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Measurements of electrochemical impedance on the alloy Al 2024T3: an analysis of parameters used to predict the quality of the anodic film

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Using the electrochemical impedance technique, the deterioration process of the alloy Al 2024T3 was followed in the presence of NaCl and Na_2SO_4. It was verified that the resistance obtained as the extrapolation to the null frequency in the impedance diagram, even though significant, is not sufficient to characterize the protecting quality of the anodic film. This parameter is only considered as a measure of anticorrosive protection when it is preceded by a capacitive loop at high frequencies. This phenomenon in the high frequency range gives a measure of the sealing quality of the film.

1. Introduction

When aluminium is exposed to air a thin oxide film naturally develops over its surface which usually confers self protection. In order to enhance this protection, a thick and controlled anodic film may be produced by anodizing. It is believed that the films obtained under these circumstances are composed of two oxide layers: a thin first layer in direct contact with the metal, known as a barrier film, and a second layer consisting of a hexagonal cell structure and termed the porous layer [1].

Due to the technological importance of the protection given by anodic films this topic has been the subject of many studies and, recently, the electrochemical impedance measurement was proposed as a fast method of evaluating the quality of anodic films on aluminium alloys [2]. The impedance diagrams obtained show the existence of two capacitive loops, one at frequencies higher than 10 Hz and another at frequencies lower than 1 Hz. Hitzig *et al.* [3] suggest that the presence of these two loops is associated with the anodic film structure: the capacitive loop at high frequencies, whose extrapolation defines a resistive value, R_{HF}, is related to the porous layer; and the capacitive loop at low frequencies, whose extrapolation defines a resistance, R_{BF}, is related to the barrier-type layer.

According to Bodu *et al.* [4] there is a satisfactory correlation between R_{BF} and the results of accelerated corrosion tests for anodized aluminium.

In the present paper, the deterioration process of anodic films obtained on the alloy 2024T3 is followed, and the R_{BF} value is analysed in order to determine whether it is a sufficient indicator of the quality of these films. The kinetic role of each of the two loops firstly detected by Bodu *et al.* [4] is also analysed.

2. Materials and methods

The working material consisted of aluminium alloy 2024T3 sheets submitted to sulphuric acid (10 μm) or chromic acid (5 μm) anodizing. The conditions for the anodizing process were as follows.

(i) chromic anodizing: voltage, 40 V; current density, 0.3 A dm^{-2}; time, 50 min; 5 g l^{-1} Cr_2O_3 and a temperature of 40° C;

(ii) sulphuric anodizing: voltage, 10–20 V; current density, 1.1–1.7 A dm^{-2}; time, 30–40 min; 230 g l^{-1} H_2SO_4 and a temperature of 18–20° C.

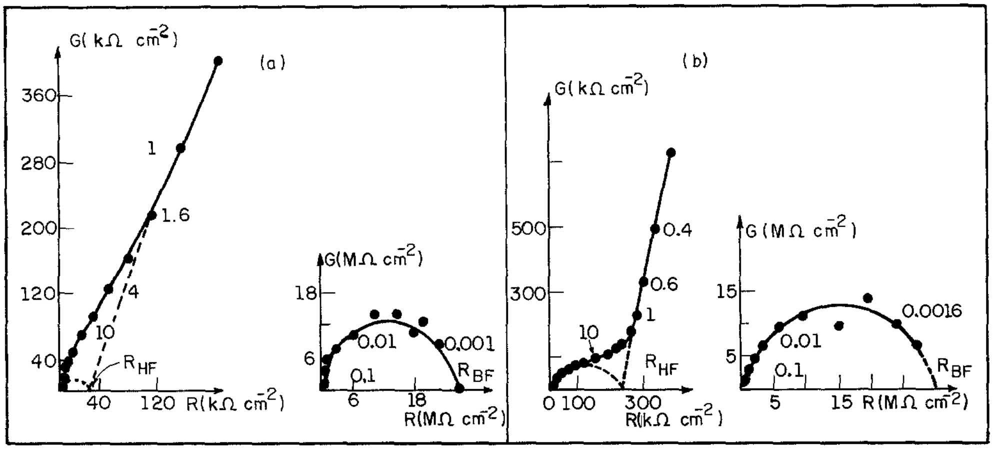

Fig. 1. Impedance diagrams obtained for (a) sealed chromic anodized and (b) sealed sulphuric anodized aluminium alloy 2024T3 immersed in 0.17 M NaCl for 1 day. (a) $R_{HF} = 28\,k\Omega cm^{-2}$; $R_{BF} = 24\,M\Omega cm^{-2}$. (b) $R_{HF} = 235\,k\Omega cm^{-2}$; $R_{BF} = 30\,M\Omega cm^{-2}$. Frequency in Hz.

