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On the electrochemical machining of some titanium alloys in bromide electrolytes

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The current efficiency was determined for the dissolution of a number of titanium alloys (IMI 115, 230, 318 and 550) in a variety of electrolytes based on potassium bromide. It was found that these materials in general dissolved at efficiencies somewhat greater than 100% based on the 4-valent dissolution reaction:

$$\mathrm{Ti} \rightarrow \mathrm{Ti}^{4+},$$

although at lower current densities the efficiency was a little lower. Using sodium chloride as an additive to the potassium bromide, slight improvements in the stray-current attack properties of the electrolyte and in the surface finish were obtained. All the alloys dissolved in the transpassive region of the polarization curve but produced etched surfaces, and evidence is presented to show that the dissolution kinetics is modified by acid generation at the anode and, in the case of the two-phase alloys, also by the occurence of differential dissolution.

1. Introduction

Titanium and its alloys are becoming increasingly important in the aerospace industries because, in addition to offering good tensile, creep and corrosion properties, the materials have very low densities and very high strength/weight ratios are attainable. Problems, however, exist with the mechanical machining of these alloys due to the formation of surface cracks and the application of electrochemical machining (ECM) has considerable potential.

A study of the thermodynamic behaviour [1] of titanium shows it to be a base metal which will dissolve, in theory, via 2-, 3- and 4-valent processes. Armstrong *et al.* [2] noted dissolution to Ti(III) in acid which was supported by Griess [3], and Cowling and Hintermann [4] examined the anodic dissolution product of TiC in H_2SO_4 and found Ti(IV) but did not rule out the possibility of a Ti(O) → Ti(III) reaction. Armstrong and Firman [5] electrolysed titanium in 10 M H_2SO_4 for a long time and found by polarographic and ring-disc analysis that only Ti(III) was present in the solution. Armstrong *et al.* [2] found that the anodic polarization curve of a rotating-disc sample was not rotation dependent showing that the dissolution process was not a dissolution–precipitation mechanism but rather was due to surface adsorption. Titanium owes its corrosion resistance to the existence of a surface film of tenacious, passivating oxide. This corrosion resistance presents a problem to the electrochemical machinist in finding an electrolyte which will dissolve the metal at an acceptably low voltage. It has been shown [6] that the order of aggressiveness of the halide ions toward titanium is in the order $I^- > Br^- > Cl^- > F^-$. The corrosion resistance of titanium has been increased even further by alloying with Pd [7], and with Cr and Mo [8]. The electrochemical behaviour of more complex alloys has also been examined: αβTi–6Al–6V–2Sn, βTi–13V–11Cr–3Al, αβTi–6Al–4V, αβTi–5Al–2·5Sn and αβTi–8Al–1Nb–1V have been studied in H_2SO_4 and in HCl acids [9–11]. Following their work on Ti–8Al–1Mo–1V, and using thermodynamic considerations of the Pourbaix diagram, Chen *et al.* [12] proposed a mechanism for anodic dissolution involving interference by anodically generated H^+. Thus the evidence available indicates that titanium and its alloys might dissolve in aqueous electrolytes in either a 3- or a 4-valent process. It was a

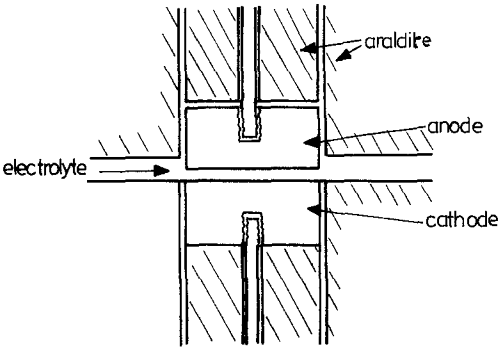

Fig. 1. Cell arrangement for the electrochemical machining.

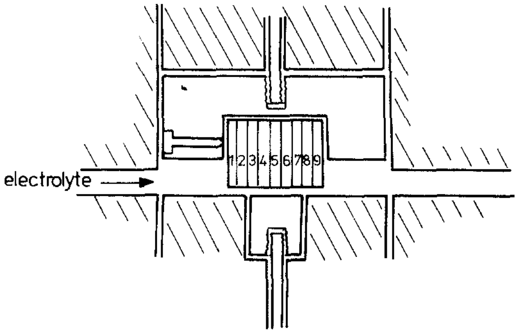

Fig. 2. Arrangement of the segmented cell.

purpose of the present work to make dissolution efficiency measurements to examine this. Additionally, it has been suggested that under conditions of ECM extreme intergranular attack is obtained, particularly for the two phase alloys [13] and in the present work this was studied in bromide-based electrolytes. Applying the principle that a compromise between aggressive ions and film-forming ions might produce the required controlling film characteristics [14, 15], the effect of additions of film-forming additives was studied. The studies made were the effect on stray current attack and the effect on dissolution efficiency. Stray attack is defined as that portion of the dissolution which is not opposite the tool and is unwanted. Efficiency is the amount of metal removed compared with the theoretical amount.

