



Changes in cold sealed aluminium oxide films during ageing

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Abstract

EIS in the 100 kHz–1 MHz frequency range was applied to the study of changes in cold sealed aluminium oxide films exposed to highly wet and extremely dry atmospheres. Information about these changes was obtained from evolution of the impedance diagrams and, in particular, from film resistance and capacitance values determined from them. Results show that sealing quality, assessed from EIS, increases over months and years as ageing proceeds in a natural atmosphere. The analysis was completed with the aid of XPS and EDX techniques and standard quality control tests. Measurements show that specimens aged very rapidly in wet atmospheres, so that they passed all sealing quality tests within 72 h. The sealing quality improves with ageing even in highly dry atmospheres despite the fact that pores lose part of their initial filling water. XPS analysis revealed that fluorine and nickel concentrate in the outer layers of cold sealed anodic films; on the other hand, films obtained by the traditional HTS procedure exhibit a uniform composition throughout their thickness.

1. Introduction

Anodized aluminium is widely used in architectural applications [1]. The porous nature of anodic films requires sealing of their pores, which has traditionally been accomplished by immersion in boiling deionized water. The slowness and high cost of hydrothermal sealing (HTS), however, has fostered the development of cold sealing procedures based on nickel fluoride solutions since the 1980s [2–10].

Cold sealing differs markedly from HTS in the underlying sealing mechanism, as well as in the composition and properties of the anodic films obtained. Anodic films sealed at ambient temperature do not meet the minimum quality standards immediately upon treatment. Depending on the particular standard, materials must age for up to 30 days following cold sealing in order to pass the tests originally designed for conventional HTS [2, 3]. This shortcoming can be circumvented by immersion in aqueous solution of NiSO₄ at 60–80 °C following the sealing treatment [11].

Given the high significance of the post-sealing step, where industrial standards are eventually met when cold sealed films are fully hydrated, we believed it of interest

to examine changes in such films under highly wet and dry conditions. We also investigated the extent to which immersion in hot water after impregnation in the cold sealing solution was necessary.

Electrochemical impedance spectroscopy (EIS) has been used for the study because it has proved in other investigations [1, 12–19] to be a highly sensitive tool for discriminating sealing quality. Since the impedance data can be insufficient to interpret all aspects of the phenomenon, the analysis has been completed with results from XPS, SEM and EDX techniques and standard sealing quality control tests.

2. Experimental details

2.1. Materials

The specimens used were 5 cm × 10 cm × 0.1 cm aluminium plates of 99.5% purity that were anodized under technical conditions in 18% sulphuric acid at 20 °C and 1.5 A dm⁻² for 45 min, followed by repeated washing and final drying with pressurized air. The oxide films thus obtained were approximately 20 μm thick.

2.2. Conditions

Following anodization, specimens were impregnated in a cold sealing bath in compliance with the specifications of the European Aluminium Anodisers Association (EURAS) for 20 min [11]. The materials thus obtained were allowed to age at ambient temperature in small closed vessels under a highly wet atmosphere or at a very low relative humidity imposed with concentrated sulphuric acid.

2.3. Methods

Impedance diagrams were made over the frequency range 100 kHz to 1 mHz under controlled potentiostatic conditions, at the open-circuit potential. The cell and experimental set-up were described in detail elsewhere [12–14]. Changes in cold sealed films during ageing were also monitored as in previous work by recording water absorption or desorption, an using standard quality control tests.

The effect of post-sealing on the composition of cold sealed anodic films at the surface and in the middle of anodic films (following mechanical abrasion to a thickness of 10 μm) was examined by X-ray photoelectron spectroscopy (XPS). Spectra were obtained on a Fisons MT500 spectrometer equipped with a CLAM 2 hemispherical electron analyser and an MgK_α X-ray source at 300 W. XPS analyses were done following argon bombardment for 5 min; this treatment was equivalent to stripping a 5 nm specimen thickness (calibrated with a Ta_2O_5 sheet), which was considered the optimized minimum to ensure acceptable cleanliness without altering the chemical composition of the surface tested.

Finally, specimen cross-sections were examined under a scanning electron microscope (SEM), as well as by energy-dispersive X-ray (EDX) analysis, in order to determine the concentration profile for the elements in the anodic films.

3. Results

Figure 1 compares the impedance diagrams for unsealed and cold sealed anodic films, the latter immediately after treatment and after ageing for one month at a very high or very low relative humidity, and for a specimen exposed successively 100 days to a very dry atmosphere and after in a wet chamber for 30 days. The diagram obtained immediately after removing the specimen from the sealing bath was much more similar to that for an unsealed film than to that for a specimen subjected to correct sealing. The diagrams for anodic films exposed

