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Formation of carbonaceous-coatings on aluminium using poly(vinyl alcohol)

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Abstract

Uniform and adhesive carbonaceous-coatings were formed on the aluminium by the following two-step process: first, aluminium specimens were anodized in acid solutions to form porous anodic oxide films; they were then heated with powder of poly(vinyl alcohol) (PVA) in flowing argon at 300°C for 30 min then at different temperatures of 450–550°C for 1 h. The coatings showed mirror-like smoothness on the electropolished and anodized specimens. The coating failed on specimens without the porous oxide films. The penetration of the fluid materials formed in the course of the decomposition of PVA into the pores of the porous oxide film was accordingly important for adhesion. This anchor effect was confirmed by scanning electron microscopy. The Vickers hardness of the surface was increased by coating and by increasing temperature of the coating process. The highest value was $Hv_{50} = 850$. The resistance to pitting corrosion in a NaCl solution was markedly increased in specimens coated at 450°C. The coating is resistant also to 1 mol l^{-1} HCl solution and to organic solvents such as acetone and hexane. © 2000 Elsevier Science Ltd. All rights reserved.

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1. Introduction

Carbon coating on aluminium is useful to improve the chemical and physical properties of the metal and its alloys. It confers resistance to environmental attack such as corrosion, abrasion and scratching, and helps during the formation of carbon/aluminium composites and during joining with other carbon materials. The direct formation of uniform and adhesive carbonaceous-layers on aluminium, however, is known to be difficult, even by CVD or PVD. Surface pretreatment of aluminium is essential for adhesive coatings.

We have developed a simple method to coat ceramic powders with carbon: it is accomplished by heating mixed powders of ceramics and of poly(vinyl chloride) (PVC) under inert atmospheres.[1] The process utilizes the characteristic thermal-decomposition behavior of PVC and the fact that it forms a low viscosity fluid above 200°C.[2] It was found that the process can be applied to aluminium plate,[3] for which the pretreatment of the aluminium surface was found to be an important factor in achieving a uniform and adhesive carbonaceous-layer. The process is useful but has the disadvantage that PVC produces hydrogen chloride gas by decomposition. By preliminary experiment, poly(vinyl alcohol) (PVA) was found to be useful as an alternative material which is classified as a precursor of soft carbon; the precursors to hard carbon such as poly(ethylene terephthalate) (PET) and poly(vinylidene chloride) (PVDC) were not suitable.

In the present work, a process using PVA was developed in which the suitable heating conditions and a preferred surface pretreatment for uniform and adhesive carbonaceous-coatings were developed. In addition, for the aluminium with carbonaceous-coatings, the hardness, corrosion resistance in a chloride medium, and protective ability against hydrochloric acid and organic solvents were evaluated.

2. Experimental

A1100 aluminium sheets cut into appropriate sizes were etched or electropolished by conventional methods,

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and anodized under the conditions shown in Table 1. Unless otherwise noted, electropolished specimens were used. In a neutral borate solution a non-porous anodic oxide film which is called barrier-type is formed and the thickness is 0.5 μm under the conditions shown in Table 1. In acid solutions, porous anodic oxide films are formed and some of the specimens with such films were kept in the solutions after anodizing for pore-widening. Oxide films having different pore diameters of 20–100 nm and having thickness of 0.42–33 μm were formed. The geometry of the porous anodic oxide films, such as pore diameters and the number of pores, is well established (e.g. Refs 4–6), though we have again measured a part of them in the present work by the pore-filling method.[6] Hereafter, anodic oxide films formed in an oxalic acid solution are denoted as ‘oxalate’ film, and similarly for other solutions.

For coating, the specimens were put in an alumina or quartz boat filled with PVA powder (average degree of polymerization = 1700) and heated at 400 K h^{-1} under flowing argon. The composition of the carbonized PVA was determined by elemental analysis for carbon and hydrogen.