2. Experimental

2.1 *Materials*

Laboratory reagent grade chemicals were used of purity > 99% with the exception of KBr which was > 98·5% pure. The compositions of the titanium alloys were as follows:

IMI 115 commercially pure titanium (99·5%),
IMI 230 Ti–2·5Cu,
IMI 318 Ti–6Al–4V and
IMI 550 Ti–4Al–4Mo–2Sn–0·5Si.

The first two (115 and 230) are single phase α alloys and the latter two (318 and 550) are two phase $\alpha + \beta$ alloys. All were cut from annealed bar supplied by Imperial Metal Industries (Kynoch) Ltd.

Table 1. Dissolution efficiencies for Ti alloys (%)

Current density (10^{-4} Am^{-2})	*IMI 115*		*IMI 230*		*IMI 318*		*IMI 550*	
	2·5	25	2·5	25	2·5	25	2·5	25
1 M KBr	90·0	105·3	81·0	95·2	–	–	105·8	116·3
2 M KBr	103·7	101·3	81·0	93·7	102·6	110·0	112·3	127·6
3 M KBr	94·9	104·5	81·8	111·5	106·7	110·0	107·4	121·2
4 M KBr	89·2	110·9	92·9	111·5	101·0	110·8	100·2	120·4
2 M KBr + 0·25 M Na_2SO_4	96·5	108·5	96·7	105·6	110·0	116·6	103·4	117·9
4 M KBr + 0·35 M KF	107·7	110·9	87·7	98·1	64·0	112·5	111·5	126·0
4 M KBr + 1 M KF	83·6	112·5	74·3	98·1	85·4	119·9	93·7	119·5
2 M KBr + 2 M NaCl	93·2	112·5	84·8	104·1	87·0	121·5	88·9	122·0
2 M KBr + 0·5 M KF + 2 M NaCl	66·5	113·3	80·3	104·8	108·4	118·2	116·3	126·8
4 M KBr							martensitic sample	108·2

2.2 *Experimental procedure*

In the efficiency work, samples were prepared using a flow rig constructed of QVF glassware, two Stuart–Turner type 12 pumps in tandem and a cell arrangement shown in Fig. 1. The flow was sufficient for a Reynolds number of ~20 000. The stray current attack studies were made using a segmented-anode cell, shown in Fig. 2. The cathode sits opposite the middle five of the nine-segment anode. The polarization plots were made using stationary electrodes in an air-free glass cell but using a nitrogen bubbler to agitate the solution; ancillary equipment included a Chemical Electronics potentiostat 403, Philips microvoltmeter PM 2435 and Simpson digital voltmeter, model 460.

3. Results

3.1 *The efficiency of the dissolution of some titanium alloys*

The efficiency for the dissolution of titanium and some of its alloys in bromide-based electrolytes is given in Table 1. The efficiency for titanium dissolution was based on the 4-valent reaction, $Ti \rightarrow Ti^{4+}$, for which a 100% efficiency is equivalent to the dissolution of 0·1244 mg C^{-1}. For the titanium alloys the effective electrochemical equivalent depends upon the amount of alloying constituent and upon the e.c.e. of that constituent. Thus for IMI 230 100% efficiency is equivalent to the dissolution of 0·1345 mg C^{-1}, for IMI 318 it is 0·1218 mg C^{-1}, and for IMI 550 it is 0·1238 mg C^{-1}; IMI 115 is a commercially pure titanium (99·5%). A microscope study showed the titanium alloys machined in KBr to be etched; in the case of the two phase alloys, 318 and 550, the etching was so extreme that one phase appeared to stand proud of the surface and when touched a black powder could be wiped off easily. This was also observed earlier [13]. A sample of IMI 550 was heated for 60 min in argon at 1200° C and then quenched. A martensitic structure was formed under these conditions. The electrochemical machining of this sample in 4 M KBr gave a finish showing the microstructure of the anticipated acicular structure with very little differential dissolution. The dissolution efficiency of this sample is given in Table 1. X-ray diffraction analysis using the Debye–Scherrer powder method was carried out on a sample of the loose black film, removed from the surface of electrochemically machined IMI 550. From the X-ray photography the *d*-spacings were calculated and were found, by comparing with ASTM *d* values, to be consistent with titanium metal and KBr (the electrolyte). EDAX analysis of etched 318 showed the loose material to be the vanadium-containing β-phase.

