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A model for the mechanism of nickel fluoride cold sealing of anodized aluminium

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The sealing of porous anodic oxide films on aluminium by the use of nickel fluoride solutions at ambient temperatures has been proposed as an alternative to hydrothermal sealing methods, on energy grounds. The process of cold sealing shows some promise and a mechanism is proposed as to how it may operate. As fluoride ions enter the pores, a place exchange mechanism occurs causing a shift in the local pH which is sufficient to cause nickel ions to precipitate. The nickel hydroxide blocks the pore mouths, effectively sealing the film. A slow step then occurs whereby water from the atmosphere diffuses into the film, effectively hydrating the film and causing general pore blocking. This slow step explains the ageing effect seen with such films. Eventually a film is produced which is effectively sealed.

1. Introduction

Aluminium is a highly reactive metal. To improve its durability and resistance to corrosion it is often subjected to anodization whereby a thick oxide film, typically up to 25 μm in thickness, is grown on the aluminium by making it the anode in an electrochemical system [1]. The mechanism of film growth produces a porous layer. While this film improves mechanical properties such as abrasion resistance, it only marginally improves the corrosion resistance of the underlying aluminium. Hence a method of sealing the pores is required. Traditionally this has been done by immersing anodized samples in boiling water, the hydrothermal method. This tends to be very expensive in energy terms. After the oil crisis of the 1970's, alternative methods for sealing anodized aluminium films were investigated, one of which was based on nickel fluoride [2]. The process appears to be reasonably effective and several patents have been issued on the process [3–5].

In recent years a number of attempts have been made to explain the mechanism of cold sealing [6, 7]. However these have not always been satisfactory. It is now clear that after the initial sealing reaction due to precipitation of nickel hydroxide, a secondary reaction involving the hydration of the alumina film takes place in a similar fashion to that occuring during hot water sealing [8]. The rate at which the reaction occurs in the pores with hot water sealing is greater (temperature effect) whereas with nickel fluoride cold sealing the reaction is long term and depends on the nature of the film, humidity and temperature, and may last up to one year [9].

The mechanism of nickel fluoride cold sealing can be explained as a series of reactions occurring in the pores of the anodic film and can be summarized as: absorption, ion exchange reaction, dissolution, precipitation and hydration.

2. Experimental details

2.1. *Processing*

The pretreatment sequence employed on 1080 alloy samples (75 mm × 50 mm × 0.5 mm) prior to anodizing has already been described in a previous paper [10]. Direct current (d.c.) anodizing was carried out in an electrolyte containing 180 $\mathrm{g\,dm^{-3}}$ sulphuric acid in deionized water at 18–20° C at a constant current density of 2 $\mathrm{A\,dm^{-2}}$. The aim was to obtain a film thickness of 20 μm.

After anodizing sealing was carried out by one of three methods: (i) sealing in nickel fluoride solution without additives at different temperatures (Set 1, Seal I.D. No. 1–3); (ii) treatment in nickel acetate, formate, chloride and sulphate in order to study the effect of various nickel salt solutions (Set 2, Seal I.D. Nos. 1–4); and (iii) Using a pre-dip in nickel salt of sulphate or acetate and then immersing in sodium fluoride solution or vice-versa (Set 3, Seal I.D. Nos. 1–4). Between each stage of the process samples were throughly rinsed.

Set 1 . Guide to sealing composition and operating conditions

Seal identification number	*Sealing composition and operating condition(s)*
1	5 $\mathrm{g\,dm^{-3}}$ $NiF_2.4H_2O$ pH 6, 25° C, 15 min
2	As above, 30° C
3	As above, 40° C

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Set 2. Guide to sealing composition(s) and operating condition(s)

Seal identification number	*Sealing composition and operating condition(s)*	*pH adjustment procedures with diluted solution*
1	0.05 M $(CH_3COO)_2Ni \cdot 4H_2O$ pH 6, 25° C, 30 min	CH_3COOH
2	0.05 M $(HCOO)_2Ni \cdot 2H_2O$ pH 6, 25° C, 30 min	HCOOH
3	0.05 M $NiCl_2.6H_2O$ pH 6, 25° C, 30 min	HCl
4	0.05 M $NiSO_4.7H_2O$ pH 6, 25° C, 30 min	H_2SO_4

Set 3. Guide to sealing composition(s) and operating condition(s)

Seal identification number	*Step 1*	*Step 2*
	Sealing composition and operating condition(s)	*Sealing composition and operating condition(s)*
1	0.05 M $NiSO_4.7H_2O$ pH 5.5, 25° C, 5 min	3 g dm^{-3} NaF pH 6.5, 25° C, 10 min
2	3 g dm^{-3} NaF pH 6.5, 25° C, 10 min	0.05 M $NiSO_4.7H_2O$ pH 5.5, 25° C, 5 min
3	0.05 M $(CH_3COO)_2$ $Ni \cdot 4H_2O$ pH 5.6, 25° C, 5 min	3 g dm^{-3} NaF pH 6.5, 25° C, 10 min
4	3 dm^{-3} NaF pH 6.5, 25° C, 10 min	0.05 M $(CH_3COO)_2$-$Ni \cdot 4H_2O$ pH 5.6, 25° C, 5 min

