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Anodization of niobium in sulphuric acid media

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Niobium oxide films of different thicknesses can be produced on niobium electrodes by anodic polarization. The films produced by a galvanostatic method show different interference colours following the expected theoretical succession of colours. An electrical breakdown was observed which showed a significant dependence of the electrolyte concentration and current density. The relationship between the colour and the current density during the anodization of niobium samples are reported for sulphuric acid solutions. In addition the method for preliminary surface preparation of the niobium electrode is described.

1. Introduction

Anodic oxidation occurs when valve metals such as Ta, Zr, Nb and Ti are anodically polarized in suitable electrolytes. The film grows to a thickness approximately proportional to the formation voltage impressed across it. In aluminium the anodizing process can be performed by using either a two-stage or one-stage procedure. The conventional two-stage procedure consists in the anodization of aluminium in sulphuric acid, yielding a porous, colorless oxide film followed either by dyeing [1] or electrolytic coloring with metallic salts [2]. The one-stage procedure produces a self-colored anodic coating in which the optical characteristic of the film depends on the alloy composition and adjustment of the anodizing parameters [3-5].

During the oxidation of valve metals like Ti, Nb or Zr a transparent film is formed and the phenomenon of interference is responsible for the colours of the films. In aqueous solutions the anodic oxidation of Ti presents great difficulties due to the elevated electronic conductivity of TiO_2 which leads to intense oxygen evolution during the film formation [6-8]. The kinetics of anodic oxidation of tantalum and zirconium in different electrolytes has been studied earlier [9-14] and the authors found that the composition of the oxide can change with the film thickness.

Niobium is a light metal and, like other valve metals, owes its corrosion resistance to a readily formed, adherent, passive oxide film. In addition to being very stable, the anodic niobium oxide film has a high dielectric constant and a high breakdown potential [15]. This is the reason why this metal is generally considered in all applications requiring valve metals like titanium or tantalum. Seeley [16] discussed the technique for surface preparation and the conditions for the anodization of niobium. Nevertheless, we have not found in any of these papers a systematic study of the colours obtained after anodizing niobium. In this investigation we determine the conditions that produce, after anodization, uniform colours on large area samples and we explain the phenomena that are responsible for these colours.

2. Experimental details

Rectangular anodes were cut from a sheet of niobium (99.5% wt % — CBMM-Brasil) with the following dimensions: 45 mm × 40 mm × 10 mm. These rectangular anodes were later used to characterize the colour of our samples. For the electrochemical measurements the electrode was made from a niobium rod (99.5 wt % — CBMM — Brasil) with a geometric area of 1.54 cm^2.

The niobium electrodes were degreased in acetone, polished with 400 and 600 grit sandpaper, polarized for 60 s at -1.0 V (against Pt auxiliary electrode) in a mixture of concentrated acids in the following proportions (by volume) 1(H_3PO_4): 2(HNO_3): 5(H_2SO_4): 9(H_2O) and then rinsed with distilled water. Finally the niobium electrode was placed in a two electrode cell and galvanostatically anodized at constant current density. The counter electrode was a platinum sheet with a surface area of several square centimeters.

The electrolyte was a dilute solution of pure sulphuric acid (p.a., Merck). The concentration of the solutions varied from 0.05 M to 0.5 M and the electrolyte was deoxygenated using pure nitrogen. Experiments were performed at a constant temperature, held by a thermostat at 25° C.

The galvanostatic experiments were performed with a regulated power supply and the potential drop between the anode and auxiliary electrode was continually recorded by means of a ECB model RB 101 *x–t* recorder.

In order to describe accurately the colour of the

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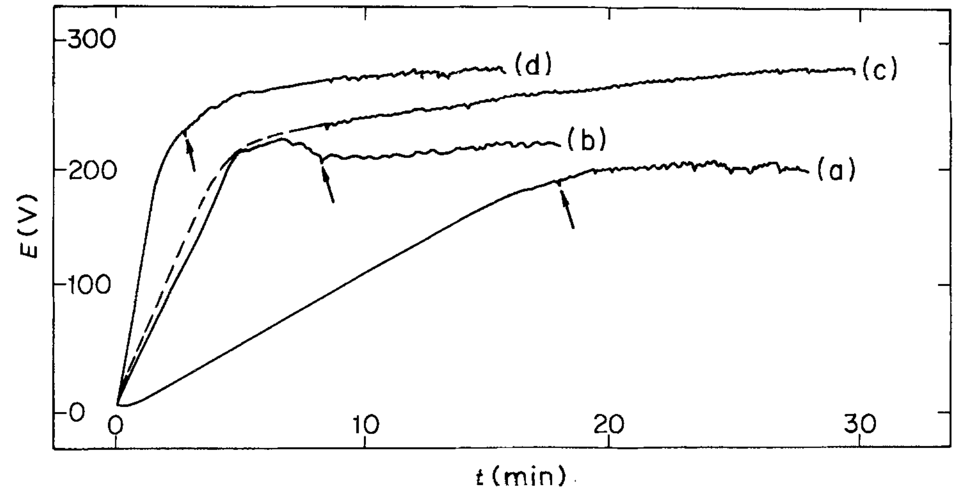

