

The mechanism of anodic oxidation of alloys

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The mechanism of formation of barrier-type anodic films on alloys containing valve and non-valve metals is considered in terms of data yielded by electrochemical methods, a.c. impedance measurements, conventional and scanning electron microscopy and chemical and electron probe micro-analysis. The alloying elements enter the film virtually in their alloy proportions. With alloys giving oxides essentially insoluble in the electrolytes, such as Nb-Zr, the metal constituent concentration profiles across the film are determined largely by the cationic and anionic transport numbers and the cationic mobilities. Where one of the alloying elements tends to give soluble compounds, such as vanadium in V-Nb alloys, this situation is complicated by preferential dissolution of that element. The film properties depend on the solution used but the main result, that relatively small additions of valve metals to metals such as vanadium permit thick barrier-type films to be formed, is unaffected. All the as-formed films are initially pore-free, but those produced on alloys rich in non-valve metal are prone to subsequent leaching, with detectable pore formation. Analysis proves that the films on V-Nb alloys are enriched in valve metal, particularly towards the outer surface. This explains why these films can be formed and also why the impedance characteristics and resistance to leaching improve as the film thickens, with the material rich in valve metal developing into an outer, more protective and possibly thicker sheath. The presence of a mass-transfer boundary layer, rich in non-valve metal dissolution products, also promotes film formation. Films formed in certain non-aqueous electrolytes are richer in the non-valve metal and so are more readily leached in water subsequently, but apparently are also chemically different. Special experiments, involving leaching and reanodizing in various solutions, and the formation of duplex films, provide important data, appearing to indicate substantial anionic movement during film growth.

Introduction

The ability to anodize alloys composed of valve metals alone, and of valve metals with other metals which themselves cannot normally be anodized, is potentially desirable in the fields of corrosion protection, capacitors and possibly catalysis. Surprisingly, few fundamental or applied results exist, especially for alloys rich in non-valve metal. The data from these largely empirical studies, taken mainly from the patent literature, are summarized in Table 1 [1-26].

More fundamentally oriented studies of aluminium alloys were made with barrier-type

anodic films formed at 10 mA/cm² and 0.1 mA/cm² in 3% w/v ammonium tartrate solution and 20% w/v ammonium pentaborate solution in ethylene glycol at 25°C [27], and with porous films formed at 25 mA/cm² in 15% w/v sulphuric acid at 20°C [28]. For Al-Mg (up to 5 wt% Mg), Al-Zn (up to 2 wt% Zn) and Al-Cu (up to 4 wt% Cu), the alloying elements apparently entered the films in their alloy proportions, and were largely retained there, except for Al-Cu alloys where copper was preferentially leached from the outer porous structure of the films formed in sulphuric acid. Ageing of the Al-Cu alloys increased this copper removal and the

Table 1. Data on the anodizing of alloys

Reference	Author(s)	Alloy composition (wt%)	Anodizing solution	Other operating conditions	General remarks and observations
1	Kolski	Nb-Ti	0.01% (w/v) propionic acid	25°C	Essentially anodic oxidation of pure Nb after prior evaporation of Ti. Similar to ref. [1].
2	Hand	Nb-10 to 70% Ti and Nb-2.5% V	0.01% phosphoric acid	31 mA/cm ² to 200 V at 25°C	
3	Mandelkorn and Dakin	Nb (20 to 80%) -Zr (5 to 60%) -Ti (5 to 65%)	0.01% phosphoric acid and aged in ethylene glycol-ammonium-boric acid solution at 60 V and 125°C	3.8 mA/cm ² to 120 V at ambient temperature	
4	Dakin and Divens	Nb-(4 to 50)% Zr Nb-(2 to 34)% Ti	0.03% tartaric acid solution (pH 5.5) or orthophosphoric acid + water and glycol. Ageing as in ref [3]	Up to 300 V at 25°C or occasionally up to 100°C	Preferred compositions, Nb-25% Zr and Nb-20% Ti, claimed superior to Nb, giving films of higher capacitance, lower dielectric loss, and greater resistance to recrystallization. Nb, Nb ₃ Sn, Nb ₆ Sn ₅ and NbSn ₂ gave blue, violet, dark violet and brown films respectively.
5	Hoffman and Maier	Nb-Sn	1% phosphoric acid	26 V	
6	Rudiger and Fischer	Ti-30 at.% Mo	Fluoride-containing solution		
7	Ince and Margolin	Ti-30% Fe-6% Mn Ti-54.5% Mn	Hydrofluoric acid, nitric acid and glycerine Hydrofluoric acid and glycerine	100-300 V 100-300 V	Differential etching or oxidation for phase identification.
8	Tomashov and Matveeva	Ti alloys	Sulphuric and phosphoric acids	5 mA/cm ² at 80°C	Similar properties to pure Ti.
9	Bogoyavlenskii and Borodina	Ti-4.5 to 6% Al	20% sulphuric acid	6 mA/cm ² , 20°C	Films resisted attack by 40% sulphuric acid. Oxides could be TiO, Ti ₂ O ₃ and TiO ₂ mixture. Breakdown at 60 V,

10	Beck and Henderson	Ti-6% Al-4% V Ti-2% Fe-2% Cr-2% Mo	230 g/l Na ₃ PO ₄ · 12H ₂ O 115 g/l K ₃ PO ₄ 70 g/l Na ₂ HPO ₄ · 12H ₂ O, 70 g/l KH ₂ PO ₄ 60 g/l (NH ₄)H ₂ PO ₄	Up to 50 V Up to 50 V	perhaps by oxygen evolution. Brown film.
11	Cotton and McQuillan	Ti-2.5 to 10% Nb			High breakdown potential in chloride. Mo additions were not beneficial. Choice of alloying elements not explained. Better stability of capacitance and lower dissipation factors than with pure Ti. Films were more stable at elevated temperature. Less gas evolution with ternary alloys than with Ti.
12	General Electric Co.	Ti-2.5 to 20% Ta Ti-5 to 45% Sn Ti-5 to 45% B	Ethylene glycol, water, boric acid and ammonium hydroxide	Up to 75 V and held there for 15 min	
13	General Electric Co.	Ti-35% Nb, Ti-35% Ta Ti-11 to 30% Mo Ti-25% Mo-15% Nb Ti-25% Mo-15% V Ti-30% Mo Ti-0.1% Pd	Ethylene glycol, water, boric acid and ammonium hydroxide 70% glyconitrile 70% glyconitrile	Up to 75 V 250 V at 25°C 25-75 V, followed by current decay for 30-90 min	
14	Salomon and Caron				
15	Salomon	Ti-13% V-11% Cr-3% Al	Phosphoric acid, water and ethylene glycol	20-50 V	Vastly improved dissipation factors and leakage factors compared with pure Ti. Good leakage properties and capacitance stability.
16	Shreir and Piggott	Ti-8% Al Ti-20% Sn Ti-5% Mn Ti-5% V Ti-5% Al -2.5% Sn Ti-6% Al-4% V Ti-8% Al-1% Mo -1% V Ti-13% V-11% Cr -3% Al	Alkali/formate or formic acid	5 mA/cm ²	Micropitted surfaces were the main objective but some anodic film formation occurred. Active to passive transition and transpassivity study.
17	Peters		1-10 N sulphuric acid		

Table 1 (continued).