2.2. *Sample evaluation*

2.2.1. *Seal quality.* To assess the seal quality of the various samples, three tests were used according to British/ISO standard (BS6161–Parts 3, 5 and 6):

Seal quality assessment	*Acceptance limit*
Phosphoric acid/chromic acid (BS 6161–Part 3/ISO 3210)	$\leqslant 30$ mg dm^{-2}
Dye spot (absorption) (BS 6161–Part 5/ISO 2143)	$\leqslant 2$
Admittance (BS 6161–Part 6/ISO 2931)	$\leqslant 20\,\mu S$ for $20\,\mu m$ film thickness

2.2.2. *Analysis of the coating.* Cross sections of samples for microscopic examination were mounted in conductive Bakelite and prepared by standard metallographic techniques. The cross sections were examined and analysed by either a Cambridge Stereoscan 2A scanning electron microscope (SEM), with a Link 860 energy dispersive X-ray analyser (EDX), or a Cambridge Microscan 5 electron probe microanalyser (EPMA).

The morphology of sealed and unsealed oxide films was examined by the replica technique [11] using a Jeol 100 CX STEMMA transmission electron microscope (TEM).

Table 1. Electrical conditions for ESCA investigations

Instrument	VG ESCA LAB
Background pressure	– 10^{-8} mbar
XPS analysis parameters	
X-ray energy	1486 eV AlK
Anode voltage	12 kV
Anode current	20 mA
Analysis area	0.4 cm^2
Emmision angle	Normal
Pass energy	100, 20 eV
Ion beam parameters	
Ion species	Ar^+
Ion energy	5 keV
Ion current	$20\,\mu A$
Gas pressure	– 10^{-5} mbar

The amount of nickel absorbed in the pores of the cold sealed anodized aluminium was measured by atomic absorption spectroscopy. The film was dissolved in an aqueous solution containing 35 ml phosphoric acid (density 1.7) and 20 g of chromium(VI) oxide per dm^3 held at a temperature of about 90° C for 45 min, for $20\,\mu m$ film. Complete removal of the film was checked using a Fischer Permascope.

A Vacuum Generators ESCA LAB electron spectrometer was employed with operating conditions as summarized in Table 1, to study the chemistry of the sealed anodized finishes by analysing the depth of penetration of an element in the pores of the anodic film and the chemical binding between the elements. Primary analysis was carried out on the surface of the anodized and sealed samples which were then mounted by double sided adhesive tape on a thick glass plate, mechanically abraded with 400 grit size silicon carbide papers until the required residual thickness was obtained and reanalysed. Film thickness was checked using a Fischer Permascope. This procedure was carried out from outside the vacuum chamber using gloves in the enclosed glove box adjacent to the ESCA instrument enabling direct insertion of samples into the vacuum chamber so limiting contamination being absorbed on the surface and hence making it possible to study the surface chemistry by mechanical depth profiling without involving any liquid (chemicals) which may cause misleading results. The effectiveness of the procedure had previously been demonstrated [12].

3. Results

3.1. *Sample evaluation*

Figure 1 shows the weight gain of unsealed and nickel fluoride cold sealed finishes as a function of number of days aged at room temperature (Set 1, Seal I.D. No. 1). The weight gain approached maximum after 28 days of ageing.

The results of phosphoric acid/chromic acid, dye absorption and admittance tests for samples treated in nickel salts of acetate, formate, chloride and sulphate

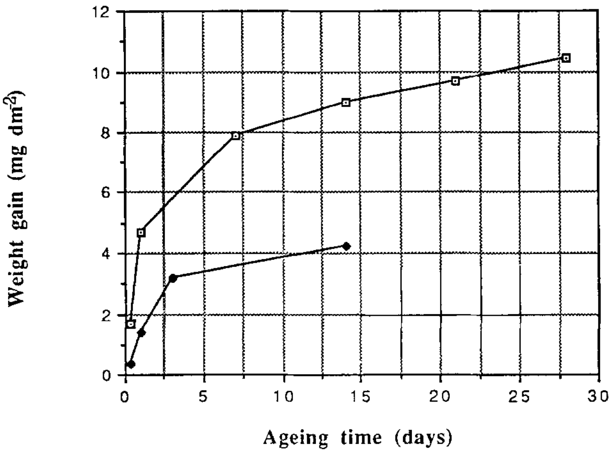

Fig. 1. Weight gain of cold sealed finishes with ageing (Set 1, Seal I.D. No. 1): (□) sealed, (◆) unsealed.

(Set 2, Seal I.D. No. 1–4) indicated (Table 2) that the films do not show any sealing effect. Similar results (Table 4) were also obtained with samples treated by double salt sealing using a predip in nickel salt of sulphate or acetate and then immersing in sodium fluoride or vice-versa (Set 3, Seal I.D. No. 1–4). According to the results of dye absorption tests on samples treated with double salt sealing, a limited sealing effect is achieved but this was found to be insignificant in overall seal quality performance.

3.2. *Surface morphology and compositional analysis*

The surface morphologies of unsealed and nickel fluoride cold sealed samples (Set 1, Seal I.D. No. 1) are shown in Fig. 2a and b, respectively. It is apparent from Fig. 2b that the pores become obliterated by cold sealing treatment and give a smooth surface appearance which is very desirable.