To observe the cross-section of the coated specimens they were broken off after making a shallow cut on the reverse side. The observation was carried out using a field emission type SEM at an acceleration voltage of 10 kV. It is known that lower acceleration voltage is preferable to observe the detailed micro-structure of carbon materials, though high voltage provides higher magnification and better resolution. The 10 kV was a compromising condition in the present work.

Micro-Vickers hardness, Hv, was measured on the surface of the carbonaceous layer with a 25 g load and on the cross-section of the anodic oxide film with a 50 g load at the middle point between the surface and the oxide/metal interface. The cross-sectional measurements are applicable to the samples thicker than about 15 μm. With three different specimens, 10 points were measured for each.

For the corrosion test, 5×5 mm^2 areas of the specimen surface were exposed using epoxy resin. The test specimens were immersed in a 0.07 mol l^{-1} NaCl–0.002 mol l^{-1} $CuCl_2$ solution (pH = 3.0, adjusted with acetic acid) in petri dishes open to the air for a maximum of 12 days: the solution is the same type on that used for the salt spray test.[7] Every 24 h the solution was changed and the number of areas that showed a pit, n_p, was counted. The survival probability against pitting, P, was calculated by $P = (n - n_p)/n$, where n is the total number of test areas; n = 20 in the present work. Details have been described elsewhere.[8]

For the acid contact test, a short silicone rubber tube of 0.8 cm^2 cross-section (inner area) was put on a coated specimen with epoxy resin and 1 mol l^{-1} HCl solution was poured into it. Ten specimens were tested for each coating condition and every 24 h the number of specimens that showed exfoliation of the carbonaceous layer was counted. The organic solvent test was done in acetone and hexane for 60 min with an ultrasonic rinsing apparatus.

Table 1
Conditions to form anodic oxide film on Al

Solution	Temperature (°C)	Anodizing	Time (min)
0.5 mol l^{-1} H_3BO_3 −0.05 mol l^{-1} $Na_2B_4O_7$	20	$i = 5$ A m^{-2} $E_{\mathrm{final}} = 360$ V	6.5
0.635 mol l^{-1} $(COOH)_2$	20	$i = 50$ A m^{-2}	10–30
	20	$i = 200$ A m^{-2}	15–60
10% H_2SO_4	15	$i = 300$ A m^{-2}	0.5–30
4% H_3PO_4	25	$E = 100$ V	3–60

3. Results and discussion

3.1. Determination of heating procedure

The results of thermo-gravimetry and differential thermal analysis (TG-DTA) of PVA were nearly the same with those reported by Dollimore and Heal,[2] so that they are not repeated here. The results indicated that the decomposition of PVA starts around 250°C and mass loss reaches a steady value around 450°C. Decomposition results in a fluid in the region of ca. 250–350°C. For the formation of uniform coatings, the following two types of heating pattern were tested using the specimens appropriately pretreated: type (a), the temperature was increased linearly to a certain value between 450 and 600°C and kept for 1 h at each temperature, and type (b), specimens were heated to a temperature of 250, 300 or 350°C and kept for 30 min, followed by heating to a temperature between 450 and 600°C and kept for 1 h. Heat treatment above 600°C is impractical due to the melting point of aluminium (660°C). These survey experiments indicated that the above type (b) is useful and that the temperature profiles shown in Fig. 1(a) are most preferable in terms of uniformity. By this process, specimens are coated with uniform carbonaceous-layer and lumps of decomposed PVA over the coatings are easily removed by scrubbing. When the specimen was electropolished, the formed carbonaceous layer showed mirror-like smoothness similar to the results with PVC.[3]

The yield and composition of the carbonized PVA at each temperature [indicated by the dots in Fig. 1(a)] are shown in Fig. 1(b). The thermo-gravimetric data in Fig. 1(b) are basically the same as those detailed by TG-DTA. It should be noted here that the results shown in Fig. 1(b) were obtained by using PVA powder only. Though the yield of carbonaceous material reaches a steady value above 400°C, the composition in terms of H/C mol ratio gradually decreases with increasing temperature. Accordingly, carbonization is not completed in the present process. The coatings at 400°C were dark brown and not uniformly colored, indicating that the temperature was too low. The coatings at 600°C often showed cracks and the substrate metal became soft. Therefore, useful coatings are obtained in the region of about 450–550°C.