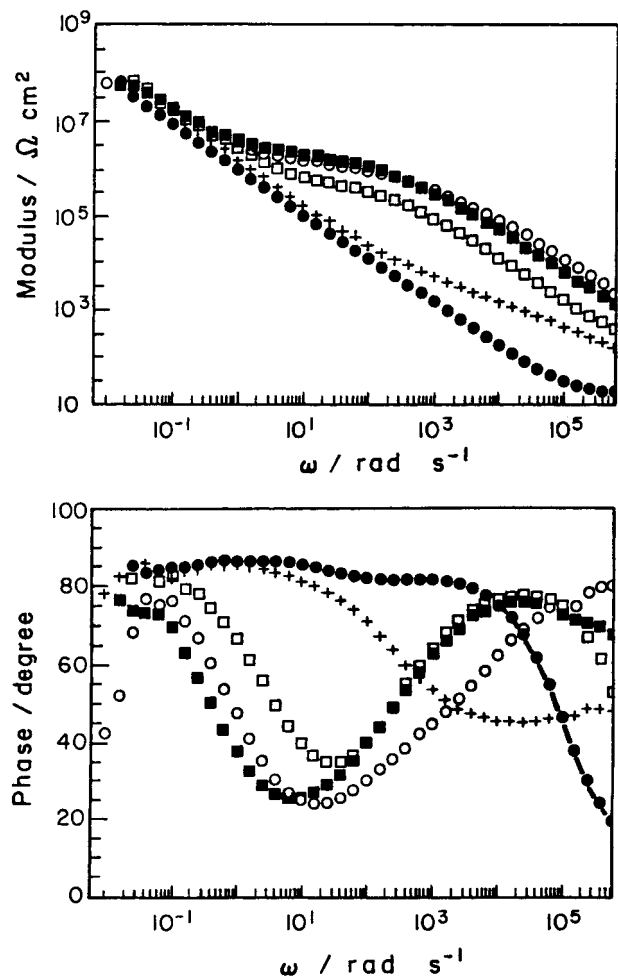


Fig. 1. Impedance diagrams for unsealed specimens (●) and cold sealed specimens immediately after sealing (+), after 1 month of exposure to a highly wet (■) or highly dry atmosphere (□), and after 100 days to dry plus 30 days to wet atmospheres (○).

to very high and low relative humidity environments for 30 days are markedly different between themselves within a wide range of frequencies ($1\text{--}10^5$ Hz). However, the diagrams obtained in alternately highly dry and wet environments were virtually identical to diagrams for films permanently stored under high RH conditions.

Figure 2 shows a fast initial evolution of the impedance spectra in humid environments. This evolution proceeds for years, as happens after traditional HTS [14]. A capacitive behaviour (impedance inversely proportional to the frequency) is usually obtained at low frequencies, although a second resistive section, which defines another semicircle at low frequencies—probably related to the resistance of a defective barrier layer (R_b)—can occasionally be seen.

Figure 3 shows the mass gain due to water absorption by cold sealed specimens in wet and dry chambers. Cold

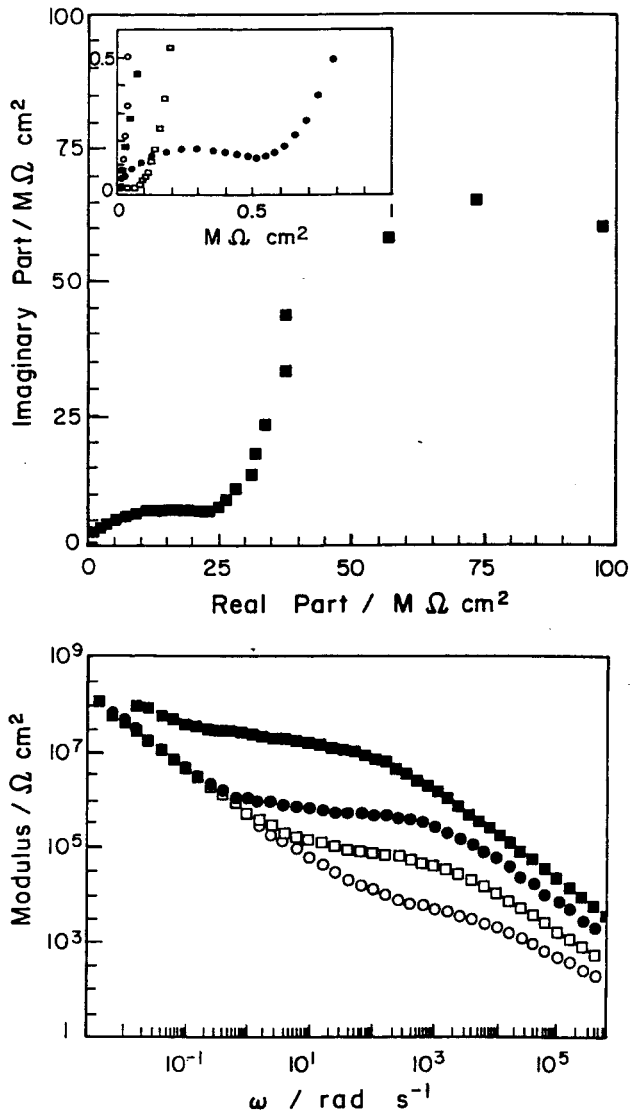


Fig. 2. Impedance diagrams for cold sealed specimens immediately after sealing (○) and after ageing for 1 day (□) and 1 month (●) in wet chamber and 3.5 years (■) in the urban atmosphere of Madrid.

sealed films absorbed more than 30 mg dm^{-2} water during the impregnation step, but continued to absorb it to complete pore saturation in the wet atmosphere. Transferring the cold sealed specimens to a desiccator containing sulphuric acid resulted in water desorption and a mass loss of about 15 mg dm^{-2} . It is interesting to confirm that after 100 days in these conditions the cold sealed films retain their ability to absorb water vapour from a moist atmosphere, filling their pores. This causes significant changes in their characteristics, as will be seen later.