Figure 3 shows the variation of nickel absorption as a function of nickel fluoride cold sealing solution temperature (Set 1, Seal I.D. Nos. 1–3) determined by AAS. The quantity of nickel absorbed is adversely affected by increasing temperature. The AAS results of samples treated in various nickel salts such as acetate, formate, chloride, sulphate and fluoride are shown in Table 3. The quantity of nickel present in the pores was found to be about one third of that obtained with nickel fluoride.

The compositional analysis of cross-sections of nickel fluoride cold sealed finishes was determined by EDX for traces of nickel. The quantity of nickel absorbed in the pores is at a maximum near the oxide-air interface and reduces towards the oxide–base metal (Table 5). This suggests that a higher degree of sealing or porous oxide films takes place with nickel in the outer surface layer adjacent to the sealing solution, with incomplete sealing at depths far from the surface of the oxide film.

Table 2. Results of H_3PO_4/CrO_3 acid dissolution, dye absorption and admittance tests for samples sealed with various nickel salts (Set 2)

Seal identification number	*H_3PO_4/CrO_3 acid dissolution (mg dm^{-2}) 3 days aged*	*Dye absorption 6 h aged*	*Admittance (µS) Time aged*	
			6 h	*6 days*
Set 2, 1	415	5	> 300	> 300
Set 2, 2	403	5	> 300	> 300
Set 2, 3	389	5	> 300	> 300
Set 2, 4	390	5	> 300	> 300
Set 1, 1 [10]	< 20	1	142	32

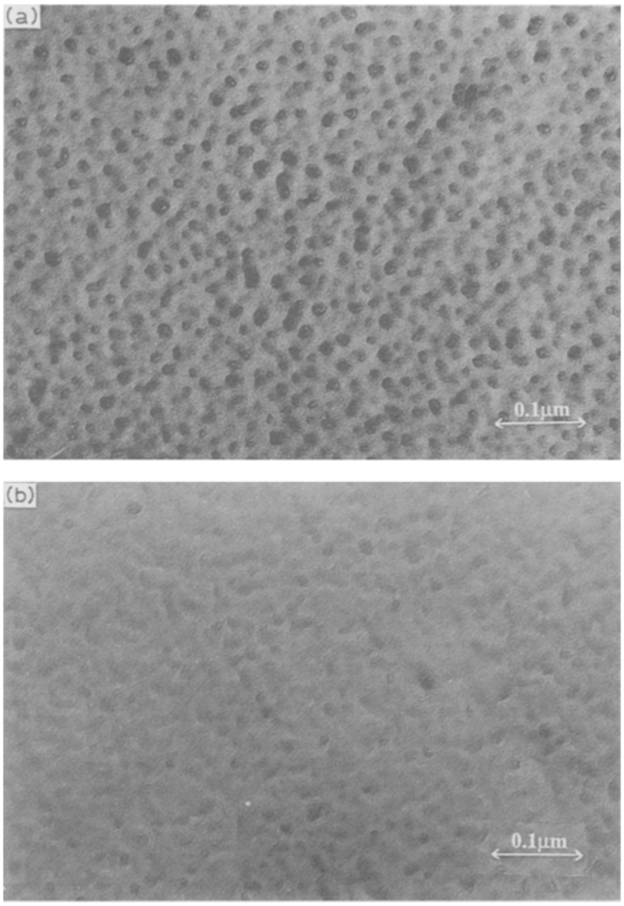

Fig. 2. Transmission electron micrographs of replica of anodic film surfaces (a) Unsealed anodic film, (b) Anodic film after treatment in nickel fluoride solution (Set 1, Seal I.D. No. 1).

The quantitative surface analyses by EPMA of samples treated in nickel salt solution of acetate, formate,

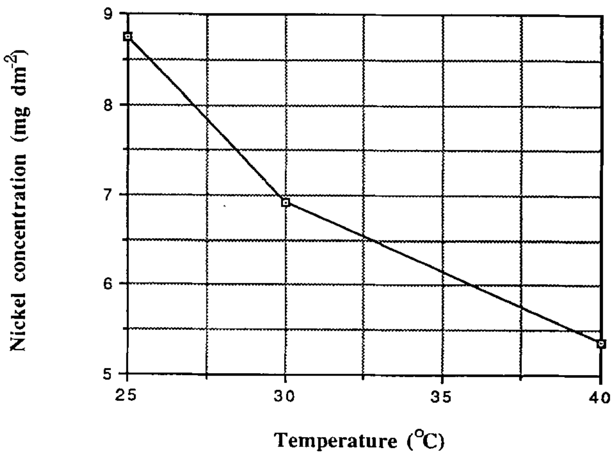

Fig. 3. Concentration of nickel in anodic oxide film as a function of sealing temperature (Set 1, Seal I.D. No. 1).