Fig. 1. Growth curves for films grown on niobium metal in 0.05 M H_2SO_4 solutions at different anodic currents: (a) 1 mA cm^{-2}, (b) 3 mA cm^{-2}, (c) 5 mA cm^{-2} and (d) 7 mA cm^{-2}. The arrows mark the first spark occurrence.

samples a Gardner AC-ZA (CIE) colorimeter was employed. The colour of each sample was defined as a point in the X-Y diagram of the International Commission of Lighting [17].

3. Results and discussion

Figure 1 shows the potential drop as a function time for four different current densities. The initial linear increase of the potential with time indicates that the film is of a barrier type [18]. The anodization rate given by the slope (dE/dt) increases with current density, as depicted in Fig. 2. There is no discernible effect of the electrolyte concentration on the anodization rate. In this region the anodization produces films displaying the normal sequence of interference colours.

The decrease of the anodization rate in the growth curves is interpreted as an indication of the beginning of film breakdown. This behaviour occurs in the region of the first sparking phenomena, as shown in the Fig. 1, suggesting that the breakdown is electrical. The first spark voltage (V_{FS}) was reproducible and was almost independent of the current density.

In Fig. 3 the dependence of breakdown voltage (V_b) and current density on sulphuric acid concentration is

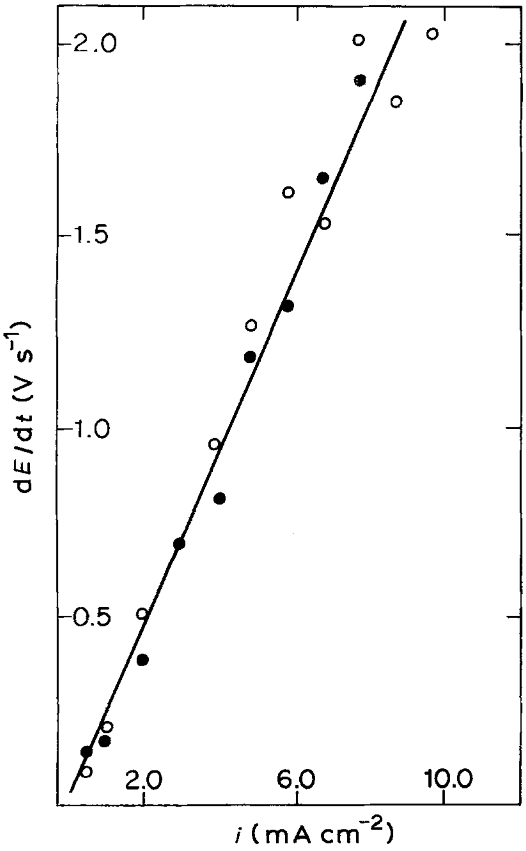

Fig. 2. Anodization rate as a function of current density in different solutions: (○) 0.05 M H_2SO_4; (●) 0.5 M H_2SO_4.

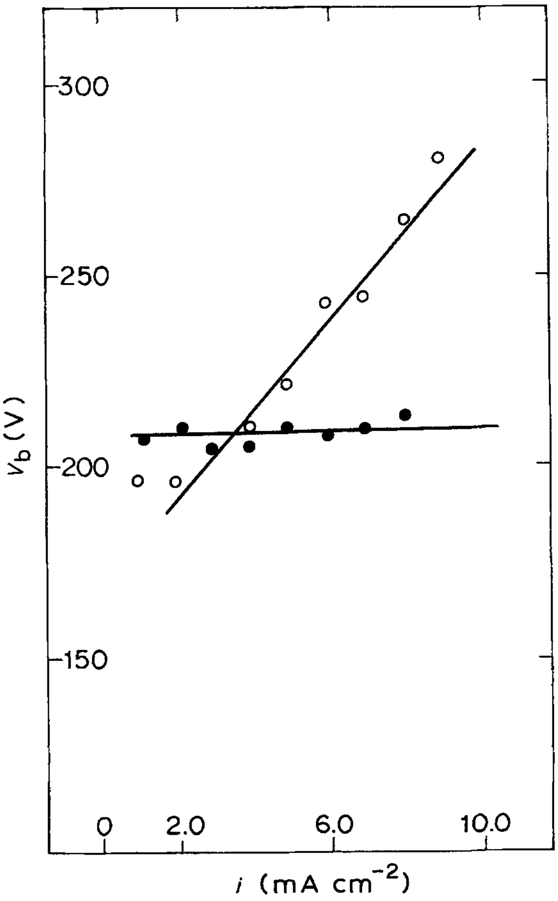

Fig. 3. Breakdown of voltage as a function of current density for films in different solutions: (○) 0.05 M H_2SO_4, (●) 0.5 M H_2SO_4.