Reference	Author(s)	Alloy composition (wt%)	Anodizing solution	Other operating conditions	General remarks and observations
18	Hoar and Mears	Ti-0.16% Pd Ti-4% Al-4% Sn -4% Mo Ti-5% Al Ti-2% Mo Ti-16% Mo Ti-5% Nb Ti-5% Ta Ta-0.3-16.5% Ti	1-8 M chloride solutions		Studies of breakdown potentials.
19	Lorenz and Michael	Ta-Ti alloys	Ethylene glycol, oxalic acid and water		Ti increased scintillation voltage of Ta. Impurity effects were important. Anodizing after prior volatilization to remove Ti.
20	Ling and Kolski	Ta-4.3 to 28.6% Ge	0.01% propionic acid/glycol solution of boric acid	0.15-0.31 mA/cm ² at 125°C	As for ref. [21].
21	Mohler and Tragert	Ta-4.3 to 28.6% Ge	Ethylene glycol, water, boric acid and ammonium hydroxide	75 V	
22	Misch and Gunzel	Zr-1.4 to 2.5% Sn	Saturated boric acid	500 V at ambient temperature	
23	Misch	Zr-10 to 95% Ti	1% (w/v) potassium hydroxide	2-40 V	Ti decreased a.c. resistance of films.
24	Salomon, Graven, and Adams	Zr-2% Hf	Sodium borate-boric acid buffer at pH 9. Sodium phosphate buffer at pH 9	30-200 V	
25	Braun, Kieffer, and Sedlatschek	W-50% Ta	0.1 N phosphoric acid	240 V at 20°C	Oxide film thickness depended on alloy composition.
26	Wolff	W-10% Re W-30% Mo W-5% Nb W-10% Ta	0.1 N phosphoric acid	60-80 V 5-30 sec	W-10% Re gave non-uniform film, with Re-rich regions giving yellow interference colours in an homogeneous blue-green matrix. W-30% Mo gave mottled films. W-5% Nb and W-10% Ta did not anodize. Alloys with more than 50 at.% Mo did not give an adherent film but etched.

copper generally promoted extensive macroscopic film thinning. Silicon particles in Al-10 wt% Si and FeAl₃ particles in Al-5 wt% Fe were incorporated, apparently unchanged, into porous films. The Å/V ratio, dielectric constant and high current efficiency of formation of barrier-type films did not appear extensively affected by this minor alloying, although high copper levels can inhibit film formation. Unfortunately, the alloying proportions were not sufficiently high for the electron probe microanalysis to be particularly accurate.

Young [29] showed that the capacitance and overpotential required to produce a given current on Ta-Nb alloys were linear functions of the composition in at.%. Study of films on Nb-25 at.% Ta and Nb-75 at.% Ta by spectrophotometric methods indicated that the refractive index of the mixed oxide, produced at 10 mA/cm² in 0.2 N sulphuric acid at 25°C, was approximately a linear function of the composition in at.%. This assumed that the ratio of elements in the film was the same as in the alloy [30]. The a.c. conduction of Zr-1.5 wt% Sn and Zr-1.0 wt% Fe did not appear significantly different from that of zirconium itself [31]. In another study of the anodic oxidation of dilute binary alloys below the oxygen evolution potential, a correlation was found between the barrier height, the field and the local current for alloys with different amounts of the same alloy constituent [32]. An increased percentage of alloying element decreased the height of the activation barrier and the local current.

Studies of the properties of barrier-type anodic films formed on Nb-Zr, Nb-W, Nb-Ti, Nb-V and Nb-Mo alloys, containing up to 50 at.% of the alloying element, under conditions similar to those of reference [27], were made using several techniques [33]. Although variations in the residual current density after current decay at the final formation voltage, Å/V ratio, dielectric constant and refractive index were qualitatively in agreement with the expected trends, these variations were relatively small compared with the overall similarity of all the properties to those of corresponding films on pure niobium. Further work [34] demonstrated a progressive decrease in the dielectric breakdown voltage in the order Nb-Zr > Nb > Nb-Ti > Nb-Mo > Nb-V >

Nb-W, largely in agreement with the corresponding effects of alloying on the a.c. resistivities of the films.

This work was extended to include vanadium-base and molybdenum-base alloys containing up to 95 at.% V or Mo [35-37]. It was shown that metals such as vanadium and molybdenum, which cannot themselves normally be anodized, can be made to produce films by alloying with relatively low proportions of valve metals such as niobium and titanium (the exact value depending on the anodizing conditions and solution). Equally, the properties of films on metals like titanium and tungsten, which are relatively poor due to oxygen evolution and film dissolution, can be improved by alloying with metals which themselves develop superior films. There was evidence that films on niobium-rich alloys were non-porous and that the alloying elements enter the film in their alloy proportions. A 'parting limits' theory, in which the valve metal oxide prevented dissolution of the non-valve metal oxide seemed more relevant than consideration of the valencies and sizes of the incorporated ions.

The present study [36, 37] comprised a detailed study of film formation on a range of alloys, using voltage-time curves at constant forming current density and a.c. impedance measurements to characterize the film electrical properties, conventional and scanning electron microscopy to depict film morphology, electron diffraction measurements to comment upon its crystal structure and electron probe and conventional chemical microanalysis to yield its chemical composition. It is now possible to describe a detailed, although still largely qualitative, model for the anodic oxidation of alloys.

Experimental procedure

The alloys used were V-5, 15, 30, 50, 80 and 95 at.% Nb, V-5, 15, 30, 50 and 80 at.% Ti, V-5, 10 and 30 at.% Ta, V-5, 15 and 30 at.% Al, Nb-50 at.% Ta, Nb-50 at.% Ti and Nb-20 at.% Zr, prepared by melting metals at least as pure as 99.7% by weight and generally considerably purer. After homogenization for 3 h at 1,400°C, as checked subsequently by electron probe microanalysis, the material was rolled and

cut into small spade-shaped sheets, or prepared as large grain-sized, circular discs about 1–1.5 cm in diameter and 0.5 mm thick by spark machining from the ingots. After mechanical polishing to 600 g and 1 μm diamond suspension, most samples were chemically polished but samples mechanically polished only or vigorously etched for a few seconds gave very similar results.