Table 3. Compositional analysis of anodized samples treated in nickel salts solution for traces of nickel

Seal identification number	*AAS*	*EPMA*
	Nickel concentration (*mg dm*$^{-2}$)	*Wt % composition of nickel* (*top surface of the films*) AV_3*
Set 2, 1	2.9	0.16
Set 2, 2	2.8	0.06
Set 2, 3	2.4	0.01
Set 2, 4	2.7	0.05
Set 1, 1	8.75	2.14

* AV_3 = average of three specimens

chloride, sulphate and fluoride are shown in Table 3. The results correlate with those obtained by AAS where the amount of nickel detected in the film treated in nickel fluoride is some 10–50 times greater than that detected in films treated in the other nickel salts.

ESCA examination was carried out on the surface of anodized specimens sealed in nickel fluoride solution (Set 1, Seal I.D. No. 1). The abrasion technique was used to remove various amounts of anodic oxide film before analysis. The results of ESCA examination are shown as an atomic percentage of the element analysed for various film depths (Table 6) and as the binding energy of the peaks observed during analysis together with values for a sample of pure aluminium fluoride (Table 7). Carbon was used to calibrate the binding energy scale. The concentration of Al, S, C, Ca, O, Ni or F was measured at each level in the film examined. Most of the carbon present was due to contamination, hence the values for carbon in Table 6 have been deleted and the figures for the remaining elements have been renormalized.

Figure 4 shows the distribution of nickel and fluorine produced on sealing. The nickel and fluorine levels are maximum at the top surface and reduce with depth into the film. Murphy *et al.* [13] indicated 9 at % of nickel by RBS at the outer surface for hot sealing in nickel acetate solution, here, with cold sealing, the nickel content was found to be 16.3 at % determined by ESCA (Table 6, Set 1, Seal I.D. No. 1). This indicates that the rate of reaction which occurs in the pores is very high, possibly preventing the nickel from penetrating deeper into the pores. Therefore, more nickel is detected at the top surface (oxide-air) in the present case.

Table 4. Results of H_3PO_4/CrO_3 acid dissolution, dye absorption and admittance tests for samples cold sealed by double salt technique (Set 3)

Seal identification number	H_3PO_4/CrO_3 *acid dissolution* (*mg dm*$^{-2}$) *1 day aged*	*Dye absorption 1 day aged*	*Admittance* (*μS*) *Time aged*	
			1 day	*30 days*
Set 3, 1	415	3–4	> 300	> 300
Set 3, 2	403	3–4	> 300	> 300
Set 3, 3	389	3–4	> 300	> 300
Set 3, 4	390	3–4	> 300	> 300
Set 1, 1 [10]	< 20	1	111	18

Table 5. Approximate compositional analysis of sealed anodic film using EDX technique (Set 1, Seal I.D. No. 1)

Depth (*μm*)	*Wt % Composition of Ni*
0	2.6
4–5	1.2
7–8	0.6

Although fluoride levels, as with nickel, are a maximum at the outer surface and reduce further into the film, the rate of decrease for the two elements was different (Fig. 4) with some evidence that the penetration of fluoride ions is greater than that of nickel ions. This is in agreement with the results reported by other investigators [7].

The binding energy of the elements analysed (shown in Table 7) are an indication of the chemical state of the element. The values obtained in this analysis do not correspond to AlF_3. As shown in Tables 7 and 8, the binding energy for aluminium does not correspond to that obtained from standard (pure AlF_3) and the published value [14].

Short and Morita [7] used oxygen as the element to calibrate their binding energy scale. This raises the question as to the interpretation of their results since oxygen is present in many forms such as Al_2O_3, SO_4^{2-}, H_2O etc. and the principle form of oxygen may change with depth. During the ESCA experiments, the source of carbon containing contamination of the film surfaces appeared to be from the same source in each instance. Hence it appeared appropriate to use it to calibrate the binding energy scale. From the analytical values obtained in Table 6, about 20–25% of nickel could be present as nickel fluoride (NiF_2); also a peak was found with a binding energy (Table 7) that corresponds to the published value for nickel fluoride and hence it is assumed to be nickel fluoride. Due to the absence of a satellite peak, the remaining nickel is not present as nickel oxide [15] but as compared with Table 8 [15], is probably nickel hydroxide.

The presence of a small amount of oxy fluoride as reported by Short and Morita [7] cannot be discounted. However, no direct evidence was seen for this

Table 6. Composition depth profile ESCA analysis of nickel fluoride cold sealed finishes for 20 μm anodic film (Set 1, Seal I.D. No. 1)

Depth (*μm*)	*Atomic percent*					
	Al(2p) *%*	*S(2p)* *%*	*Ca(2p)* *%*	*O(1s)* *%*	*Ni(2p*$^{3/2}$*)* *%*	*F(1s)* *%*
0	13.8	1.6	0	54.7	19.1	10.9
1.0	28.0	2.1	0.14	62.0	4.5	3.2
2.5	29.2	3.1	0.24	62.3	2.8	2.3
4.0	30.0	3.1	0.24	63.0	1.1	2.3
5.0	32.3	2.0	0.9	63.0	0	1.8
10	35.5	3.1	0.34	60.4	0	0.9

Table 7. ESCA analysis of nickel fluoride cold sealed finish for 20 μm anodic film

Seal identification number	Binding energies (eV) eV(± 0.3 eV)*				
	Al(2p)	F(1s)	F(Auger)	Ni($2p^{3/2}$)	Ni(3p)
Set 1, 1	74.8	684.2	657.6	855	69
Standard AlF_3	76.0	686.1	653.3		

* Measured against C(1s) at 284.6

compound. Also there appears to be no published values available for such a compound.