shown. As can be seen V_b is affected by the current density for values higher than $2\,mA\,cm^{-2}$ when the anodization is performed in a 0.05 M H_2SO_4 solution. In the more concentrated solution, 0.5 M H_2SO_4, V_b is constant over the range of current density reported and is lower than the values obtained in the previous case at current densities higher than $5\,mA\,cm^{-2}$. This behaviour may be associated with the incorporation of anions into the film which increases the electronic injection current at the oxide/electrolyte interface [14, 19].

Quantitative analysis of this phenomenon requires a knowledge of the laws governing electronic injection at this interface for each metal/oxide/electrolyte (MOE) system. The dependence of breakdown voltage on the solution concentration and current density are in agreement with Ikonopisov's model [19] of electrical breakdown for MOE systems.

The analysis of the different steps of growth of an anodic film on niobium in our experimental conditions can be described by the thickening of the natural oxide film, in the linear region of the *E–t* curve, and simultaneous oxygen evolution in the breakdown region.

The existence of a previous film of niobium oxide, about 3 nm thick, was confirmed by Di Quarto *et al.* [20] based on the analysis of the capacitance as a function of the formation voltage recorded during the growth of the film.

The thickening of the film in the linear region of the growth curve can be explained by hopping theory [21–23], considering that there is no discharge of oxygen on the surface of the anode and neglecting the dissolution of the oxide film in sulphuric acid.

The discharge of oxygen, observed during the present experiments, begins at the end of the linear region of the potential-time curves. This behaviour has already been observed with other valve metals [24, 25].

Finally, in order to establish a correlation between the colours and the electrochemical data six niobium samples, representing one of the colours of the visible spectrum, were analysed.

Figure 4 shows the reduced trichromatic coordinates of these samples in the diagram of the International Commission of Lighting [17, 26]. In this diagram every possible colour is uniquely represented by a point which can be specified by giving the X and Y chromaticity coordinates. The colours at the outer boundary of the diagram (solid curve) have maximum saturation, and the colours gradually become more faded toward the center of the diagram. The colour hue changes on a path going around the central region.

An unknown colour can be located on the chromaticity diagram by direct measurement using a colorimeter or, alternatively, its position can be calculated from the spectral distribution of the radiation.