Table 1 summarizes the results of the conventional control tests for specimens aged at ambient temperature

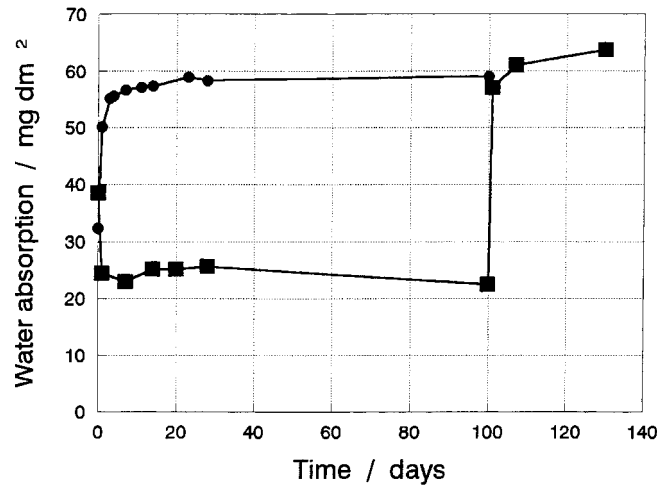


Fig. 3. Weight changes in cold sealed specimens during ageing at a very high (●) or very low relative humidity (■).

at very high and very low relative humidities, and also at 50°C and very high RH. Cold sealed specimens pass the dye spot and acid dissolution tests after ageing at ambient temperature and high RH for less than 24 h. Passing the admittance test entails ageing for three days. Raising the ageing temperature to 50°C leads to cold sealed specimens meeting the quality standards imposed by the dye spot and acid dissolution tests almost immediately, whereas those of the admittance test require 4 h of ageing. Surprisingly, even those anodic films that aged in a highly dry atmosphere – in which a large fraction of the pore length was empty – passed the dye spot and acid dissolution tests very rapidly (within 24 h).

Figure 4 shows the variation with time of sealing quality determined by the admittance test, the most demanding of all the standard tests. In a very dry environment, the cold sealed anodic films shows a too high value of admittance, about three times higher than the maximum value industrially accepted ($20 \mu\text{S}$). However, as the results prove, the films keep their reactivity latent, and improve their quality quickly when the relative humidity of the environment rises.

The XPS analyses revealed the presence of oxygen, aluminium and some carbon – as consequence of surface contamination – on the surface of hot sealed specimens. Cold sealed specimens aged at a high or low moisture were found to also contain nickel and fluorine, in addition to a markedly decreased amount of aluminium relative to hot sealed specimens (Table 2). Aluminium was present as Al^{3+} ion (in oxide form) and no trace of Al^0 was detected [20].

Peak O 1s for the surface of cold sealed specimens exhibited two components at binding energies similar to

Table 1. Effect of ageing time of cold sealed aluminium oxide films on the results of standard quality control tests as function of the temperature and atmospheric relative humidity

Results sealing type	Exposure time /days	Mass change /mg dm ⁻²	Acid dissolution /mg dm ⁻²	Admittance / μ S	Dye drop test number [†]
Unsealed	0	0	436	>300	5
Boiling water	0	41.2	8.4	16	0
Cold sealed (ageing at high RH and room temperature)	0	38	36.6	>300	4
	1	54	12.9*	38	0*
	3	60	8.5	20*	0
	8	61	7.4	12	0
	28	63	4.6	7	0
Cold sealed (ageing at high RH and 50 °C)	0 h	38	36.6	>300	4
	2 h	56	4.3	35	<1*
	4 h	56	2.4	20*	0
	6 h	57	1.8	15	0
	12 h	62	2.4	8	0
	18 h	64	2.7	7	0
Cold sealed (ageing at low RH and room temperature)	0	38.5	53.5	304	3
	1	24.4	14.6	129	1*
	7	22.9	12.5	138	0.5
	30	25.6	5.8	70	0.5
	100	22.4	13.2	64	0.5
	101	56.9	–	76	0.5
	107	61	–	40	0
	130	63.7	–	10*	0