The pH of nickel fluoride cold seal solution was monitored as anodized samples were processed. When eight samples were processed at 25° C for 5–20 min, a pH of 6.5 was found, whereas the same number of samples with the same surface area, anodic film thickness and sealing time at 40° C gave a pH of 6.66 (both having an initial pH of 6). This indicates that with an increase in sealing temperature the sealing solution pH increases. The rise in pH with temperature of sealing may be connected with the AAS results (Fig. 3), which showed a corresponding decrease in nickel in the film, to indicate that the nickel in the pores becomes hydrolysed more rapidly, thus increasing the rate of plugging of the pores and hence limiting the amount of nickel precipitation there. This was found to have a direct effect on seal quality [9]. Hence higher temperature is detrimental in many aspects.

4. Discussion

This section covers two parts; one explains the hydration process associated with nickel fluoride cold sealing and the second part compares and discusses the results of seal quality with samples which have been treated in other nickel salt solutions (Set 2, seal I.D. No's 1–4) and samples which have been treated in two steps (Set 3, seal I.D. No's 1–4).

It has been noted [10] that when freshly precipitated nickel hydroxide is produced, it will usually redissolve in acid fairly readily. However, if it is allowed to stand for some time, often the rate of dissolution in acid is much slower. This has been assumed to be due to a crystallization effect of the materials precipitated in the pores of the anodic oxide film. Such a crystallization effect was particularly noted with nickel fluoride sealing [9, 10]. This, in part, explains the ageing effect observed with cold sealed finishes. Ageing appears to be a two stage process. There is a rapid ageing process taking place in the first five hours [10] whereby the nickel hydroxide/hydroxy fluoride precipitate is stabilized which allows tests such as phosphoric acid/chromic acid and dye absorption to be passed. This is followed by a slow ageing process which seems to involve the general hydration of the film and more complete pore blockage. This is exemplified by the weight gain measurements (Fig. 1) and the admittance measurements [10] which may take 14–30 days to reach a satisfactory level.

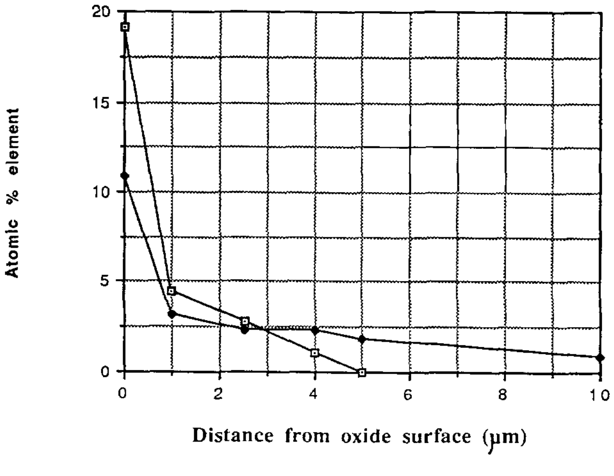

Fig. 4. Distribution of nickel (☐) and fluorine (◆) produced on sealing determined by ESCA analysis (Set 1, Seal I.D. No. 1).

The difference in response to the various standard seal quality tests may be explained as follows. Many of the tests are essentially acid dissolution tests. On an unsealed anodic oxide film, the acid probably first attacks the pore wall which tends to have a looser general structure [8]. On a freshly nickel fluoride cold sealed anodized film, the test acid can attack the nickel hydroxide, dissolve it, and subsequently carrying on attacking the oxide film. After about 5 h of ageing of nickel fluoride cold sealed samples, the nickel hydroxide in the pores has crystallized sufficiently to resist the attack of the acid and hence protect the more vulnerable pore wall structure. This seems to apply quite well as far as the phosphoric acid/chromic acid test is concerned. As far as acetic acid/sodium acetate and acidified sodium sulphite dissolution tests are concerned, the ageing time required to pass the test would seem to depend on the pH, temperature of the solution and the effect of other ions in tests solution on the redissolution of the partially crystallized nickel hydroxide. This also helps to explain why the cold sealed samples will pass the dye spot test relatively shortly after sealing. In this case, the acid activator is applied for one minute (at room temperature) before application of the dye tests, compared to the 15–30 min of the acetic acid/sodium acetate and acidified sodium sulphite dissolution tests [10]. In the case of the admittance test, the physical properties of the whole film are being measured. In the freshly sealed film only near the top surface of the film is plugged and essentially the remainder of the film down to the aluminium substrate is unaffected. However with extended periods of time much of the remainder of the film becomes hydrated and the pores become plugged. Hence eventually a satisfactory admittance value is achieved. The question may arise as to why the alumina film should continue to hydrate with time, especially since the pore mouths have been plugged. An unsealed film will gain weight with time, but only at about one half the rate of cold sealed samples (Fig. 1). Also such a film never seems to produce a satisfactorily sealed