After attachment to an aluminium wire lead and subsequent masking, chemical polishing and cleaning, anodizing was performed at 10 mA/cm² or occasionally 0.1 mA/cm², at 25°C, generally without subsequent current decay upon reaching the set anodizing cell voltage. The main anodizing solution was 3% w/v ammonium tartrate solution with its pH adjusted to 7 with a few drops of 0.1 M ammonium hydroxide solution. Approximately 0.3%, 0.6%, 6% and 30% w/v ammonium tartrate solutions at pH 7, and tartrate solutions, initially 3% w/v but adjusted to give pH values in the range 2 to 10 were also used (the pH 2 solution was tartaric acid itself). Considerable use was also made of 20% w/v ammonium pentaborate, $(\text{NH}_4)_2 0.5\text{B}_2\text{O}_3 \cdot 8\text{H}_2\text{O}$, in ethylene glycol and a solution of anhydrous glacial acetic acid (S.G. 1.05) saturated with sodium tetraborate decahydrate was occasionally employed. Anodizing was terminated when the voltage reached 10, 50 or 100 V, corresponding to films approximately 230, 1150 and 2,300 Å thick, using the niobium Å/V ratio as a crude thickness criterion. Apparent current efficiencies were determined using voltage/time curves plotted on a recorder and optical thicknesses determined with the aid of niobium and tantalum optical step gauges. Samples were generally washed in distilled water after preparation, except for vanadium-rich films where ethanol was used to minimize film leaching.

A.c. impedance measurements were made using a General Radio Capacitance Measuring Assembly, Type 1610-B, with either M sodium chromate solution with its pH adjusted to 7.2 with sodium dichromate solution, or 3% w/v ammonium tartrate solution (pH 7.0), as the measuring solution.

The only films which could be stripped mechanically were those formed on V-95, 80 and 50 at.% Nb in tartrate solution, to which 0.2%

NaF had been added, and similar films on Nb-50 at.% Ta and Nb-20 at.% Zr. The current efficiency of film formation did not appear to be affected with these niobium-rich alloys but it is conceivable that the film properties were modified by the fluoride. Conventional electron microscopy of two-stage formvar-carbon replicas, direct carbon replicas, stripped films and fractured films produced under various conditions was performed extensively with an E.M.6 electron microscope. Electron diffraction was also performed in this instrument and a few specimens were viewed in a Cambridge 'Stereoscan' scanning electron microscope. Films were analysed, where possible, using electron probe microanalysis of stripped films in plan and atomic absorption spectroscopy of dissolved stripped films. Anodizing solutions were analysed using chromatography.

Results and Interpretation

The experimental results are too numerous and involved to be presented in a single paper, so will be detailed in a series of papers elsewhere. Nevertheless, they are all necessary to formulate the overall mechanism, so the main findings are enumerated here. Most of the work involved examination of a typical general case, namely films formed on V-Nb alloys in aqueous tartrate and non-aqueous borate solutions, by conventional anodizing methods. However, valuable information emerged from similar studies of other vanadium-base alloys and selected niobium-base alloys, and from special experiments on the V-Nb system involving leaching and re-anodizing, growth of duplex films and current decay at constant formation voltage.

(1) It is possible to anodize alloys of a valve metal and non-valve metal which are relatively dilute in the valve metal (at least as low as 15 at.%) in aqueous solutions. This is true for all surface preparations but the best results are obtained if the surface is very smooth, avoiding excessive flaw formation and product streaming from these surface defects. The properties of films produced on borderline valve metals (e.g. Ti and W) are significantly improved by alloying with a little superior valve metal (e.g. Ta or Nb).

(2) The voltage/time curves at constant formation current density in aqueous solution are similar, indicating similar current efficiencies, for all alloys in the V-Nb series, except V-15 at.% Nb and to a much lesser extent V-30 at.% Nb, where substantial vanadium or vanadium product dissolution occurs. The results are relatively independent of solution concentration and pH except at the extremes of pH.

(3) The impedance characteristics indicate that thin (10-V) films on the vanadium-rich alloys in tartrate have poor dielectric properties, largely due to leaching by the forming and measuring solutions. With V-15 at.% Nb the impedance values change rapidly with time due to this behaviour, whereas with V-50 at.% Nb the effect is only just detectable. Except for certain very vanadium-rich alloys, the impedance properties improve substantially with increasing film thickness. Impedance methods are much more sensitive than electron microscopy and chemical analysis in detecting relatively minor flaws in the films. Alloying a valve metal with relatively small proportions of a non-valve metal (less than 50 at.%) usually leads to some small but detectable deterioration in impedance characteristics, as witnessed by the increase in dissipation factor and increased slope of the plot of series capacitance against frequency. All these results provide supporting evidence for the existence of a niobium-rich sheath at the outside of the film, which tends to screen the inner vanadium-rich material from the solution.

(4) Use of a niobium optical step gauge and capacitance measurements, supported by film weight gains and chemical analyses, indicate that there is an increase in film $\text{\AA}/V$ ratio with increase in the vanadium content of the V-Nb alloys and therefore of the film. The thickness predicted by capacitance is usually higher than that predicted from the optical step gauge. Approximate considerations of the likely effects of alloying indicate that vanadium reduces the dielectric constant of the film.

(5) Alloys as dilute in niobium as V-5 at.% Nb anodize in the non-aqueous borate/glycol solution. Vanadium itself can be anodized in a saturated acetic acid solution of borax containing some water at voltages up to 80 V, with a relatively low leakage current, whereas V-5 at.%

Nb and V-15 at.% Nb can sustain at least 100 V in this solution.

(6) Films formed on niobium and niobium-rich alloys with vanadium in the borate/glycol solution have a lower apparent optical thickness, a lower capacitance and take a shorter time to reach the final formation voltage at constant current density, compared with the corresponding films formed in tartrate. There is little variation in apparent current efficiency with alloy composition for the niobium-rich alloys. With the vanadium-rich alloys, this behaviour is modified by reaction of the vanadium compounds with the solution, thereby reducing the apparent current efficiency considerably. These reaction products may become partly incorporated into the film.

(7) The films formed on relatively vanadium-rich alloys in the borate/glycol bath dissolve faster in water and have poorer impedance characteristics than the corresponding films formed in tartrate.

(8) Electron microscopy indicates that there is no visible porosity for most of the as-formed films, even if fluoride is added to the forming solution. The evidence for V-15 at.% Nb is less convincing because the film has a semi-fluid consistency, particularly when thin. The unwashed films show no obvious pores for this alloy but washed films show some surface roughening, due to disturbance of the material. It is possible that some unresolved 'porosity' exists at inter-crystallite regions in the films, including those on V-30 at. % Nb and possibly to a small extent on V-50 at.% Nb. 100-V films on V-15 at.% Nb exhibit a phenomenon which resembles breakdown, possibly dielectric breakdown. Micrographs from thick (100-V) films fractured by bending appear to show greater flexibility for films formed on V-95 at.% Nb than on V-50 at.% Nb.

(9) Electron diffraction yields only diffuse rings, indicating that the films are essentially amorphous.

(10) Chemical analysis and weight change experiments for anodizing of V-Nb alloys, particularly V-15 at.% Nb, confirm that vanadium or its compounds dissolve in the solution during anodizing, effectively enriching the film in niobium compared with the alloy. Films

formed on V-15 at.% Nb in the borate/glycol solution contain more vanadium than the corresponding films formed in aqueous tartrate solution. As the film thickens during tartrate anodizing its vanadium concentration increases. As the impedance characteristics also improve, this is additional evidence of the continued thickening and/or perfecting of the outer-niobium-rich sheath, preventing leaching. There is also chemical analytical evidence that a vanadium gradient exists in the films formed in aqueous solution, with the niobium concentrating towards the film exterior. The amount of vanadium entering the solution depends to a lesser extent on the concentration and pH of the anodizing solution. Little niobium enters the solution.