Most test samples presented a 1 cm^2 surface; however, some tests were made for samples with 20 cm^2 to verify the area effect on the reproducibility of the results. The graphite rod auxiliary electrode was 600 cm^2 in area. The electrolytes were 0.17 M Na_2SO_4 and 0.17 M NaCl, both solutions being buffered at pH 4.6 with acetic acid. All tests were reproduced at least four times, but only two results for each type of sample and electrolyte are presented.

The working cell had a conventional three-electrode construction and the apparatus was that initially developed and adapted by Epelboin and co-workers [5, 6], and now widely adopted for impedance measurements. The experimental set-up contains a wide-band potentiostat [6] and a Transfer Function Analyzer based on a numerical correlation technique (Solartron–Schlumberger 1174).

3. Results and discussion

Fig. 1 shows the impedance diagrams obtained for sealed chromic anodized and sealed sulphuric anodized aluminium alloy in the presence of 0.17 M NaCl. As can be observed, the diagrams show the presence of two capacitive loops, one for frequencies over 10 Hz and another at very

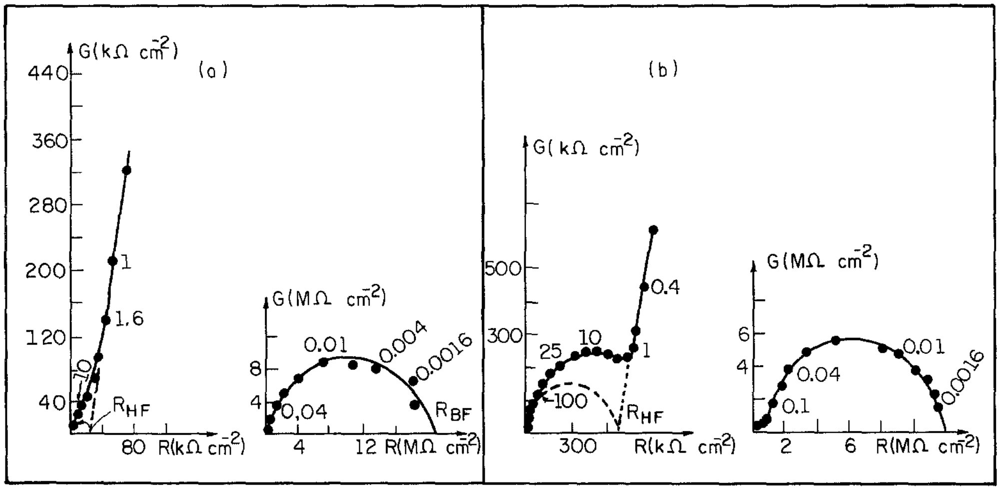

Fig. 2. Results corresponding to conditions as for Fig. 1 but in 0.17 M Na_2SO_4. (a) $R_{HF} = 28\,k\Omega cm^{-2}$; $R_{BF} = 24\,M\Omega cm^{-2}$. $R_{HF} = 580\,k\Omega cm^{-2}$; $R_{BF} = 12\,M\Omega cm^{-2}$. Frequency in Hz.

low frequencies, below 1 Hz. It is noticed that the capacitive loop at high frequencies is clearer for the sulphuric anodized specimen than for the chromic anodized specimen [4].

Fig. 2 shows results corresponding to those of Fig. 1 where NaCl was replaced by 0.17 M Na_2SO_4 solution. Again, the presence of two capacitive loops is noticed in the same frequency range. Comparing Figs 1 and 2, it is observed that the electrolyte change does not cause any significant modification in the frequency domain of any of the capacitive loops seen in the impedance diagrams.