Table 8. Possible chemical/binding assignment

Reference number	*Al_2O_3*	*AlOOH*	*$Al(OH)_3$*	*AlF_3*	*NiO*	*$Ni(OH)_2$*	*F(1s)*	*F(Auger)*
7						855.9		
14	74.2	74.2	74.2	76.1		856.1	684.8	655.7
15					854 ± 0.15	855.6 ± 0.3		
16						853		

finish no matter how long it is aged [10]. Analytical values obtained (for nickel fluoride cold sealed samples) in Tables 6 and 7 suggest that the pores contain nickel fluoride, nickel hydroxide, aluminium, and sulphur probably as aluminium hydroxide, aluminium sulphate and the presence of hydroxy fluoride could not be discounted [7]. The authors believe that in nickel fluoride cold sealing, the nickel ions have a catalytic effect on the hydration process (as has also been suggested by another author [17]), and in the presence of fluoride a suitable pH condition is created for aluminium to hydrate at a greater speed than with unsealed films (Fig. 1).

Therefore the material in the pores and the walls swells causing complete plugging of the pores. When such a surface has been aged, it shows a low solubility in the acid dissolution test, and a good score in the copper accelerated acetic acid salt spray (CASS) test [10].

The seal quality assessed by phosphoric acid/chromic acid dissolution, dye absorption and admittance tests indicated (Table 2) that the films treated in nickel acetate, formate, sulphate or chloride do not show any sealing effect. This can be explained by the results of analysis of the films determined by AAS (see Table 3) in which the quantity of nickel absorbed in the pores was found to be about one third of that obtained with nickel fluoride. The EPMA results also show (Table 3) that the amount of nickel detected in the films treated in nickel fluoride is some 10–50 times greater than that detected in film treated in the other nickel salts. Therefore the high absorption of nickel in the pores was assisted by fluoride in solution. Other ions do not contribute a great deal to sealing when assessed by the seal quality tests, bearing in mind that the aim is to deposit enough nickel in the pores for plugging to occur.

The seal quality of samples treated by two-step sealing determined by phosphoric acid/chromic acid, dye absorption and admittance tests also showed (Table 4) no sealing effect and also indicated that the presence of nickel and fluoride ions together in the sealing solution is necessary for sealing to occur and hence, as is also shown above, the role of fluoride in sealing is significant for cold sealing to occur in order to obtain optimum protection.

5. Proposed mechanism of cold sealing

The anodic oxide film formed on aluminium in sulphuric acid contains a large number of pores. These pores are long and thin (20 μm long and about 10–20 nm in diameter). On completion of anodizing, the aluminium is removed from the sulphuric acid. At this point the sample is washed. Some of the residual acid will be leached out, especially from near the surface, but further into the film the pores will contain acid. Acid leaching was confirmed by boiling an anodized sample for 20 minutes and measuring the pH of the water before and after treatment. Wefers [18] in his study of the sealing mechanism also found that the pH of the water dropped during hydrothermal sealing. The degree of acidity in the pores is further influenced by a number of causes:

The reaction between aluminium and water also generates some hydrogen ions, which tend to effect the pH in the pores.

$$2Al + 3H_2O \longrightarrow Al_2O_3 + 6H^+ + 6e^- \quad (1)$$

There is a reaction of sulphuric acid with Al_2O_3

$$Al_2O_3 + 6H^+ \longrightarrow 2Al^{3+} + 3H_2O \quad (2)$$

According to Greenwood and Earnshaw [19], aluminium has a small ionic size and a high charge density, forms a strong bond with oxygen in water and weakens the oxygen-hydrogen (O—H) bond and increases the preponderance of H^+ released in the water making the solution acidic.

$$Al^{3+} + xH_2O \longrightarrow [Al(H_2O)_{x-1}OH]^{2+}_{(aq)} + H^+_{(aq)} \quad (3)$$

Other authors [20] suggest that the above hydrolysis equation is too simple and that the main species present are the ions $[Al_2(OH)_2]^{4+}$ and $[Al_{13}(OH)_{32}]^{7+}$. However, the pH drop that is observed after boiling of the anodized samples in water, could be explained by the above reaction plus the diffusion of sulphate species (aluminium sulphate/sulphuric acid) from the pores.

According to the Pourbaix (potential/pH) diagram [21] from aluminium, at low pH the oxide film will dissolve. Therefore for sealing to take place the cold seal solution should have a pH in the range of 3.8–8.5 where aluminium oxide is stable and preferably, by analogy with hydrothermal sealing a pH in the range of 5.5–7.0 [1]. For this to happen, the ions from the seal solution should be able to penetrate deep into the pores and mop up the hydrogen ions.