*The standard industrial sealing requirement is surpassed

[†] <2-good sealing, 5-no sealing

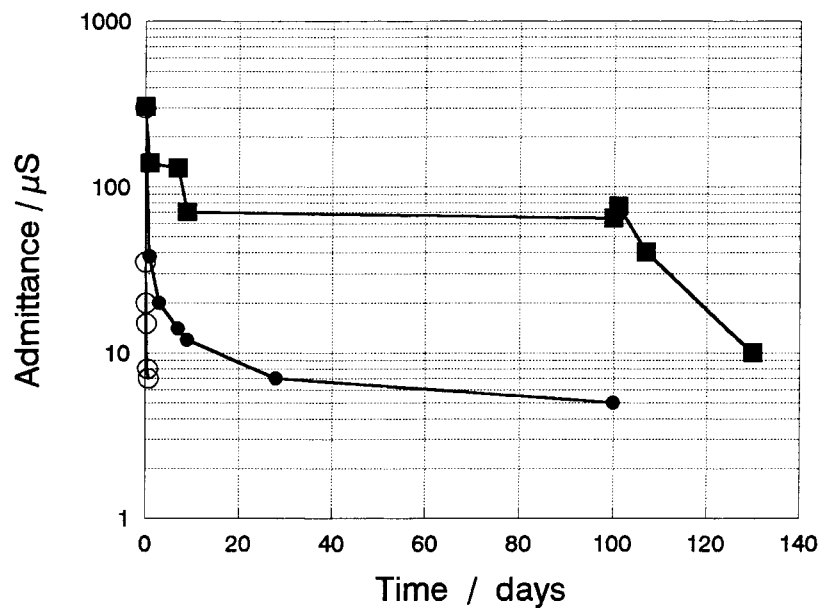


Fig. 4. Results of the admittance test during ageing as function of the temperature and humidity degree of the atmosphere: high (●) and low relative humidity (■) at room temperature and high relative humidity (○) at 50 °C.

Table 2. Percentage composition and binding energies (BE) of the chemical species studied at the specimen surface following surface cleaning (argon bombardment for 5 min)

Sealing type	Al 2p			O 1s			S 2p at %	C 1s at %	F 1s at %	Ni 2p at %
	at %	BE	% area	at %	BE	% area				
HTS during 45 min	28.2	75.0	100	65.5	531.0 532.4	59 O ²⁻ 41 OH ⁻	–	6.3	–	–
Unsealed specimens	27.5	75.0	100	62.2	531.0 532.4	55 O ²⁻ 45 OH ⁻	1.7	8.5	–	–
Cold sealing (aged in high RH)	9.5	75.3	100	45.8	531.6 532.9	52 OH ⁻ 48 H ₂ O	–	19.7	8.4	16.6
Cold sealing (aged in low RH)	6.3	75.3	100	39.9	531.6 533.0	49 O ²⁻ 51 OH ⁻	–	42.6	5.2	6.0

those of peak O 1s for unsealed or hot sealed aluminium, 531.0 and 532.4 eV. The first component can be assigned to oxygen in aluminium oxide and to oxygen in hydroxide ion associated to nickel [21]. The second component can be ascribed to oxygen in hydroxide form associated to aluminium or water [20]. Peak Ni 2p for the surface of the cold sealed specimen aged in a wet chamber was observed at the typical energy for nickel in hydroxide form [22]. As can be seen in Figure 5, the Ni 2p peak for the surface of the cold sealed specimen aged at a very low moisture also exhibited a second component at the typical energy of nickel oxide [22], that was not detected in the specimens aged at a high moisture. Finally, peak F 1s appeared at the typical energy of fluoride ion.

Table 3 gives the percent composition of the anodized aluminium surfaces studied after stripping a thickness equivalent to 10 μm . The sole elements detected in the surfaces thus examined were oxygen, aluminium, sulphur and carbon. It is worth noting the absence of nickel and fluorine from the cold sealed specimens. However, the sulphur is preferentially detected inside the anodic films, although its exact amount is difficult to estimate due to the low concentration. Both components of peak O 1s appeared at the typical binding energies for the oxide (531.0 eV) and hydroxide (532.4 eV).

Figure 6 shows the variation of the aluminium, oxygen and sulphur contents, determined by EDX along lines normal to the specimen surface. As can be seen the three species were uniformly distributed across the oxide film.

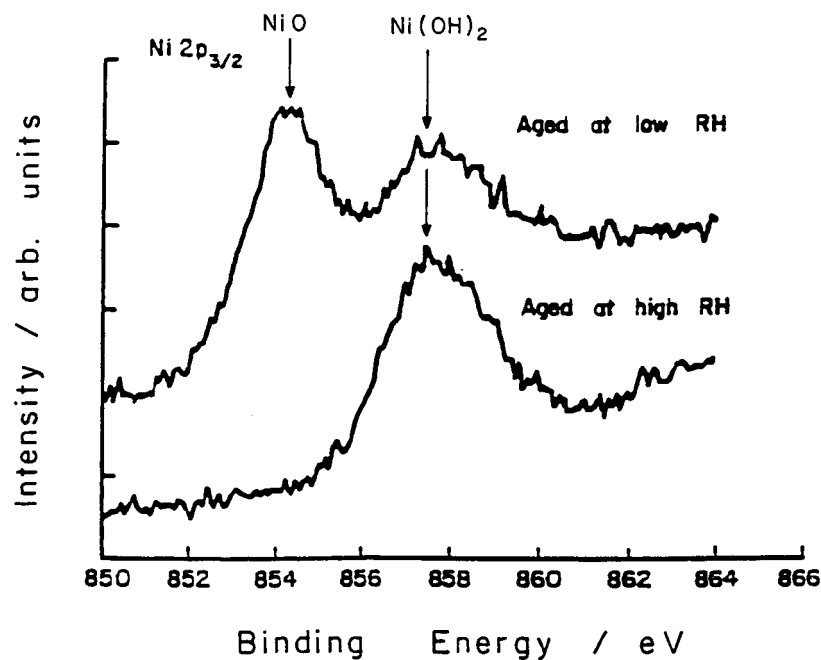


Fig. 5. Ni 2p spectra for cold sealed specimens aged at a very high or very low relative humidity.