Fig. 3 shows the effect of a longer immersion time as compared with Figs 1 and 2. It is noticed on this figure that in both electrolytes the R_{HF} and R_{BF} values undergo a significant decrease with time. After a few days of immersion the R_{HF} value goes to zero; that is, the capacitive loop at high frequencies tends to disappear. This phenomenon is slower for the NaCl than for the Na_2SO_4 solution (sample 'a'). However, this aspect is not further explored in this work, due to a complex acetate–sulphate and acetate–chloride interaction with the aluminium alloy [7].

It is noticed that the change of electrode impedance is qualitatively independent of electrolyte and anodizing process. Since chromic anodized specimens are generally thinner, their impedance changes faster with immersion time compared with sulphuric anodized specimens. This is the reason why more detailed examinations are made for chromic anodized aluminium alloys.

Fig. 4 gives the time dependence of electrode impedance for sealed specimens in the NaCl (Fig. 4A) and in the Na_2SO_4 solution (Fig. 4B). In each figure, two independent results for the same conditions are shown to illustrate the reproductibility of results. In both solutions a similar change with time was observed.

At the beginning, two capacitive loops are seen, allowing the R_{HF} and R_{BF} values to be determined. As the immersion time extends, the capacitive loop at high frequencies tends to disappear. At the same time, new additional phenomena are observed: the specimen in the Na_2SO_4 electrolyte always starts to behave in an inductive–capacitive manner (5th and 6th day diagrams for samples III and IV). On the contrary, in NaCl, only one additional capacitive loop can generally be seen (11th day diagram for sample II). However, in this electrolyte, an inductive–capacitive behaviour has also been observed (10th day diagram for sample I) in a few cases. It is certain that new additional phenomena appear at the lower frequency branch because the impedance change was

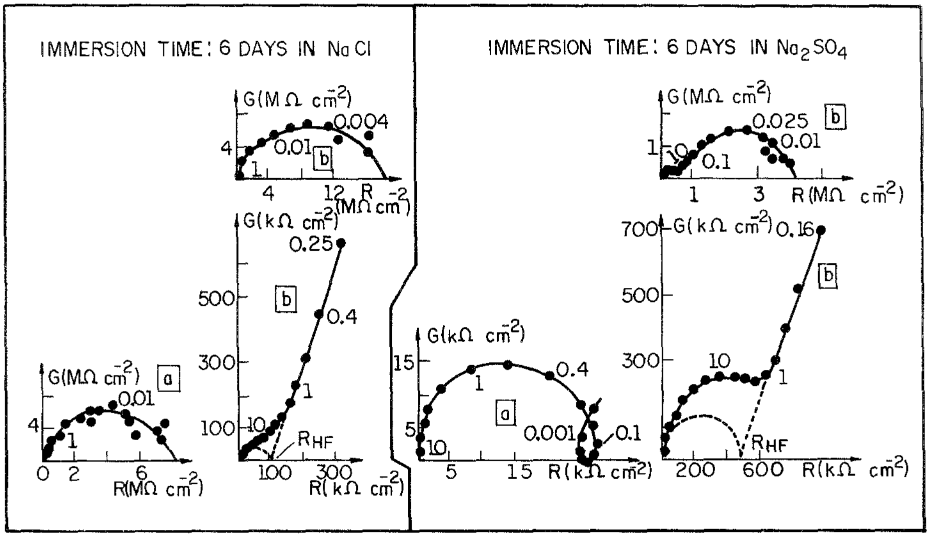

Fig. 3. Effect of immersion time on the electrode impedance. (a) Sealed chromic anodized alloy; $R_{HF} = 0$; $R_{BF} = 8\ M\Omega\,cm^{-2}$ for 0.17 M NaCl solution and $R_{HF} = 0$; $R_{BF} = 30\ M\Omega\,cm^{-2}$ for 0.17 M Na_2SO_4 solution. (b) Sealed sulphuric anodized alloy; $R_{HF} = 110\ k\Omega\,cm^{-2}$; $R_{BF} = 17\ M\Omega\,cm^{-2}$ for 0.17 M NaCl solution and $R_{HF} = 480\ k\Omega\,cm^{-2}$; $R_{BF} = 4.2\ M\Omega\,cm^{-2}$ for 0.17 M Na_2SO_4 solution. Frequency in Hz.