The study of cold sealing shows that the nickel fluoride solution possesses such properties, which after processing the anodized aluminium the pH was found to have increased, implying the solution reacts with ions in the pores resulting in neutralization of some of the hydrogen ions causing a rise in pH. A similar rise in pH was found by Short and Morita [7]. Such an increase was not observed with nickel salts of sulphate, chloride, acetate and formate. According to a study carried out by Schmitt and Pietrzyk [22] on liquid chromatographic separation of inorganic anions on an alumina column, the retention of various ions on alumina was

$$F^- > SO_4^{2-} > Cr_2O_7^{2-} > HCO_2^- > \text{benzoate}$$
$$> ClO_2^- > BrO_3^- > Cl^- > NO_2^- > Br^- > ClO_3^-$$
$$> SCN^- > I^- > ClO_4^- > C_2H_3O_2^-$$

Assuming that the oxide film on anodized aluminium is not too dissimilar to the alumina used in the above study, it is apparent that the sulphate ion is fairly strongly bonded to the alumina. This bond appears to be stronger than either formate, chloride or acetate. However, it appears to be weaker than the bond for fluoride ion. Hence it suggests that formate, chloride and acetate will be unable to displace sulphate from the aluminium, whereas the possibility arises that fluoride may do so. It is therefore possible that in nickel fluoride sealing, the reaction involves a degree of fluoride-sulphate exchange. Analysis of nickel fluoride solution after processing of anodized aluminium using gas chromotography and AAS showed [9] traces of SO_4^{2-} and Al^{3+}. This may imply an ion exchange reaction as well as simple outward diffusion of $Al_2(SO_4)_3$.

As suggested by Schmitt and Pietrzyk [22] fluoride is able to bond strongly on alumina in the ion exchange column and in addition to the exchange reaction with sulphate may be able to find new sites exchanging with hydroxyl groups and releasing OH^- to cause a rise in pH. The reaction which occurs may be

$$\rightarrow Al^+\ O\text{–}H^- + F^- \longrightarrow \rightarrow Al^+\ F^- + OH^- \qquad (4)$$

Lorking and Mayne [23] added sodium fluoride of pH 5.4 to anhydrous aluminium oxide in water. After a period of four weeks the pH of resulting solution was found to be 10.6. This further implies the release of OH^- group by attachment of fluoride ion to aluminium probably as a oxy-fluoride.

Fluoride ion is retained via the formation of an electrical double layer at the alumina surface. This happens when the surface charge appears due to dissociation at surface $\equiv$AlOH groups and detachment of hydroxide ions. As a result of the charge site, ions of opposite charge are attracted from the bulk of the solution with the resulting formation of two charged planes at the interface [22].

With ESCA analysis (Table 7) there was no evidence for aluminium fluoride. However, the compound is probably in the form of oxy or hydroxy complex fluoride [24]. Since there is no ESCA data for this compound it cannot be confirmed that such ions are present. Also the concentration of any fluoride compound may be below the ESCA detection limit.

The increase in pH of sealing solution observed after processing of aluminium may be derived from Equation 4, also the reaction between fluoride ions and hydrogen ions in the pores, shifts the reaction to the right causing a rise in pH.

$$H^+ + F^- \longrightarrow HF \qquad (5)$$

Since the HF is a weak acid in water, its conjugate base F^- is a strong base which reacts with H_2O [25] as

$$F^- + H_2O \longrightarrow HF + OH^- \qquad (6)$$

Therefore OH^- is produced and H^+ absorbed thereby the pH in the pores increases. Some of the hydroxyl ions formed also from Equations 4 and 6 neutralize the hydrogen ions produced from Equation 3.

The amount of hydroxyl ions formed by processing anodized samples in nickel fluoride solution is sufficient to cause an increase in pH of the bulk solution, therefore the local pH causes the precipitation of nickel and it may also be possible to cause some dissolution of the oxide film in the first few minutes of sealing. The TEM study of unsealed and sealed films shows the porous structure became obliterated after nickel fluoride sealing (Fig. 2a and b) and when the specimens were viewed they had a smooth surface appearance. The analysis of nickel fluoride solution after processing of anodized samples showed the presence of aluminium and sulphate confirming some dissolution of the film resulting in a smooth appearance. Dito and Tegiacchi [6] reported that both aluminium and sulphate dissolution in the sealing bath are mainly from the top surface of the film and they reach their normal values towards the base metal. This is a result of rapid pore closure that occurred during the first few minutes of treatment, and pore plugging prevents any decrease in sulphate and aluminium from outward diffusion from the pores into the solution. The ESCA analysis is also in agreement with the above claim.

Short and Morita [7] proposed that the fluoride ion in the solution is absorbed by the anodic oxide film ($Al_2O_3 \cdot H_2O$) forming a complex ion, which subsequently dissolves. This dissolution of the anodic film and the observed loss in sulphate ions will result in a localized reduction in the pH in the pores which will accelerate the dissolution and result in a pH gradient in the pores. When the aluminium in solution in the pores mixes with the higher pH solution at the entrance to the pores it will precipitate, along with nickel ions present in the form of a mixture of hydroxy-fluoro aluminium and hydroxy aluminium and hydroxy nickel. This is a rather contradictory statement to their results because, if there was any dissolution by reduction in pH in the pores/surface, the pH of nickel fluoride solution would also decrease with use. Nevertheless, the above authors also show an increase in pH with the processing of the samples in nickel fluoride which is in agreement with the result obtained in this present work. Therefore the sealing occurs at a high pH due to hydroxyl ion formation, and the precipitation achieved by increase of the pH with fluoride in the pores/oxide surface.