3.2. Surface pretreatment of aluminium for uniform and adhesive coating

The coating failed on specimens which has been just polished or covered with non-porous barrier-type oxide film, similar to the case of PVC.[3] Coating was attempted using specimens etched in alkaline solutions, but this also failed. The coating was successful only when the aluminium surface was covered with porous oxide film having the appropriate geometry. The present results and those previously obtained with PVC[3] clearly indicate that the formation of a porous anodic oxide film on the aluminium is a necessary pretreatment to form a uniform and adhesive carbonaceous-layer.

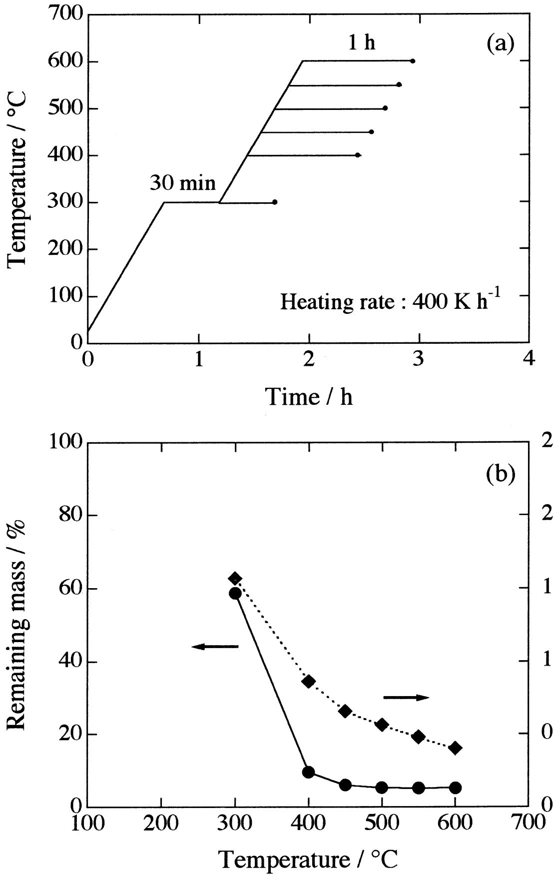

Fig. 1. (a) Temperature profiles for coating process and (b) the yield and composition of carbonized PVA.

By extensive survey of the specimens covered with an anodic oxide film having different pore diameters and film thickness, the domain diagrams shown in Fig. 2 were obtained. Initially the diagrams were made by pore diameter, but the border between the uniform and adhesive coatings and the failed ones was found to be

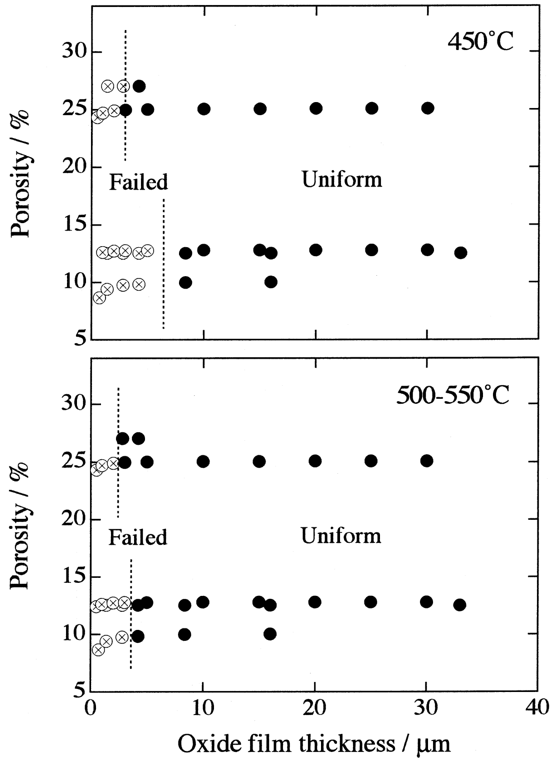

Fig. 2. Domain diagrams showing the optimum condition for coating as functions of the porosity and thickness of anodic oxide film.