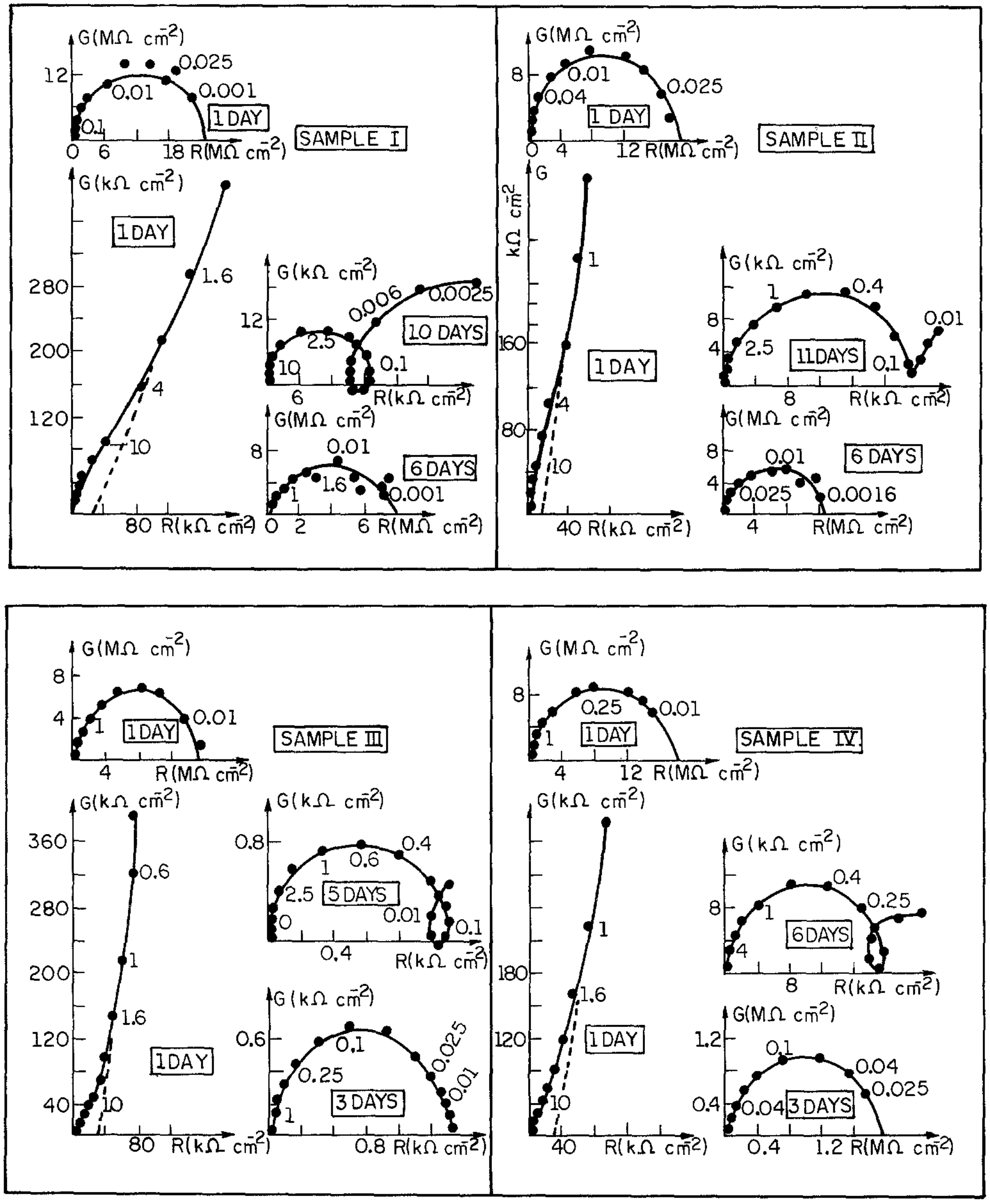

Fig. 4. Impedance diagrams obtained for the sealed chromic anodized aluminium alloy. (a) 0.17 M NaCl; (b) 0.17 M Na_2SO_4.

followed every day to check a continuous transformation from one feature to another.