The amount of hydroxyl ions produced mainly depends on the temperature of the sealing solution in which an increase in temperature causes rise in pH of sealing solution, thereby preventing the efficient entry of solute ions into the pores by a more rapid initial plugging at the pore mouth. As shown by AAS analysis (Fig. 3) the higher temperature of sealing decreases the absorption of ion(s) such as Ni^{2+} or vice versa.

The fact that nickel starts to hydrolyse as nickel hydroxide above pH 6, may imply that during the sealing once such a high pH has been reached the nickel is precipitated, but the extent of precipitation may be influenced by local conditions within the pores, such as residual sulphate and aluminium content. The precipitation of nickel is more extensive in the outer film regions where the pH is probably highest, gradually declining towards the oxide-base metal. The EDX, EPMA and ESCA analysis all indicate that for cold seal solution the precipitation plug is completed very quickly mainly near the outer surface, severely limiting further entry of sealant into the pores and therefore further precipitation.

The quantity of material absorbed/precipitated (mainly nickel) is determined by the fluoride present in solution (the combination of the two ions in solution was found to be necessary for sealing). It has been shown from the results of quantitative analysis using AAS that the nickel concentration is three times greater for nickel fluoride than nickel salts of SO_4^{2-}, Cl^-, $HCOO^-$ and CH_3COO^- and by EPMA analysis of the top surface 10–50 times greater for the nickel fluoride. This suggests the relative reaction is increased in the presence of fluoride. ESCA analysis shows that the fluoride penetrates deeper in the pores than nickel and promotes the absorption of positively charged ions such as Ni^{2+}.

The analytical values obtained from ESCA showed that fluoride concentration at the top surface is about half the nickel or about 20–25% of the nickel is present as NiF_2, the remainder of the nickel is probably nickel hydroxide. This may suggest that the precipitate formed is a mixture of nickel hydroxide and fluoride with a relatively small amount of aluminium at the top surface.

It is likely that once the pH in the pores increased (above 3.8), the aluminium ions precipitated possibly forming a hydroxide:

$$Al^{3+} + 3OH^- \longrightarrow Al(OH)_3 \qquad (7)$$

or

$$2Al^{3+} + 6OH^- \longrightarrow Al_2O_3 \cdot 3H_2O \qquad (8)$$

or a compound containing aluminium hydroxide and fluoride with the nickel compound.

As shown by ESCA analysis, the middle portion of the anodic oxide film (the area devoid of nickel) contains substantial amounts of aluminium, oxygen, sulphur and some fluoride. Probably fluoride in these areas will cause a rise in pH leading to the precipitation of aluminium hydroxide. In this area pores however may not be fully plugged with probably incomplete sealing occuring at depths far from the surfaces of oxide film.

The nickel fluoride cold sealed samples immediately after sealing show a poor seal quality. However with ageing the samples passed the seal quality tests [9]. This indicates that the compound precipitated in the pores initially is insufficiently crystallized. The reaction cannot therefore be considered a major sealing process but with ageing the film becomes stable and shows significant improvement in seal performance.

The gravimetric measurement of cold sealed finishes showed that samples gain in weight with time (Fig. 1). Campanella [17] in his mechanism of ageing of hot nickel salt sealing postulated that the nickel has a catalytic effect and possibly absorbs water molecules from the atmosphere causing the hydration of the film. The presence of water in the pores of sealed anodized aluminium in this current study was implied by a long pumping down time in the ESCA vacuum chamber prior to analysis.

The absorption of water molecules in the pores results in a long term pore filling process with some increase of material volume, in which case the pores become compact and tightly blocked preventing entry of dye stuff or corrodent products.

The humidity and temperature of the environment are important factors in the continuous process of nickel fluoride sealing. For the same reason if the samples are exposed in a dry (very low humidity) environment, a post-treatment after nickel fluoride cold sealing is strongly recommended [26] in order to stabilize the sealing process.

6. Conclusions

The overall conclusion is that the following main reactions occur in the pores due to nickel fluoride cold sealing.

(i) Absorption of nickel fluoride on the surface and walls of the pore structure.

(ii) Diffusion of fluoride ions in the pores, promoting the absorption of positively charged ions (Ni^{2+}).

(iii) Ion exchange between fluoride and sulphate causes an increase in concentration of sulphate in the pores leading to outward diffusion of sulphate into the bulk solution.

(iv) The ion exchange between fluoride and hydroxyl groups on aluminium causes a rise in pH.

$$\rightarrow Al^+O\text{–}H^- + F^- \longrightarrow \rightarrow Al^+F^- + OH^-$$

(v) Reaction between fluoride ions and hydrogen ions in the pores, shifts the reaction to the right causing a rise in pH

$$H^+ + F^- \longrightarrow HF$$

and since HF is a weak acid in water, its conjugate base F^- is a strong base which reacts with water as

$$F^- + H_2O \longrightarrow HF + OH^-$$

Therefore OH^- is produced and H^+ absorbed thereby the pH in the pores increased.

(vi) Some dissolution of aluminium sulphate.

(vii) Precipitation of metal compounds such as nickel hydroxide.

(viii) The film ages in two stages. The first stage involves the crystalization of nickel hydroxide and other metal compounds and takes place in a first few hours of sealing.

(ix) The second stage involves atmospheric hydration of the film and results in swelling and pore plugging.

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