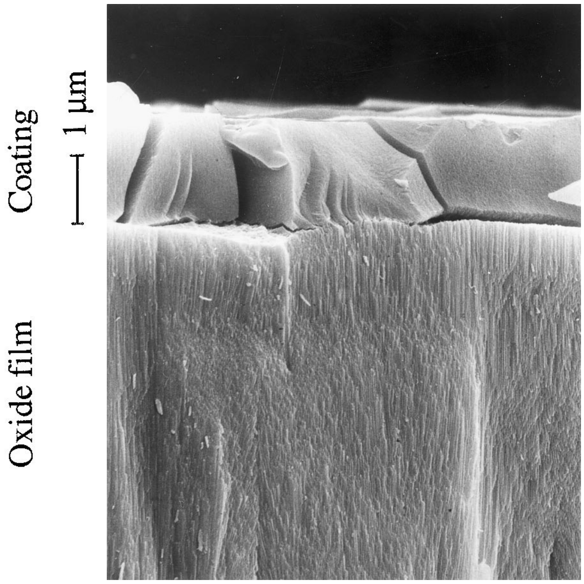

Fig. 3. Cross-section of coated specimen at 500°C on the 30 μm thick 'sulfate' film having pores of 20 nm in diameter.

indicated unequivocally as by the porosity and thickness of the anodic oxide film. Here, the porosity is the percentage of pore volume to the total film volume, and it can be calculated approximately from the pore diameter and the number of pores. The region for good coatings is wider for higher coating temperature. It is seen that larger porosity is required for thinner anodic oxide films to obtain uniform coatings. It may be related to the anchor effect to ensure adhesive coatings. The thickness of the carbonaceous-layer was 1–2 μm as shown for example in Fig. 3. There is the possibility of changing the thickness by using different heating processes, but the magnitude remains close to a micrometer. Actually, the coatings obtained by the heating pattern of type (a) were always less than a few micrometers, though they were checked by the Eddy-current method using commercially available equipment. It suggests that the coating thickness is mainly determined by the viscosity of the fluid formed by the decomposition of the PVA.

As mentioned above, adhesive coatings were not formed on the specimens which have been just polished, etched, or covered with a barrier-type anodic oxide film. It suggests that pores in the porous oxide film function to form anchors for the carbonaceous-layer. The observation of carbonaceous materials in pores by SEM was fairly difficult, since these materials spall by bending to expose the cross-section and do not give good contrast with electrons. In Fig. 4, two examples of a cross-section are shown: (a) was coated on 'sulfate' film (pore diameter is about 28 nm which has been increased from the original diameter of ca. 20 nm by chemical dissolution) and (b) was on 'phosphate' film (pore diameter is ca. 100 nm) . In Fig. 4(a) the carbonized PVA looks like an array of beads having diameters similar to those of the pores, whereas in (b) it forms a pillar-like structure. In both cases, carbonized materials are only filling the outermost part of the porous layer, a few hundreds nanometers in (a) and a few micrometers in (b). In Fig. 4(b), the end of the carbonaceous material in a pore is indicated by the arrow, showing that it reaches to about 2 μm in depth. It is about a half of the film thickness (ca. 4.2 μm). These differences in morphology and the filling