The appearance of these new kinetic phenomena is always associated with the disappearance of the capacitive loop visible at an early stage of immersion (R_{HF}). Furthermore, it is related to the appearance of attack points on the sample surface. This correlation between the disappearance of R_{HF} and the attack on the samples indicates a possible significance of this loop in the protection of the anodic film.

In Fig. 5 the impedance diagrams obtained for the non-sealed chromic anodized specimens in the NaCl and Na_2SO_4 solutions are shown. It can be seen that, even with a short immersion time, there is no capacitive loop in the high frequency domain; that is, R_{HF} is *not* observed for non-sealed material. For these non-sealed specimens a fast degradation of the protective effectiveness of the anodizing film occurs, indicated by a steep decrease of electrode impedance. A comparison of Figs 4 and 5 suggests an

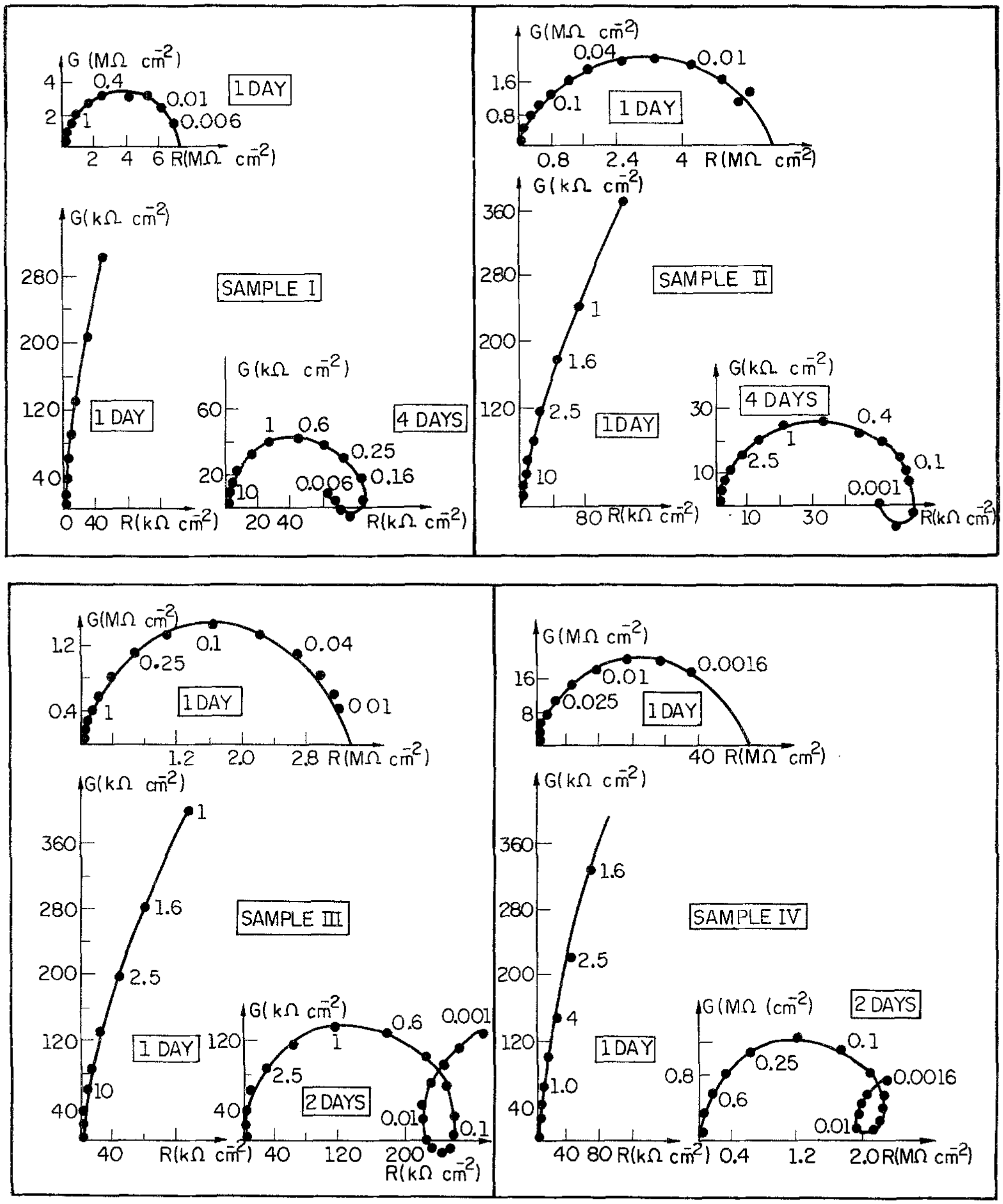

Fig. 5. Impedance diagrams obtained for the non-sealed chromic anodized aluminium alloy. (a) 0.17 M NaCl; (b) 0.17 M Na_2SO_4.

association of the R_{BF} values with the presence of a barrier layer, and the R_{HF} values with the presence of a porous layer in the same film. Further evidence for this hypothesis is presented in the analysis of Figs 6 and 7.