(11) Electron probe microanalysis of the niobium-rich V-Nb alloys indicates a concentration gradient through the film, with vanadium concentrated near the alloy and niobium towards the outer surface. The apparent composition near the alloy/film interface tends towards that expected from the ratio of alloying elements in the alloy. The distribution of niobium and zirconium through the film is essentially uniform and the concentrations of niobium and zirconium in the film correspond to the alloy proportions, for the Nb-Zr system, where neither oxide is significantly soluble in the tartrate electrolyte. However, for the corresponding Nb-50 at.% Ta system and Nb-50 at.% Ti systems, some niobium enrichment occurs towards the outside of the film. Neither electron probe microanalysis nor chemical analysis is sufficiently sensitive to predict the degree of sharpness between the variously enriched layers.

(12) Chemical analysis and the other tests, impedance characteristics etc., suggest the likely formation of some pentavalent vanadium compounds in the film at high current density (10 mA/cm²), with some conversion to tetravalent compounds on standing. Ignition of films formed in tartrate indicate carbon, suggesting tartrate incorporation into the film during anodizing. Alloying may alter the structure and chemical nature of the film as well as its actual composition.

(13) Low current density, circulation of the anodizing solution, excessive vanadium content of the alloy, low concentration of the electrolyte,

extreme pH values and other aggressive features of electrolytes (e.g. the presence of fluoride or ammonia) all exert their individual adverse influences in suppressing film formation or in causing inferior coatings to be formed. For example V-15 at.% Nb, when polarized at 0.1 mA/cm² instead of 10 mA/cm², often does not give a film. Film formation is strongly favoured by the existence of a mass-transfer boundary layer enriched in the dissolving ions. Factors such as circulation of the solution tend to disperse such layers and make film formation more difficult. When the films are themselves sludge-like the flowing solution tends to erode them.

(14) Better films are obtained when vanadium is alloyed with niobium than when it is alloyed with a corresponding atomic percentage of titanium, the films having superior impedance characteristics and being less soluble. Relatively small additions of vanadium actually greatly improve the anodizing characteristics of titanium in tartrate solution, the characteristic oxygen evolution at 20 V being largely suppressed, possibly due to a reduction in flaw density. The impedance characteristics of titanium-rich alloys deteriorate with increased film thickness because of the eventual effects of gas evolution at the higher voltage. By contrast, films on vanadium-rich alloys show improved properties with increased thickness, as with V-Nb alloys.

(15) Films on tantalum and niobium are quite comparable in properties, yet V-30 at.% Ta tends to give films with poorer properties than V-30 at.% Nb. This may be partly related to the poorer surface finish achieved on V-30 at.% Ta with the usual chemical polishing solution, although alternative explanations are given later.

(16) V-Al alloys containing 5-30 at.% Al do not anodize in aqueous tartrate solution, exhibiting streaming and no compact film. In the borate/glycol solution they yield films which are very soluble upon immersion in water.

(17) As expected, films on all the alloys are thicker after current decay following formation to a set cell voltage. However, with vanadium-rich alloys, especially V-15 at.% Nb, streaming of soluble products is observed from certain points on the surface. The film dissolution is accentuated by the continued dispersion of the

mass transfer boundary layer developed during rapid film growth. At places where the outer niobium-rich sheath is not complete, leaching occurs to give porous films and subsequent attack of the alloy. Current concentration and Joule heating effects may occur at the weak spots.

(18) The properties of duplex films, formed initially to 50 V in tartrate followed by continued anodizing to 100 V in the borate/glycol solution, are quite different from those of corresponding films formed by the reverse sequence, particularly for V-15 at.% Nb and to a much lesser extent for V-30 at.% Nb. The apparent current efficiency is lower when the non-aqueous solution is used second because of gas evolution and particularly because of reaction between the film and the solution. However, there is also some effect, compared with 100-V films formed in tartrate alone, when tartrate is used second because of a tendency for tartrate to leach the first film and produce pores which are visible in the electron microscope. Indeed, when tartrate anodizing is performed first the films possess better impedance characteristics than when it is used second. This is because the film formed in tartrate is usually more protective than the film formed in borate/glycol and further growth tends to occur extensively under this layer, due, as is emphasized later, to the apparently substantial anionic contribution to growth. The initial electrolyte properties appear to control the final thickness, as well as the impedance characteristics to a high degree. Duplex anodizing thus constitutes a method of inducing film growth on an alloy which will not anodize normally in a particular solution which must be used for the final stages of formation.

(19) Leaching experiments were performed in various ways to attempt to detect soluble, vanadium-rich channels through the films. Reanodizing then provided information about the direction of ionic movement in films, pore filling etc. Films on V-15 at.% Nb and V-30 at.% Nb were the most readily leached, so were used for detailed studies. Anodizing in the usual tartrate solution at 10 mA/cm² to a set voltage was followed by leaching in hot or cold water, or hydrochloric acid, for known times. Certain specimens were then re-anodized under identical

conditions to the same voltage. The sequential process was also continued with certain specimens until no further significant changes could be produced, as witnessed by the voltage/time curves and film colours.

The slope of the voltage/time curves and the intercept on the voltage axis upon re-anodizing at 10 mA/cm² (essentially a measure of film thickness unaffected by leaching) are higher the lower the alloy vanadium content, the higher the formation voltage (i.e. the thicker the film) and the less severe the leaching. In addition, the increment of 'new film' (i.e. the increase in total film thickness as assessed approximately by an optical step gauge) is less. In the limiting case, where leaching has penetrated extensively almost through the entire film, this increment can approach the original film thickness.

The leaching and reanodizing procedure cannot be applied significantly to alloys containing at least 50 at.% Nb nor to V-30 at.% Nb carrying a 100-V film. It is particularly applicable to thinner films on V-30 at.% Nb and especially to all films on V-15 at.% Nb, as indicated earlier. Using boiling water to leach for 1-10 min, the leaching and reanodizing process can be repeated until the 10-V (approximately 230 Å) film is apparently about 1,000-1,400 Å thick. With cold water leaching for 10 min the cycle can only be repeated a few times and a thinner limiting film is achieved. The approximate limiting thickness for corresponding experiments with V-15 at.% Nb anodized to 50 V is 2,300 Å. Leaching in water appears to remove sufficient vanadium compounds from certain films on V-15 at.% Nb that the alloy is effectively reached but this is more difficult with V-30 at.% Nb. Only by prolonged boiling can the water leach out the vanadium-rich regions in the inner parts of films. Films on V-15 at.% Nb can also be leached rapidly in chromate solution and virtually complete film removal is achieved by more severe reagents such as 10% v/v hydrochloric acid. Undermining is probably achieved and any niobium compounds 'dragged' into solution with a magma of vanadium-rich material.