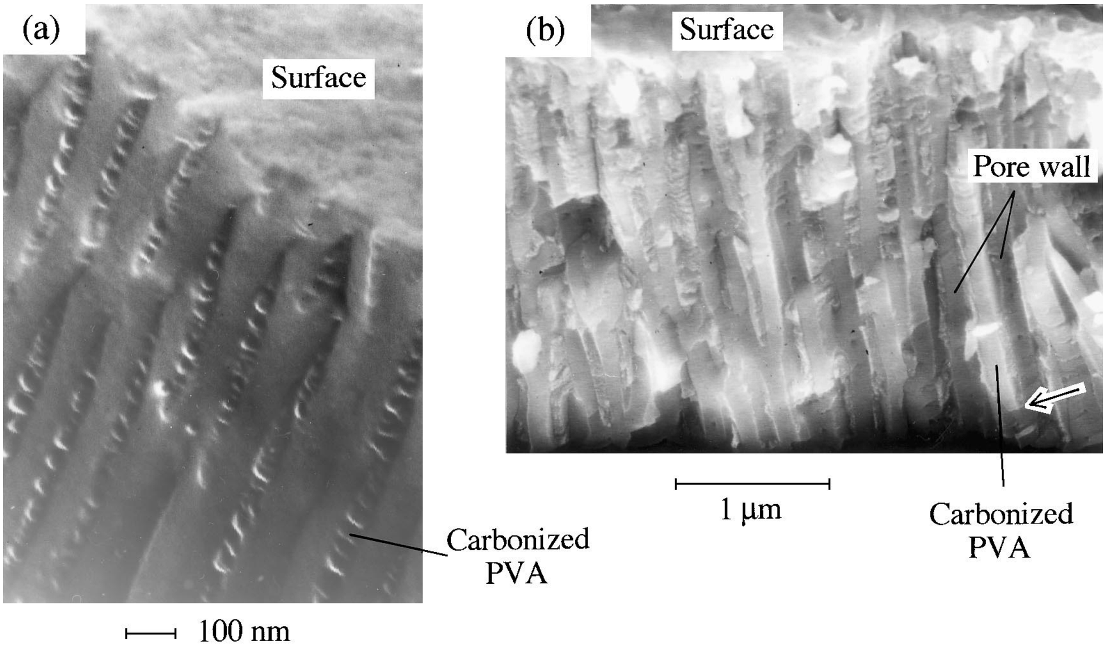

Fig. 4. Cross-section of coated specimen at 500°C: (a) on 30 μm thick 'sulfate' film having pores of 28 nm in diameter and (b) 4.2 μm thick 'phosphate' film having pores of 100 nm in diameter. See text for explanation of the arrow in (b).

Table 2
Micro-Vickers hardness, Hv_{25}, of the surface with the standard deviation ($1 \pm 1\sigma$)

Anodizing conditions	As-formed oxide film	After heating at 500°C in air	Coating temperature 450°C	500°C	550°C
10% H_2SO_4, 15°C 300 A m^{-2}, 30 min	390 ± 50	540 ± 70	605 ± 80	630 ± 70	660 ± 60
0.635 mol l^{-1} $(COOH)_2$ 200 A m^{-2}, 30 min	430 ± 60	590 ± 60	730 ± 100	800 ± 80	850 ± 80

depth of carbonized materials can also be attributed to the viscosity of the fluid formed by the decomposition of the PVA. It should be noted here that in Fig. 4 the carbonaceous layer on the surface has almostly disappeared as a consequence of the bending. At any rate, it is concluded that adhesive coatings result from the anchor effect of pores in the anodic oxide film.

3.3. Properties of the coated aluminium

The hardness, Hv, of the surface and the cross-section of specimens are summarized in Tables 2 and 3. The hardness of porous anodic oxide films on aluminium depends on the type of solution and temperature,[9] but under conventional operation conditions it is usually $Hv = 300$–450 on the surface (Table 2). The anodic oxide films are hydrated and contain electrolyte anions, so that they become hard by heat treatment in air. The surface hardness of the coated specimens, however, is much higher than that of just heat-treated samples and Hv increases with increasing coating temperature. In contrast with this, the hardness of the cross-section is almost the same with or without coatings (Table 3). This is consistent with the observations made by SEM, that is, the carbonaceous materials are penetrating only into the outermost part of the pores.