Table 3. Percentage composition and binding energies (BE) of the chemical species studied at the specimen surface following surface stripping of a film thickness equivalent to 10 μm following surface cleaning (argon bombardment for 5 min)

Sealing type	Al 2p			O 1s			S 2p at %	C 1s at %	F 1s at %	Ni 2p at %
	at %	BE	% area	at %	BE	% area				
HTS during 45 min	27.0	75.0	100	59.2	531.0	65	1.2	12.5	–	–
					532.4	35				
Unsealed specimens	34.2	75.0	100	61.9	531.0	52	–	3.9	–	–
					532.4	48				
Cold sealing (aged in high RH)	29.5	75.0	100	59.3	531.3	64	1.3	9.9	–	–
					532.6	36				
Cold sealing (aged in low RH)	31.3	75.0	100	60.9	531.3	68	–	7.8	–	–
					532.6	32				

By contrast, the content in nickel decreased markedly, and that in fluorine somewhat more gradually, with increasing depth (Figure 7), which is consistent with the expectations from XPS data. Also consistent with the XPS results, the contents in both elements in the film centre were virtually zero (Tables 2 and 3).

4. Discussion

4.1. Inferences from the impedance diagrams

The impedance diagrams obtained immediately upon removal of the specimens from the cold sealing bath resembles more closely those for unsealed anodic films than those for properly sealed specimens (Figure 1). However, changes occur very rapidly and as ageing time was extended the impedance diagrams evolve from the typical shape for unsealed anodized materials to adequate sealing (Figure 1). One day of ageing at ambient temperature or only 2 h at 50 °C suffices to obtain impedance diagrams typical of well-sealed materials

and, as can be seen from Figure 2, the favorable effect of ageing on sealing quality continued for a very long time.

Though other more complex equivalent circuits allow a better fitting in some specific cases [15–19, 23], the general performance of sealed and unsealed anodized aluminium can be modelled very approximately by the equivalent circuits in Figure 8(a) and (b) [15, 16], provided the film exhibits no deterioration reaching the metal surface.

Impedance values between 10^8 and $10^9 \Omega \text{cm}^2$ are obtained at 1 mHz (minimum frequency used during measurements) without reaching a new resistive region; that is, there is no second semicircle in the Nyquist diagram from which the parameter R_b (in Figure 8(a)) can be determined. In this cases R_b is so high that it prevents the passage of current almost completely; the equivalent circuit in Figure 8(a) can be simplified into the equivalent circuit in Figure 8(c).

The resistance and capacitance of porous layer of the cold sealed film, R_p and C_p , and the capacitance of barrier layer, C_b (and other properties) may be estimated from the impedance diagrams. Figure 9 shows some

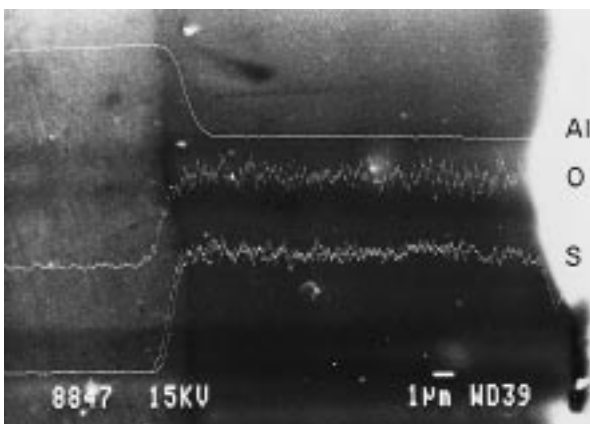


Fig. 6. Aluminium, oxygen and sulphur distributions in a cold sealed oxide film.

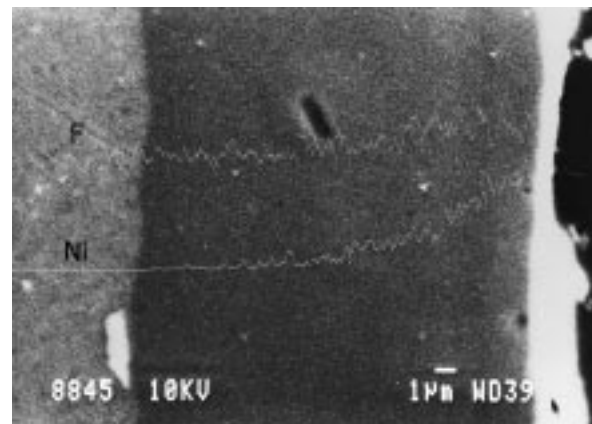


Fig. 7. Fluorine and nickel distributions in a cold sealed oxide film aged at a very high relative humidity.