During the leaching of the film on V-15 at.% Nb in water the niobium-rich skeleton 'collapses' on to the alloy. Under severe conditions crazing networks of cracks are evident in electron micro-

graphs of this residual film, but under less severe conditions pores are visible where the outer niobium-rich sheath has been penetrated locally, perhaps at flaws or impurity centres. The pores are finer and more localized, and are filled more readily on reanodizing, the less severe is the leaching agent. For a few cycles the pores can be obliterated on reanodizing, but later quite large ruts, clearly evident in the scanning electron microscope, are produced. A typical pore diameter after the first leaching for 10 min in boiling water of a 50-V film formed on V-15 at.% Nb, is 200 Å and the pore separation is 1,000-2,000 Å. Pores in similar films on V-30 at.% Nb are of similar size but are localized in groups. More severe leaching, as in hydrochloric acid, can produce much larger pores and film collapse.

The effect of leaching is therefore to enrich the residual film in niobium, whereas subsequent reanodizing thickens the film and attempts to block pores and flaws. The limit to the dual process occurs when the outer niobium-rich sheath is sufficiently compact to prevent subsequent leaching; indeed leaching becomes progressively more difficult as the processes are repeated. This argument is supported by the progressive improvement of the impedance characteristics after leaching and reanodizing for several cycles.

Discussion

Theory of film formation

A basic model of film growth is now formulated and evolved from these established facts. Anodizing in the usual aqueous tartrate solution is considered first, beginning with the case where no significant metal or oxide dissolution occurs. The implications of metal or oxide dissolution, secondary chemical reactions between the film and solution and methods of causing pores to be developed are then pursued.

Film composition and ionic movement in films.

With the Nb-Zr alloy the alloying elements are evidently incorporated into the film in their alloy proportions and this should be the case for the other alloys. This observation is supported by earlier work [27, 28, 33-35] and by an analogous study of the anodizing of the compound

InSb where indium and antimony were uniformly distributed through the film, except for the outer 100 Å where the concentration of the soluble antimony fell progressively substantially to zero at the outer interface [38]. This dissolution could have been due to slight leaching or to the dissolution mechanism discussed later.

It is expected that little, if any, preferential oxidation occurs during anodizing, as happens in thermal oxidation at elevated temperature, because the extrapolated alloy interdiffusion coefficient is very small at ambient temperature, compared with the present rate of film growth. Even if the expected vacancy level in the alloy is increased by processes such as divacancy injection, as suggested for other anodic processes [39], and interdiffusion is also assisted by dislocation pipe diffusion, preferential oxidation is still unlikely at relatively rapid film growth rates. During slow anodizing over long periods some preferential oxidation might occur. However, for the present study a mixed oxide with the alloying elements in their alloy proportions on average is considered normal.

The essentially uniform alloying element distribution through the films on the Nb-Zr alloy means either that the cationic mobilities are equal, which seems rather unlikely, or that film growth is predominantly by anionic movement. The latter conclusion is supported by observations that the oxygen ion transport number in zirconium oxide during anodizing is 0.95 and in niobium oxide is 0.70 [40]. These transport numbers could well depend on the current density (field), forming solution etc. Presumably the smallness of the cationic transport number precludes any measurable concentration differences.

With the Nb-Ta system, although equal incorporation of the metals into the film and negligible dissolution should occur, there is apparently significant cationic transport, and the niobium ion is evidently sufficiently more mobile than the tantalum ion, producing a measurable niobium enrichment towards the outer film surface. A cationic transport number of 0.3 has been reported for the anodizing of both tantalum and niobium under typical conditions [40]. It is not clear why such similar cations should have very different mobilities unless,

using a glass model, niobium is considered to be more of a network modifier and tantalum more of a network former. An apparent overall enrichment of the film in niobium is also anomalous and requires checking for a solution omitting fluoride, in which possible preferential dissolution of tantalum is eliminated.

It does not follow that the anionic distribution, i.e. O^{2-} , OH^- and tartrate, in the film is uniform; in fact it almost certainly is not. Hydroxyl ions can probably penetrate well into the film with the field and compete with the oxygen ion in providing transport [41–45]. Proton activity is more likely operative in the thin outer region of the film [42, 44, 45] and may possibly promote pore initiation or general dissolution under certain circumstances. Comparison of the films produced in tartrate and borate/glycol solutions suggests that film characteristics depend on the solution anion type, but nothing specific can be said about anionic incorporation or movement under the field. The data of other workers are conflicting and unresolved. Thus, films formed on tantalum and niobium in sulphuric acid appear to possess a relatively uniform distribution of the acid anion [46]. In contrast, films formed on niobium and tantalum in phosphoric and sulphuric acids are duplex, with only the outer layer rich in phosphorus or sulphur [47]. More recently, for zirconium anodized in 0.1 M sodium carbonate solution, 0.1 M sulphuric acid or saturated ammonium borate solution, it is reported that the carbon and sulphur tend to be concentrated towards the oxide/solution interface, whereas the boron is distributed uniformly through the film [48].

With the V–Nb system, typical of alloys in which the alloying elements are again presumably incorporated into the film in their alloy proportions, but one of them is definitely soluble, the film is enriched in niobium, particularly towards its outer surface. The metal concentration profile due to preferential dissolution is superimposed upon any such profile determined by differences in the cationic mobilities, representing a more general case. It cannot be stated whether V–Nb acts more like Nb–Zr or like Nb–Ta from the ionic movement viewpoint, because the profiles are so affected by dissolution. However, the leaching and reanodizing

experiments, discussed in detail later, favour substantial anionic movement. The Ti–Nb system, and possibly the Ta–Nb system under the conditions used, may bear some resemblance to the V–Nb system if titanium or tantalum oxides can be dissolved significantly in the fluoride-containing solution used for formation.

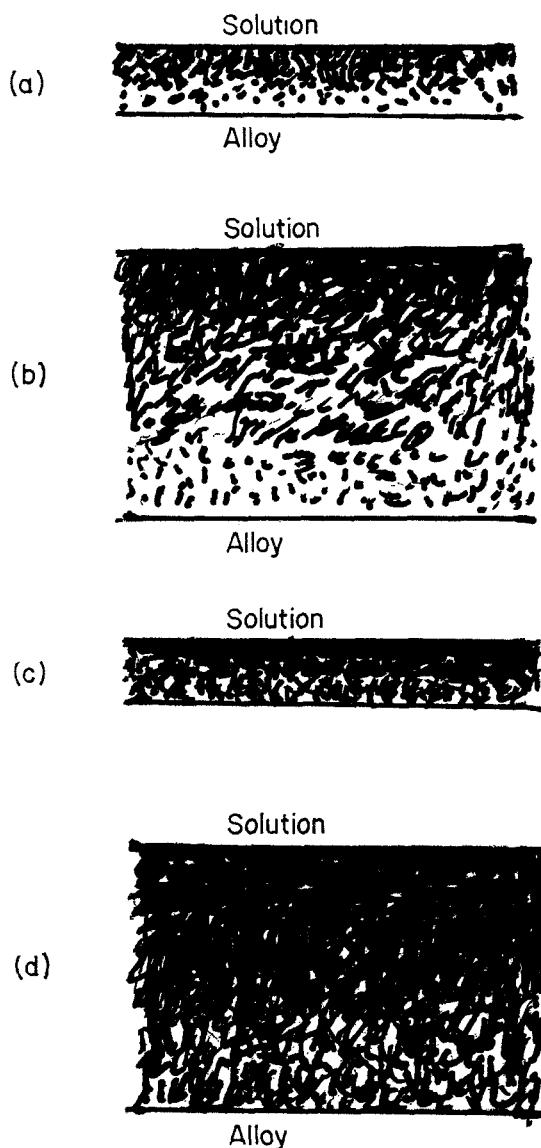


Fig. 1. Schematic diagrams of cross-sections of films formed on V–Nb alloys in aqueous solutions, showing the distribution of vanadium (light) and niobium (dark).