The results of the corrosion test for the specimens coated at 450°C are shown in Fig. 5, where the survival probability for pitting, P, is plotted as the logarithm against the immersion time (e.g. Refs. 8,10 and 11). For comparison, the results of control experiments are also shown: control specimens were sealed in boiling water for 30 min after anodizing.[8] Coated specimens show much better resistance to pitting corrosion than specimens just anodized and sealed. The protective effect of the coating is much larger on 'oxalate' films than on 'sulfate' films irrespective of the thickness of the oxide film. This is not attributable to the difference in thickness of the barrier layer present at the oxide/metal interface, since the results of control experiments do not show such a large difference in spite of a barrier layer of 'oxalate' film more than twice as thick as for the 'sulfate' films. The difference is mainly due to the larger pore diameter of the 'oxalate' film (ca. 40 nm) than that of the 'sulfate' film (ca. 20 nm). As shown in Fig. 4, when the pore diameter is small, the carbonaceous materials cannot plug the pores tightly and deeply. As a consequence, chloride ions eventually penetrate into the pores and reach the pore bottom to dissolve the barrier layer. The 'sulfate' films shown in Fig. 5 have pores of ca. 20 nm in diameter but the prolonged anodizing to form a thicker oxide film causes widening of the pores at

Table 3
Micro-Vickers hardness, Hv_{50}, of the cross-section with the standard deviation (1 ± 1σ)

Anodizing conditions	Heated at 500°C	Coated at 500°C
10% H_2SO_4, 15°C 300 A m^{-2}, 30 min	570 ± 60	560 ± 60
0.635 mol l^{-1} (COOH)$_2$ 200 A m^{-2}, 30 min	560 ± 60	580 ± 50

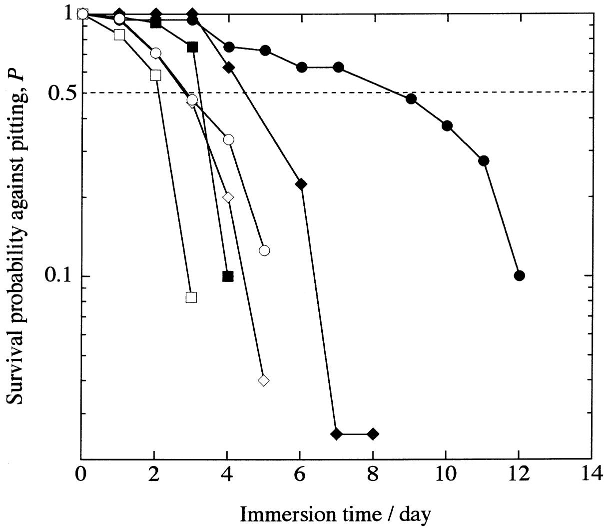

Fig. 5. Results of corrosion test. -■-, -□-: 15 μm thick 'sulfate' film, -◆-, -◇-: 30 μm thick 'sulfate' film, -●-, -○-: 16 μm thick 'oxalate' film. Filled symbols show the coated at 450°C and open ones the uncoated.