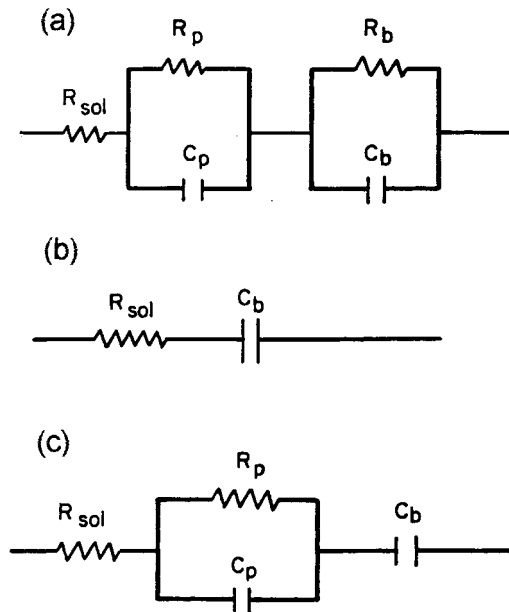


Fig. 8. Simplified equivalent circuits for anodic films.

of the results obtained as a function of the degree of ageing. The changes in pore filling hydration during ageing results in very large and opposing variations in C_p and R_p .

Since C_p and R_p can vary over 2–3 orders of magnitude as a function of degree of hydration (Figure 9), both parameters can be used as quantitative indices in analysing the effect of any factor on the

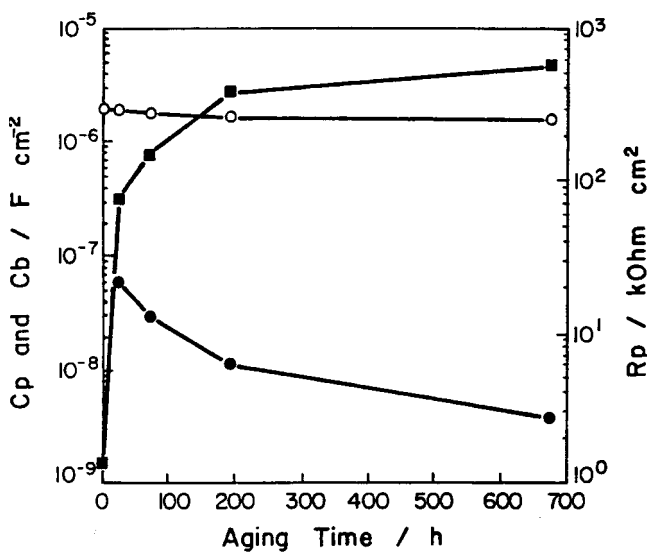


Fig. 9. Evolution of the resistance of the porous film (■) and of the capacitances of the porous (●) and barrier (○) layers for cold sealed specimens as function of the ageing time.

properties of aluminium oxide anodic films and for assessing sealing rate and completeness. R_p increases and C_p decreases as hydration reactions progress within the pores and, consequently, sealing quality improves (Figure 9). After water incorporation by the sealing treatment, aluminium hydroxide gel formation, crystallization and agglomeration processes occur at a later time [19]. As a consequence, intercrystalline water disappears during ageing and the permittivity of the pore filling, ϵ , decreases. Since the oxide film capacitance depends to a great extent on the value of ϵ [17, 19], it is understood that C_p also diminishes (Figure 9). The considerable increase of R_p with ageing must also be related to this loss of intercrystalline water. The small change in C_b during ageing suggests that the barrier layer is not significantly altered during the process.

The estimation of R_b is rarely possible since there are rarely sufficient well-defined low frequency semicircles. Exceptionally, the Nyquist diagram for the specimen aged 3.5 years in Figure 2 allows this estimation, giving a value of $R_b = 9.2 \times 10^7\ \Omega\ cm^2$. Assuming a barrier layer thickness of $180\ \text{\AA}$ (anodizing voltage 15 V, for a limiting barrier layer thickness of $10\text{--}14\ \text{\AA}\ V^{-1}$ [17]) a resistivity value of $\rho_b = 5 \times 10^{13}\ \Omega\ cm$ is calculated for the compact layer, which is at least one order of magnitude lower than that for dense pure alumina [24] or dry anodic films [25]. This difference explains the particular behaviour of the specimen and which may be attributable to the lattice defects of the barrier layer or to its contamination with SO_4^{2-} ions.

Provided that environmental conditions guarantee a period of high, or even moderate, humidity, EIS results show that cold sealed anodic films improve in quality very rapidly (Figures 1 and 2), reaching the levels demanded by the standards without any need of resorting to the two-step cold sealing method.

In general, all these results point out the usefulness of the impedance measurements for a quantitative study of the processes that come about during ageing of the oxide film after the sealing treatment.