- (a) Thin film on vanadium-rich alloy.
- (b) Thick film on vanadium-rich alloy.
- (c) Thin film on niobium-rich alloy.
- (d) Thick film on niobium-rich alloy.

A general film model. Schematic diagrams represent the behaviour of vanadium-rich and niobium-rich alloys respectively, anodized to different thicknesses. In Fig. 1(a), the thin film formed on a vanadium-rich alloy to 10 V, say, shows the oxide to have a relatively widely separated niobium-rich skeleton filled with vanadium-rich material. Owing to the surfeit of vanadium, this readily contacts the solution and dissolution occurs by leaching action. The vanadium-rich film is metastable and, given sufficient time, should dissolve completely in the forming or other aqueous solution. As the film is thickened, (Fig. 1(b)), the vanadium becomes more screened from the solution by the outer niobium-rich layer developing in compactness and, at least up to a limit, in thickness. However, this layer is incomplete for V-15 at.% Nb because of an inadequate amount of niobium and some vanadium-rich paths still penetrate the outer sheath. With V-30 at.% Nb, the outer sheath of niobium-rich material is much more complete, so prolonged leaching is generally necessary to puncture it at weak spots and leach out vanadium-rich film material from beneath it.

In contrast, the thin film formed on the niobium-rich alloy has a relatively more compact outer protective layer rich in niobium oxide and therefore very little vanadium contacts the main electrolyte (Fig. 1(c)). The thick film formed on the niobium-rich alloy (Fig. 1(d)) gives a somewhat thicker protective outer layer and vanadium-containing material is buried inside it. However, even in the outer niobium-rich layers, there is probably a low concentration of vanadium ions corresponding to the relatively small cationic transport contribution. Such ions tend to dissolve when they contact the solution but do not give a completely 'leachable' network. They are restrained further from complete dissolution by the presence of a mass-transfer boundary layer saturated with vanadium ions, especially for vanadium-rich alloys.

In all cases, most of the vanadium resides in the inner regions, as borne out by chemical and electron probe microanalysis. Indeed the V-Nb ratio in the film tends to the ratio in the alloy as the alloy/film interface is approached. In practice, the composition of the film there may tend to be

exactly that of the alloy but, if the cation transport number is significant and the cation mobilities are sufficiently different, this situation need not hold very far into the film from the inner interface, quite apart from any film dissolution effects. The inner layer would act like the ideal version of the Nb-Ta case described earlier.

The as-formed film is, therefore, generally compact and pore-free in the sense used with anodic films on aluminium but, for the spongy, sludge-like films on vanadium-rich alloys, the still relatively high concentration of vanadium at the exterior of the film is bound to result in general dissolution of vanadium compounds over the film surface. Additionally, dissolution is most rapid at flaws and impurity centres, as witnessed by the streaming of electrolytic products when the electrode is poorly polished. Some major pores can be formed on vanadium-rich alloys, especially if the films are severely leached after the completion of anodizing. As described earlier, the pores visible in the electron microscope, produced by moderate leaching *after anodizing*, are typically about 200 Å in size for reasonably stable films. It is also conceivable that leaching can occur at intercrystallite regions [49], which may be rich in vanadium compounds. Leaching *during anodizing* is presumably more significant for films growing largely by anion movement, where repair of the outer part of the film is less easy.

Apart from the contributory factors of surface finish and degree of hydration of the anodic film already mentioned, the ease of development of the outer valve-metal-rich sheath should depend on the relative mobilities of the ionic species in the film. The ease of establishment, as indicated by the general film properties, appears to be V-Nb > V-Ta > V-Al, which may mean that the mobilities are in the order niobium > tantalum > aluminium, on the not necessarily true assumption that the cation transport numbers are the same for all the films. Ionic radii in Å units, based on a co-ordination number of 6, are 0.51-0.57 for Al³⁺, 0.61-0.63 for V⁴⁺, 0.64-0.68 for Ti⁴⁺, 0.79-0.87 for Zr⁴⁺, 0.4-0.59 for V⁵⁺, 0.69 for Nb⁵⁺ and 0.68 for Ta⁵⁺ [50]. The mobility depends partly on the charge and size of the ion and there does not seem to be any obvious pattern here. The relatively poor proper-

ties of films on V-Ti are at least partly due to the inherently poor anodizing qualities of titanium itself. Perhaps surprisingly, certain oxides with a high degree of covalent bonding (e.g. V_2O_5 and MoO_3) do not readily form anodically in aqueous solution.

A further unresolved point in the anodic oxidation of metals is the distance each ion moves in the film before being captured. In one study [40] it is deduced that the metal ions and oxygen ions move right through the film by counter-current motion, although the number of replacement events is not specified, forming fresh material at the film interfaces, whereas in another [51] it is considered that fresh material essentially develops within the film. At first sight it seems most likely that each ion moves only a limited distance in the film before capture in crystallite or inter-crystallite regions. However, this need not be the case in amorphous, glassy materials where it is difficult for the moving 'interstitial' ion to find a permanent or resting site [63]. Ignorance on this point, and on the properties of transport through crystallites and inter-crystallite regions respectively, hinders establishment of a detailed mechanism of dissolution of the vanadium-containing films. If the film grows largely by anionic movement, after the establishment of the initial niobium-rich sheath by preferential dissolution of vanadium compounds near the outer surface, the new film grows inside the sheath with a uniform vanadium distribution and never comes in contact with the solution, so it can be quite rich in vanadium. Under these conditions the only vanadium subsequently entering solution results from leaching at flaws in the outer sheath or at inter-crystallite regions. If the cation also contributes to film growth there is some direct dissolution as well as leaching because the vanadium ions can pass through the outer sheath under the field, even if it is almost entirely valve oxide. Under the latter conditions, the vanadium content of the outer sheath could still be significant and the actual vanadium level at the oxide/solution interface would depend on how quickly it dissolves. The above argument also requires that the film is acting essentially like an ionic solid. Possibly on very vanadium-rich alloys it is behaving with properties nearer those of a liquid and rapid

chemical interdiffusion in a sludge occurs in the inner regions of the film.

Film and solution chemistry. In a previous study [52], the film formed on vanadium at low current density in a glacial acetic acid solution of borax is convincingly positively identified as V_2O_4 and the dissolution products in aqueous solution as vanadyl (oxovanadium) ions. In the present work, although some V_2O_4 is considered present in vanadium-rich films or anodizing solutions, some V_2O_5 (or its hydrates) is probably formed initially on V-Nb and other vanadium-base alloys for the following reasons:

(1) The current density and hence appropriate electrode potential are considerably higher, favouring V_2O_5 formation [53].