Fig. 6 represents the variation of the resistive value ($R_{HF} + R_{BF}$) with immersion time for the samples of Fig. 4. One can define in this figure three different regions. Firstly, Region I where the resistive value remains high; for instance, in NaCl, until 140 h for sample I and 180 h for sample II. After this immersion time there is a rapid decrease of the resistive value (region II). Lastly another region appears (region III) characterizing a new kinetic behaviour with low impedance values. Certainly this last change is related to the corrosion process of the base material. A similar tendency is observed for

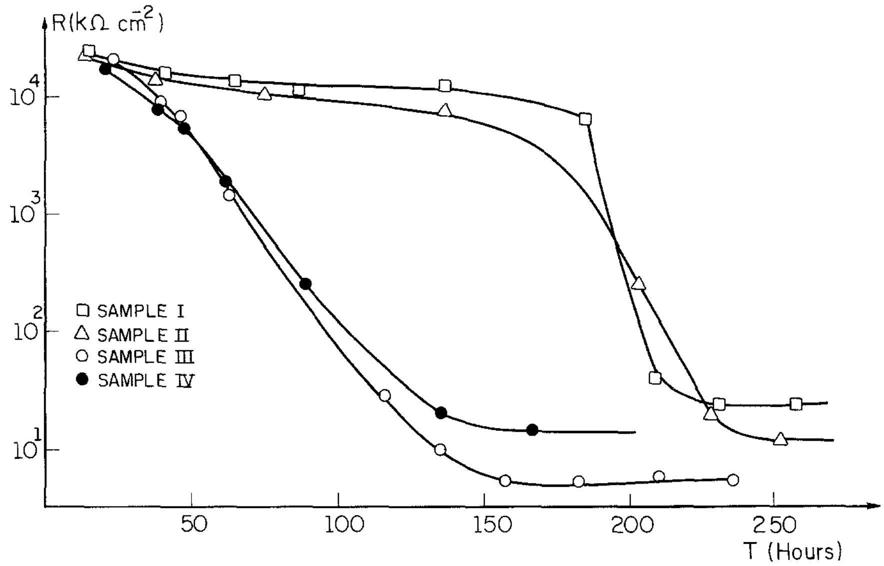

Fig. 6. Resistive value (R_{HF} and R_{BF}) as a function of the immersion time for sealed chromic anodized aluminium alloy (Samples from Fig. 4).

samples II and IV in Na_2SO_4 media, though region I is not so clearly marked as in the NaCl solution. Region III corresponds to the case where the impedance diagrams exhibit a very low-frequency capacitive loop (together with an inductive loop in certain cases) as shown in Fig. 4. This indicates a significant change in the electrode kinetics.

Fig. 7 shows the change of the resistive value (R_{BF}, since in this case $R_{HF} = 0$) with immersion time for the samples in Fig. 5. A comparison of this figure with Fig. 6 reveals the disappearance of region I; that is, as soon as a specimen is immersed in an aggressive medium a steep decrease of resistance takes place, followed by a plateau.