4.2. Conventional sealing quality control tests

The fact that specimens absorbed about $20\ mg\ dm^{-2}$ water after removal from the cold sealing bath (Figure 3) confirms that pore shutting was incomplete, in agreement with EIS results. Also, the fact that none of the sealing quality tests was passed immediately after immersion (Table 1 and Figure 4) shows the need for subsequent ageing under conditions that facilitate ulterior hydration.

The facts that water is absorbed at the beginning of ageing and the dye drop test shows levels 3 or 4 (close to the value 5 for no sealing) immediately after impregnation, suggest that the sealing solution that penetrates the pores during immersion occupies the bottom of the pores. Part of this water remains certain time as unsaturated solution or as aluminium hydroxide gel, since specimens lost after impregnation a significant amount of water (15 mg dm^{-2}) in a highly dry atmosphere (Figure 3).

Sealing quality improved very rapidly in a wet atmosphere and met all quality standards within 72 h (Table 1). As a result, immersion in the hot nickel sulphate solution, a usual practice following impregnation in the cold sealing bath, could be dispensed with [11].

Surprisingly, the outer anodic layers continued to evolve even in a highly dry atmosphere and also passed the dye spot and acid dissolution tests within 24 h (Table 1). However, they failed the 1 kHz admittance test, even after 100 days of ageing (Figure 4). The pronounced catalytic effect of the additives of the cold sealing bath in the ageing process is inhibited or dramatically reduced in very dry atmospheres (Figure 4). However, the results described herein prove that this effect keeps latent after 100 days in these atmospheres, coming out again when the specimens are moved to a humid environment, where water is absorbed until pore saturation (Figure 3). Leaving aside its theoretical implications, this result is important from a practical point of view.

4.3. Inferences from the XPS and EDX results

The different conditions used in sealing anodic films on aluminium give rise to different chemical compositions of the film surface. In unsealed and HTS specimens, the chemical composition in the middle of the layers (following removal of a $10 \mu\text{m}$ thickness, Table 2) was similar to that at the surface, which suggests a uniform composition of anodic layers throughout the film thickness. The increased significance of the second component of peak O 1s ($\text{BE} = 532.4 \text{ eV}$) in cold sealed aluminium specimens aged at very low or very high moisture (associated to the presence of water) in relation to hot sealed specimens (Table 2) suggests that the specimen surface consists largely of highly hydrated aluminium hydroxyoxides containing small amounts of nickel hydroxyfluorides. After a thickness of $10 \mu\text{m}$ is stripped off the specimen, the nickel and fluorine contents drop to zero. This difference in the nickel and fluorine contents between the surface and the centre of the anodized film suggests that the two species concentrate near the anodic film/air interface and that their

contents fall abruptly with increasing depth in the oxide layer, consistent with the concentration profiles of Figure 7.

On the other hand, the aluminium, oxygen and sulphur concentrations remain constant through the oxide film thickness (Figure 6), also consistent with previous results [8]. The fact that sulphur is often undetectable by XPS on the surface suggests a possible leaching of SO_4^{2-} ions by the sealing bath, which is consistent with the enrichment of the solution with these ions previously observed by several authors [4–6].

The appearance of a second component for the Ni 2p XPS spectrum at the typical energy for nickel oxide in cold sealed specimens aged at a very low moisture (Figure 6) [22], can be ascribed to the formation of a surface nickel hydroxide layer of smaller thickness than that observed at a high moisture and hence easier to remove by argon ion bombardment; alternatively, it can be assigned to the decomposition of the nickel hydroxide by effect of the bombardment [21].

4.4. Sequence of changes during ageing of cold sealed aluminium oxide films

It should be emphasized that the results obtained suggest that the mouths of the pores in the alumina film *complete its closing* outside of the sealing bath, during the ageing process. A schematic diagram of the different degrees of completeness of the filling and plugging of pores, depending on the cold sealing and ageing conditions, is given in Figure 10(a, b, c and d):

- (i) The bottom of the pores is filled during immersion in the cold sealing solution, but the pore mouth is only partially blocked (Figure 10(a)). This model is justified by the quite low impedance (and high admittance) values, the capability of the film of continuing absorbing water during ageing in humid atmospheres and by the high reactivity in the acid dissolution test and absorption ability in the dye spot test.
- (ii) Pores are virtually filled up at the beginning of ageing at moderate or high RH. Nickel and aluminium hydroxides precipitate at pore mouths and all quality thresholds are reached (Figure 10(b)). This hypothesis is supported by a remarkable increase in the impedance values (and a decrease in the admittance), the increase in the mass of the anodic film, which approach the maximum possible value for water absorption, and the small reactivity in the acid dissolution test and the lower capability of absorption