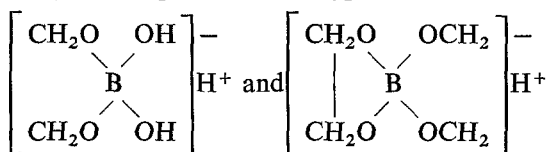
(2) Potentiostatic experiments on vanadium in acid solutions support the formation of pentavalent vanadium at high electrode potential [54].

(3) The relatively good impedance properties of most films formed on V-Nb alloys suggest that V_2O_5 , rather than V_2O_4 , is present. Thus, reduction of V_2O_5 to V_2O_4 produces a massive reduction in its resistivity at the transition temperature of 67°C [55, 56]. It should, however, be added that much of the high resistivity of anodic films on V-Nb alloys is due to the enrichment of the films in niobium compounds and the existence of the outer niobium-rich sheath. Penetration of the sheath leads to rapid deterioration of the impedance characteristics.

(4) The colour changes observed during anodizing, such as streaming and subsequent reaction with the aqueous tartrate solution, suggest the presence of V_2O_5 . Thus, both anodic films and solid V_2O_5 give viscous amber products in tartrate and tartaric acid solutions, possibly characteristic of vanadic ions or similar ions, e.g. pyrovanadate. These solutions turn blue on standing overnight, characteristic of the tetravalent state. The colour change is more pronounced with tartaric acid than neutral tartrate, because of its better reducing properties.

(5) The reaction between vanadium-rich films and the glycol in the borate-glycol forming solution (the reaction not occurring in aqueous borate solution) is characteristic of oxidation by the V^{5+} ion. Thus, it has been deduced that

V_2O_5 reacts with ethylene glycol in the same way as it does with monohydric alcohols, with no cleavage of the C-C bond [57]. In the reaction, complex compounds of the type:



may react with V_2O_5 to give the black compound, which could contain V_2O_3 .

It may be speculated that vanadium is associated with hydrogen-bonded material to give a complex polymer, rather than existing as a simple or hydrated oxide. The initial anodic products, or their reduced forms, could also react with the tartrate electrolyte to give complexes, e.g. the tetravalent ion can give the ammonium salt $(\text{NH}_4)_2 [\text{VO}(\text{tartrate})] \cdot \text{H}_2\text{O}$ [58]. Fluorides can also give complexes with vanadium [53]. The effect of electrolyte on the \dot{A}/V ratio (d.c. field), however, is applicable to niobium itself, which does not react with the borate/glycol bath, so this must be due to another effect such as anion incorporation into the film.

Glass-forming characteristics of films. As the effect of alloying is to reduce the a.c. impedance of films on niobium, irrespective of the valency of the diluting constituent, and there is no obvious correlation between d.c. formation field and the valency of alloying element, it is apparent that criteria such as the Wagner-Hauffe rules are not directly relevant to anodic films. This is not surprising in view of their mixed amorphous oxide structure and the mode of growth. Furthermore, the use of criteria such as the Pilling-Bedworth ratio in considering the degree of compactness of the oxide has limited application with anodic films.

The glass-forming characteristics of anodic films may eventually give a key to their detailed properties. In general, oxides with a low value of the ratio of cation radius to oxygen ion radius should be good glass formers but this is not obvious in practice. Thus Al_2O_3 would be expected to be a good glass former but does not vitrify very readily in the solid state. In one theory [59] the mobile interstitial tantalum ions carrying the current in Ta_2O_5 are considered as

network modifiers to distinguish them from tantalum ions held more firmly in the lattice at that stage. In an alloy anodizing situation, e.g. V-Nb in borate/glycol, it is difficult to know how to sub-divide vanadium, niobium and boron-containing ions into network formers and modifiers, since all the ions appear to contribute to some extent to conduction.

On an ion selectivity argument [60], small ions in solution might be expected to exchange with small ions in the film by an anion exchange mechanism. In particular, the inclusion of glass-forming ions such as borate into anodic films on aluminium might be expected to influence the properties of the resultant films by promoting faster anion diffusion [60]. Anodic films are also considered to have a greater preference for protons than for other monovalent ions such as Na^+ , by virtue of their smaller effective anionic radius.

The glass-forming characteristics and degree of covalent bonding of the film should determine the relative mobilities of the cations and the transport numbers in the film to some degree. It has been indicated [63] that glass formers have high covalent bond strengths whereas modifiers have lower bond strengths and only bond ionically with anions in the network. Most of the oxides involved in the present work are listed as network formers under appropriate configurations, which seem different for each material. They do, however, differ in the degree of covalency [34] which could explain differences in behaviour. Network formers are likely to favour anion movement because they have channels through which the large anion can move, while small highly charged cations are tightly bound in the network structure, and the converse is also true. These views have to be reconciled with theories that O^{2-} either does not move in Ta_2O_5 or else moves by a highly correlated movement [64], whereas it can move interstitially in ZrO_2 , as well as those described earlier in which both cation and O^{2-} are considered to be mobile [40]. Consideration of cooperative transport mechanisms and local field effects [66] may lead to a complete reinterpretation of the results.

Theory of leaching and reanodizing

Fig. 2 represents schematically the cross-sections

of films on a vanadium-rich V-Nb alloy (e.g. V-15 at.% Nb) at various stages of formation, leaching and reanodizing. A uniform, parallel-sided film, which is niobium-rich towards its outer surface, is obtained during normal anodizing in tartrate solution (Fig. 2(a)). Upon leaching, the outer niobium-rich sheath is perforated

