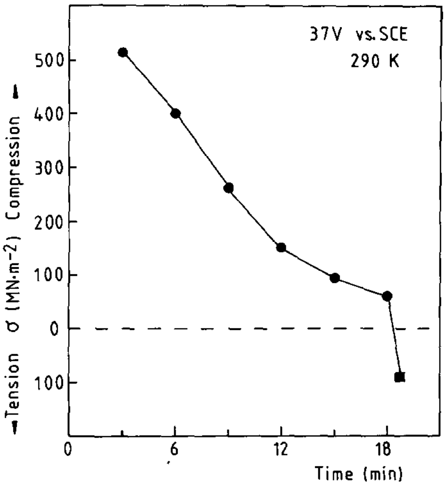


Fig. 4. Zirconium foil deflection as a function of time for anodizing zirconium in the sulphe electrolyte at pH 9: (●) during the anodization time; (■) during the open-circuit time.

Fig. 5. Internal stress in the anodic zirconium oxide, grown in the sulphate electrolyte at pH 9, as a function of time: (●) during the anodization time; (■) during the open-circuit time.

We only know the validity of the familiar relationship beween electrostrictive stress and applied electric field E_{el} in a dielectric medium.

$$\sigma_{\mathrm{electrostr}} \approx E_{\mathrm{el}}^2 \tag{3}$$

During the potentiostatic anodization of valve metals, the electric field across the growing anodic oxide is usually decreased with increasing thickness of the anodic film. Then, a minor reason for the decrease of the anodic stress with increasing anodization time (Fig. 5) may be the decrease of the electric field and accordingly of the electrostrictive stress (eqn. 3) with increasing thickness of the growing zirconium oxide. However, the major reason for the last observation must be related to the nature of ionic migration during the growth of zirconium oxide potentiostatically. At present, a more detailed analysis cannot be given because of the quantitative uncertainties regarding the anodic stress components as mentioned in Section 1.

At this point, we would like to mention another factor which may affect the anodic stress measurements. It is well known that during the galvanostatic anodization of valve metals, the temperature of growing oxides increases as a result of the Joule heat effect. Unfortunately, only one investigation has been reported for the temperature of growing tungsten oxide potentiostatically, in which the temperature of growing oxide was first found to increase suddenly and then to decrease with increasing anodization time and oxide thickness [11]. However, the relationship between the temperature change of the anodic oxides growing potentiostatically and the anodic stress is unknown quantitatively.

With respect to the development of tensile stress during the open-circuit time and after the end of zirconium potentiostatic anodizations, two possible reasons can be given. The first reason is based on the assumption that, during the potentiostatic anodizatiron of zirconium, the dominant travelling ionic species are the oxygen species. This assumption can be related to the Pilling–Bedworth ratio, *i.e.* the ratio of the volume of grown zirconium oxide to the volume of zirconium metal from which it is formed.

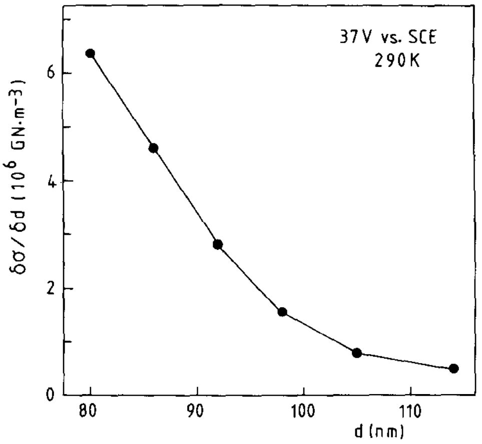


Fig. 6. Internal stress gradient in zirconium oxide as a function of the oxide thickness during the potentiostatic growth of the oxide film in the sulphate electrolyte at pH 9.

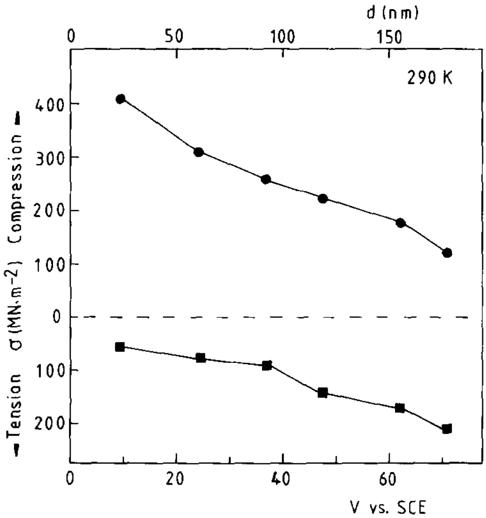


Fig. 7. Anodic stress (●) after 6 min of anodization time and open-circuit stress (■) after the end of potentiostatic anodization in the sulphate electrolyte at pH 9 as a function of applied voltage.

The Pilling–Bedworth ratio is based on the concept that ratios less than unity result in tensile strains in the oxide film. Since the oxides do not possess high tensile strengths, cracking of the oxides can occur. When the ratio is more than unity, compressive strains are developed in the oxide film. Bearing in mind these ideas and knowing that the Pilling–Bedworth ratio is equal to 1.5 for the crystalline oxide of anodized zirconium, we can expect the development of tensile open-circuit stress. The second reason is based on Vermilyea's hypothesis of structural considerations and successive field-assisted dehydration [1] in the outer layers of growing zirconium oxide, which gives rise to the development of tensile open-circuit stress.

Combining Figs. 3 and 5, we obtain the anodic stress gradient ($\partial\sigma_c/\partial d$) during the growth of zirconium oxide films, between 80 and 115 nm oxide thickness (Fig. 6). From Fig. 6, we observe that the stress gradient is a function of the oxide thickness. In fact, the stress gradient decreases rapidly between 80 and 95 nm and then decreases slowly up to 115 nm. The non-uniform change of stress gradient can mainly be attributed to the possible changing mode of ionic conduction during the oxide thickening and/or changing structure of the growing zirconium oxide.

Finally, Fig. 7 shows the anodic and open-circuit stress after 6 min and at the end of the potentiostatic anodization of zirconium, in the range of applied voltages of 8–72 V. The anodic stress is observed to decrease and the open-circuit stress to increase with increasing applied voltage, *i.e.* zirconium oxide thickness.

4. Conclusions

The anodic stress, *i.e.* the superposition of growth and electrostrictive stresses, and the open-circuit stress were measured during the potentiostatic anodic oxidation of zirconium in a sulphate electrolyte. The anodic stress was found to be compressive whereas the open-circuit stress was always tensile. With increasing thickness of zirconium oxide, the anodic stress was observed to decrease and the open-circuit stress to increase.

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