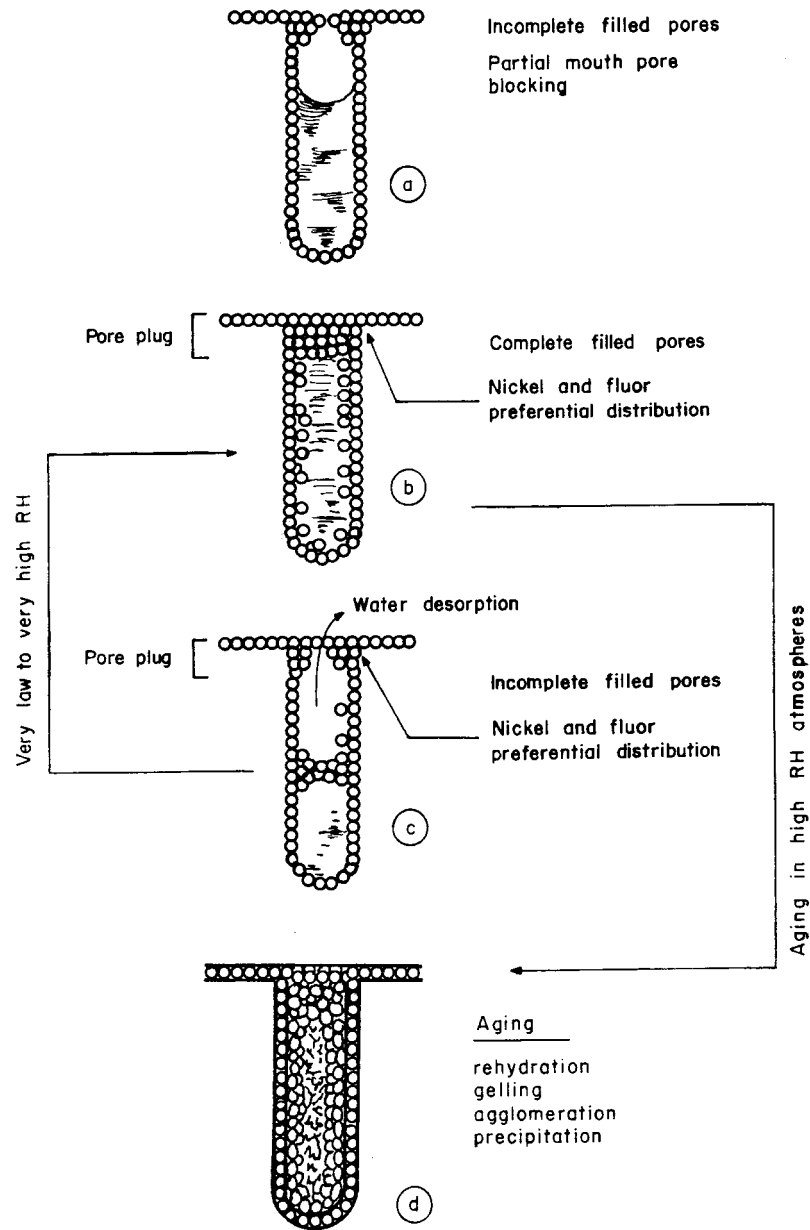


Fig. 10. Proposed mechanism for ageing of cold sealed anodic films exposed to highly wet and extremely dry atmospheres.

in the dye spot test. XPS and EDX analysis show that the Ni and F from the cold sealing bath are concentrated exclusively near the mouths of the pores.

- (iii) At very low RH, a water desorption process takes place and more than half the pore length remains empty. Nevertheless, the mouth of the pore is blocked sufficiently to surpass the dye spot and acid dissolution tests, but not the admittance test. (Figure 10(c)). In accordance with this behaviour, a moderate change towards lower

impedance values, than those for a fully sealed film is observed. XPS results prove that Ni and F are concentrated near the mouth of the pore.

- (iv) Films exposed to dry environments for months are able to pass from situation (c) to situation (b) very rapidly if they are moved to humid environments, as the above mentioned changes in the measured properties show. Inside a full pore, changes continue taking place during ageing (Figure 10(d)). This is observed in Figure 2, where sealing quality,

assessed from film impedance measurements, increases over months and years as ageing proceeds in a natural atmosphere.

5. Conclusions

The results presented in this work demonstrate the following:

- (i) No quality standard is met immediately after impregnation in the cold sealing solution.
- (ii) The last step in the cold sealing procedure involves ageing of anodic films, which starts after immersion in the nickel fluoride bath; during ageing, anhydrous alumina continues its hydration process.
- (iii) Ageing in a wet atmosphere is very rapid; thus, specimens pass all sealing quality tests within 72 h.
- (iv) The rapid ageing of anodic films impregnated in a nickel fluoride bath when exposed to high RH atmospheres makes cold sealing in two steps redundant.
- (v) In a highly dry atmosphere, pores are partially emptied after cold sealing. Nevertheless, specimens pass the dye spot and acid dissolution tests – although not the 1 kHz admittance test – within 24 h of ageing.
- (vi) Cold sealed specimens, whose hydration process has been interrupted by exposing them to a very dry atmosphere, preserve their reaction capacity latent for months in such way that they are quickly rehydrated (fulfilling all the quality indexes demanded by the industry) when moved to a humid atmosphere.
- (vii) As XPS analysis reveal that nickel and fluorine concentrate near the surface of cold sealed anodic films.

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