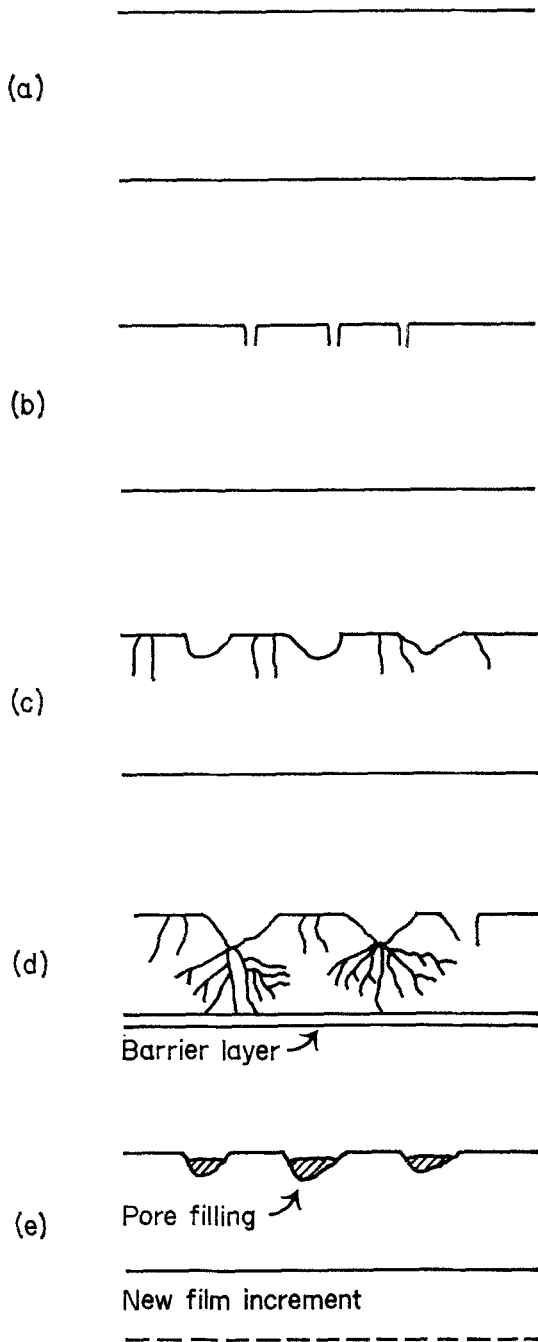


Fig. 2. Schematic representation of the sequence of changes in anodic films on V-Nb alloys during leaching and reanodizing.

- (a) As-formed, parallel-sided film.
- (b) Puncturing of outer, protective, niobium-rich sheath during initial leaching.
- (c) Leached and slightly 'collapsed' film after slight to moderate leaching.
- (d) Film after moderate to relatively severe leaching, showing the removal of fine vanadium-rich channels in the inner film regions.
- (e) Film in (d) after reanodizing, showing channel and partial pore filling by cation movement, and general film thickening by anion movement through the 'barrier layer'.
- (f) Surface of film leached and reanodized on several occasions, showing crazing, surface roughening and incipient cracks.

at weak spots (Fig. 2(b)). The subsequent decrease in film thickness occurs by film 'collapse' or subsidence on to the alloy, resulting from the dissolution and removal of vanadium-rich material from inside the sheath (Fig. 2(c)). Localized leaching between crystallite regions occurs on the inner part of the film as illustrated by the rootlike spread in Fig. 2(d). The barrier layer merely represents that part of the film which has not yet suffered significant leaching and which sustains any voltage measured at the start of reanodizing. Chemical interdiffusion in any liquid or mobile material formed initially, or developed subsequently on the inner film regions, can facilitate removal of vanadium-rich material from this region. With prolonged leaching, visible pores, as well as very fine ones invisible in the electron microscope, are formed. Fig. 2(d) represents a moderately heavily leached film.

Upon subsequent reanodizing (Fig. 2(e)) the general thickening of the film at its base occurs by anionic movement through any residual

barrier layer. After extreme leaching, the apparent incremental thickness increase, as detected by the colour change, approaches that expected if all the new material developed at the base of the film, rather than within it or by pore filling. This is strong evidence for predominant anionic movement during film growth. Some cationic movement does, however, occur, possibly causing some material development within the film material itself and promoting definite pore blocking. This blocking of pores by cation movement accounts for the greater slope of the voltage/time curve upon reanodizing than during the initial anodizing. Thicker films, a higher alloy niobium content and less severe leaching all tend to make the pores finer, so that they are more easily filled by the cation contribution to growth. The film increment at the base upon reanodizing is less under these conditions because less charge is required for the film to reassume the limiting voltage. It appears that the cation contribution is successful in partially obliterating the pores for the first few cycles of moderate leaching and reanodizing, but later the outer regions become too gross for this to occur and the pore healing occurring on reanodizing takes place in the film depths. Eventually the leached channels in the depths of the very thick films produced after many cycles are so fine that they are filled almost instantaneously, explaining why there are eventually no significant increases in overall film thicknesses. The niobium-rich sheath is now developed as a complete layer within the film (i.e. below the surface porous structure). It would be interesting to study the morphology of the alloy/oxide interface after many cycles, if the film could be stripped, to reveal any irregularity of the interface and the zone of influence of pores on the current distribution during reanodizing.

The repeated film deflation and thickening occurring on leaching and reanodizing contributes towards the cracking, which can be quite extensive and appear as a surface crazing pattern (Fig. 2(f)). This appearance applies both to leached and reanodized films after several cycles.

The theory of parting limits governing the electrochemical dissolution of alloys [61, 62] can be adapted to explain the leaching of these

anodic films during, and particularly after, anodizing [35]. The theory essentially states that dissolution of the less noble metal can be retarded and even prevented by alloying with a noble unattacked metal, provided the latter is present above a critical concentration. The precise parting limit may be sharp or diffuse, depending on the alloy and the solution, and often varies from alloy to alloy and solution to solution. In certain situations the less-noble metal is leached away, leaving a skeleton of noble metal. In the analogous case of anodic films, e.g. on V-Nb alloys, Nb^{5+} ions and V^{5+} or V^{4+} ions (or the appropriate corresponding oxide crystallites) assume the function of the noble and less-noble metals respectively. Because of the non-uniform distribution of niobium and vanadium in the films, and the susceptibility to leaching once the outer niobium-rich sheath is punctured, it is not surprising that the 'parting limit' for anodic films is relatively diffuse and depends on the conditions. Any parting limit would refer to the outer niobium-rich sheath rather than the film as a whole. It is conceivable that the general film structure is of niobium-oxide-rich crystallites intermingled with inter-crystallite regions containing vanadium cations, water and the solution anion. As with metallic alloys it may chance that a cluster of the attackable species is encapsulated by 'nobler' species within the film and so escapes attack. The outer niobium-rich sheath is really a special case of this on a macroscopic scale.

Future studies

The mechanism of transport of cations, oxygen ions, hydroxyl ions, electrolyte anions and protons in anodic films on pure metals and alloys require elucidation before the model can be developed. It would also be useful to have theoretical predictions of the distribution of cations and anions in anodic films under the influence of the electric field. Development of the parting limit and glassy film concepts is also required. Elaboration of the approaches developed here is desirable, particularly if more sensitive analytical techniques and systems can be explored in details (as with InSb[38]) and methods developed for stripping the films or

examining them by replication after fracture. The use of sputter ion source mass spectrometry [65] should yield more precise concentration profiles through alloy anodic films. Preliminary results [66] generally confirm the trends described here. Dry impedance measurements would be of interest.

Many other alloys could probably be anodized in the way described, possibly after appropriate pretreatments but these will not be listed here. It would be interesting to develop alumina films on Cu-Al, Fe-Al alloys etc., by preferential thermal oxidation and then attempt to anodize the samples. In more general terms, the influence of prior anodic films on subsequent thermal oxidation would be rewarding.

The present research also has relevance in the study of passive films developed on alloys, a subject recently discussed independently by Hoar [67]. If both alloy constituents in a binary alloy give essentially insoluble compounds, they would be expected to exist in the film in their alloy proportions when the film was formed rapidly at high current density. However, for formation at low current density, some enrichment in the less-noble metal could possibly occur, as explained earlier. This situation would be modified if the noble or less-noble metal produce soluble film products. The holding of a specimen in the passive region, with the slow leaching of one component and progressive healing of the film, could lead to an eventual enrichment in the other component.

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