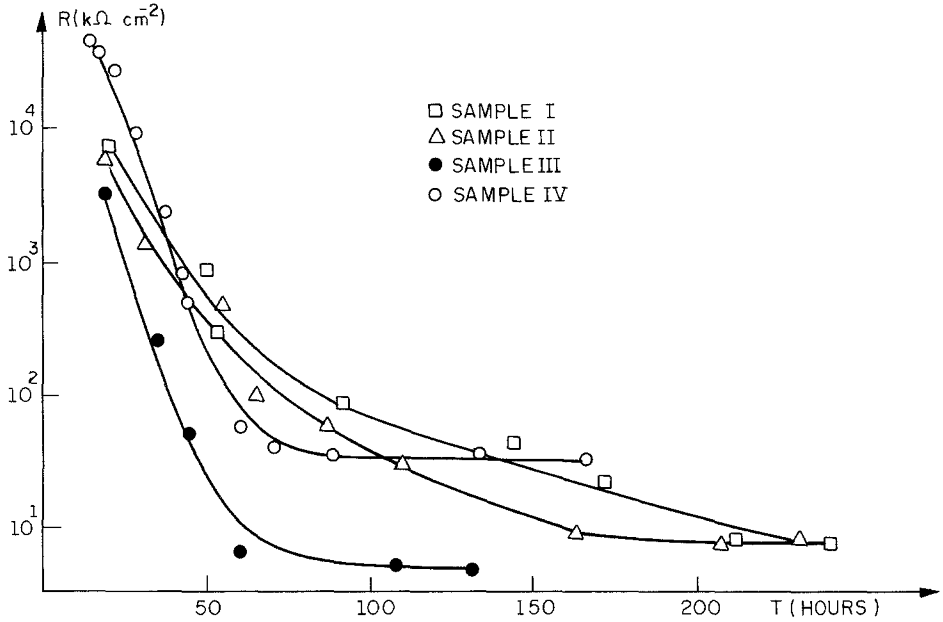

Fig. 7. Resistive value (R_{BF}) as a function of the immersion time for non-sealed chromic anodized aluminium alloy. For conditions, see Fig. 5.

The differences between Figs 6 and 7 are related to the fact that in sealed chromic anodization there is a partial occlusion on the external layer pores (porous layer). In this case there are two resistive values (R_{HF} and R_{BF}). In non-sealed chromic anodized samples, no R_{HF} can be seen. Therefore, region I of Fig. 6 corresponds to the solution attack on the sealed porous layer. Since $R_{HF} \ll R_{BF}$ in this range only a slight variation of the total resistance ($R_{HF} + R_{BF}$) with time occurs. This statement was verified by a visual examination of the surface state of corroding specimens: no degradation was observed in region I.

It can be concluded that the R_{BF} measured at an early stage of specimen immersion in aggressive media does not account alone for the protective effectiveness of anodized film. In other words, if the sealing process is omitted, the protective effect of the anodized film decays quickly even if the initial R_{BF} value is high. This is illustrated by sample IV of Fig. 7. A heavily damaged surface was observed at 60 hour immersion. On the contrary, in spite of a relatively low initial R_{BF} value, the surface degradation can be observed only after about 135 immersion hours with sample IV of Fig. 6. Consequently, both R_{HF} and R_{BF} measurements are necessary to ensure a good evaluation of the protecting quality of anodized film.

The intrinsic R_{BF} values of several specimens taken for the same immersion time in a given working electrolyte, indicate the protective action of the anodized film [4]; however, it is important to compare specimens subjected to the same sealing process. The R_{BF} value shows how effective is the protection offered by the barrier film, as has been shown in this paper and also from other experiments [7]. On the other hand, the value of R_{HF} can be used to control the sealing process.

4. Conclusion

The analysis of the change of impedance diagrams as a function of sample immersion time allows verification of the kinetic role of the two capacitive loops.

It was shown that the presence of the high-frequency capacitive loop (R_{HF}) is essential for an effective metal protection by the anodized layer. Its presence controls the velocity at which the electrolyte reaches the barrier film (R_{BF}). Since R_{BF} is more intimately related to the electrode kinetics itself this value sets the real resistance of the film to the corrosive medium attack at a given moment; however, this value alone does not provide a basis for prediction of the performance of the anodizing film. To apply the impedance technique as a test to evaluate the protective effectiveness of anodized film on aluminium alloy, both R_{BF} and E_{HF} have to be determined.

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