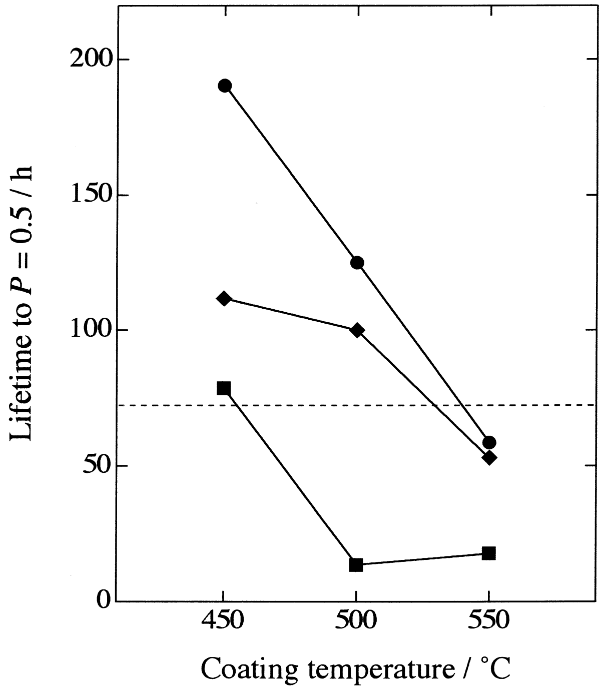

Fig. 6. The effect of coating temperature on the corrosion resistance. The broken line shows the lifetime of the uncoated 'sulfate' film of 30 μm. -■- 15: μm thick 'sulfate' film, -◆-: 30 μm thick 'sulfate' film, -●-: 16 μm thick 'oxalate' film.

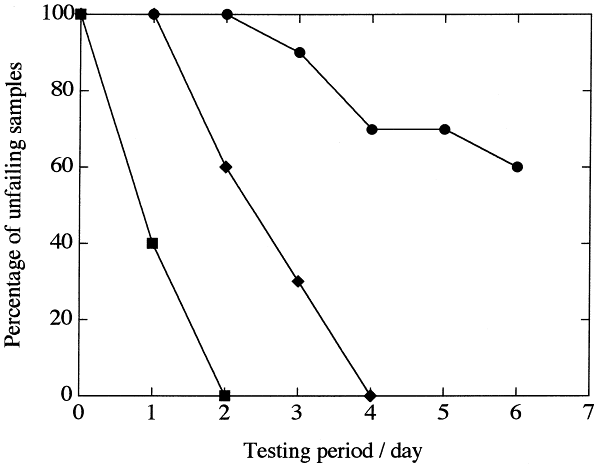

Fig. 7. Results of acid contact test with 1 mol l^{-1} HCl solution. -■-: 15 μm thick 'sulfate' film, -◆-: 30 μm thick 'sulfate' film, -●-: 16 μm thick 'oxalate' film.

the outer part due to chemical dissolution by the acid electrolyte.[12] This is preferable to the coating by the present process and may be a reason why the corrosion resistance of the coated 30 μm 'sulfate' film showed better resistance than the 15 μm film.

When the coating temperature was increased, the corrosion resistance decreased as shown in Fig. 6, where the lifetime to $P = 0.5$ which can be estimated from plots like Fig. 5 was used as a measure of corrosion resistance. By SEM observation of the coated specimens, failure was found to be due to cracks formed in the anodic oxide film during the coating at elevated temperatures. Therefore, when corrosion resistance is the primary requirement, coating should be carried out at temperatures not exceeding 500°C.

The results of the acid contact test for the specimens coated at 450°C were similar to those of the corrosion test shown in Fig. 7, where the percentage of surviving samples is plotted against testing period. From this and Figs. 4 and 5, it can be said that, when the pore diameter of the anodic oxide film is larger than 40 nm, the carbonaceous-coatings formed on aluminium by the present process function as a good barrier to the environment. On the contact test with an organic solvent, the coatings formed at 400°C dissolved slightly in acetone and hexane by ultrasonic rinsing, but those at higher temperatures did not show any degradation or exfoliation in either solvent.

4. Conclusions

Uniform and adhesive carbonaceous-coatings can be formed on aluminium by heating with poly(vinyl alcohol) (PVA) powder under inert atmospheres. The aluminium substrate must first be covered with a porous anodic oxide film and there are optimum ranges of the thickness and porosity of the oxide film for successful coating. Carbonaceous materials penetrate into the outermost part of the porous oxide layer and the penetration depth depends on the pore diameter. The thickness of the carbonaceous coatings is 1–2 μm being determined by the viscosity of the fluid formed by the decomposition of the PVA. The overall properties of the coatings including protective ability against environmental attack were found to be best following coating at 450°C. Any organic polymers which decompose and carbonize by way of liquid phase may be applied to the present process.

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