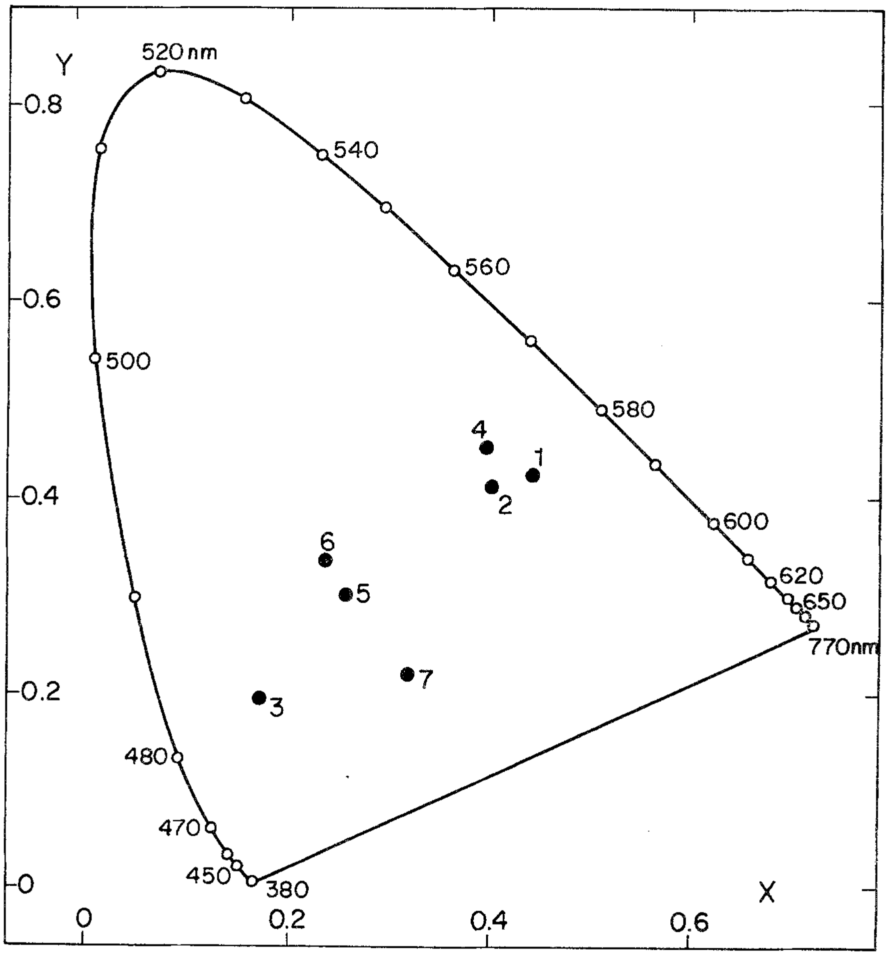

Fig. 4. Reduced trichromatic coordinates for anodized niobium samples: (1) light source, (2) brown, (3) blue, (4) yellow, (5) light blue, (6) green and (7) violet.

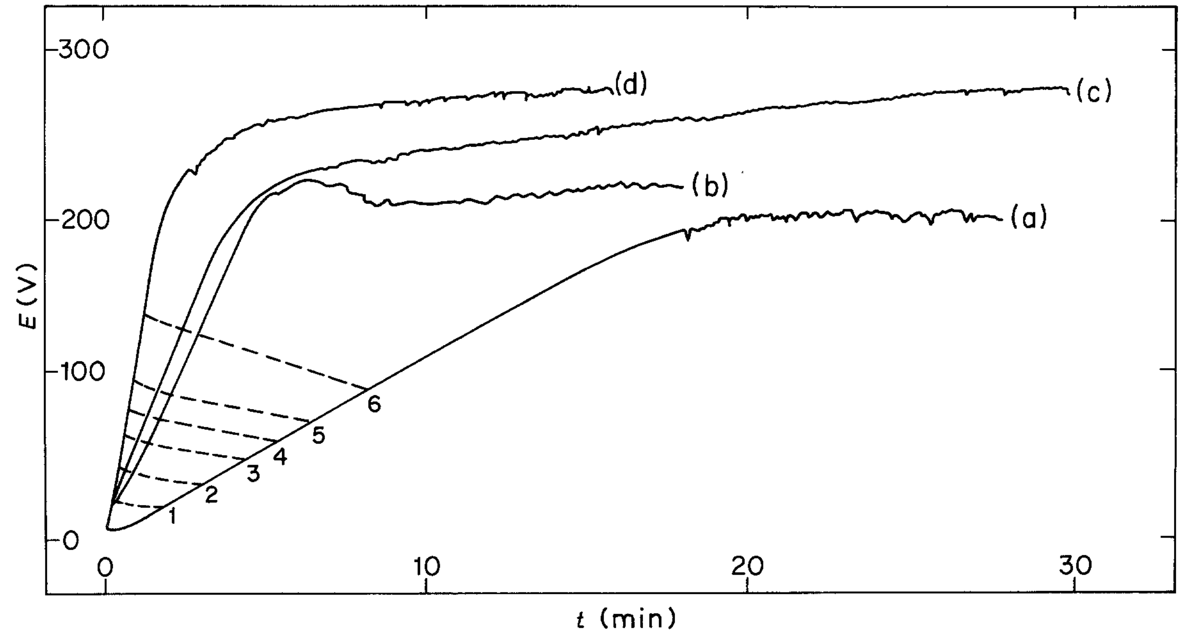

Fig. 5. Relation between the colours of the samples (- - -) and the potential drop (——): (a) 1 mA cm^{-2}; (b) 3 mA cm^{-2}; (c) 5 mA cm^{-2}; (d) 7 mA cm^{-2}. Colour: (a) brown, (2) light blue, (3) yellow, (4) violet, (5) blue and (6) green.

According to Young [21, 27], the colours of anodized niobium samples can be explained in terms of interference phenomena rather than as stoichiometric defects in the composition of the film.

In Figure 5, samples with the same reduced trichromatic coordinates were selected and represented as a function of the potential. This fact is in agreement with theoretical succession where the variation of thickness gives rise to the extinction which determines the complementary colour seen.

4. Conclusions

The growth process of an anodic film on niobium is associated with the thickening of a natural oxide film. The results of this work show the complex nature of the electrical breakdown processes in metal/oxide/electrolyte systems. This process is associated with the level of impurities in the films that increase the electronic injection current at the film/solution interface.

The experimental succession of colours observed during the growth of the film is the same as that theoretically obtained considering the conditions for the extinction and reinforcement of wave lengths in ideal circumstances, i.e. a transparent oxide film on a smooth and perfectly reflecting niobium surface.

For practical purposes we have found a surface treatment that leads to uniform films and the experimental conditions necessary for good reproducibility of a given colour.

Acknowledgments

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