In bromide–chloride mixtures the etching was much reduced, such that the single phase alloys were virtually polished, although the 'honeycomb' still occurred for the two phase materials.

3.2 *Stray attack properties of bromide–electrolyte for titanium*

It will be observed from Table 1 that there is some slight tendency for the difference between the efficiencies at the lower and the higher current densities to be widened in chloride–bromide electrolyte compared with bromide alone. This was tested by using the segmented-anode cell and the data for IMI 115 in 4 M KBr and in 2 M KBr + 2 M NaCl at 25×10^4 A^{-2} are given in Fig. 3. For minimal stray attack the ratios of weight-losses, segment 3/segment 2 and segment 7/segment 8, should be as high as possible.

3.3 *Polarization curves for titanium alloys in KBr*

The current–potential plots for titanium (IMI 115) and for IMI 550 in static 1 M KBr are given in Fig. 4. Also shown is the effect of adding chloride in differing proportions to a bromide electrolyte. The breakdown potentials in these mixed electrolytes are plotted in Fig. 5, where it will be noticed that only a small amount of bromide appears to be required to lower the breakdown potential considerably.

4. Discussion

The efficiencies for the dissolution are displayed in Table 1. It is seen that for the high current density dissolution the current efficiency is almost invariably in excess of 100% for the 4-valent process. Now efficiencies of over 100% may be obtained either if the dissolution is not all by a 4-valent pro-

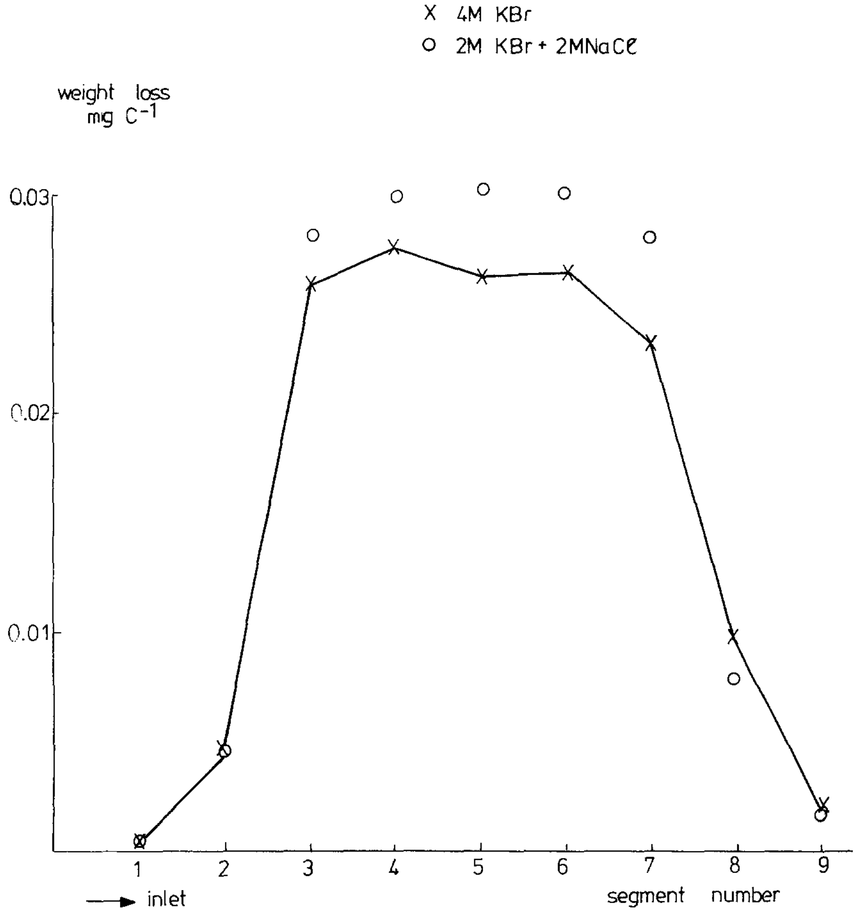

Fig. 3. Stray current attack on IMI 115.

cess, or if a proportion of the metal is failing to be electrolysed, i.e. if excessive intergranular attack is causing undissolved grains to drop away. This second mode is unlikely to be important in the case of the single phase alloys, because although the surfaces exhibit indentations of grain size [13] they are bright and clean after machining and show no evidence of undermining. Thus it must be concluded that a proportion of the dissolution, at least, is via a lower-valent mechanism. At the lower current density the efficiency is nearer 100% relative to the 4-valent process in KBr electrolyte. The multiphase alloys on the other hand machined to give a black powdery surface film and a sample of IMI 550 which was heat-treated, effectively to convert it to single phase prior to electrochemically machining, gave an efficiency more akin to the single phase materials than to the untreated 550 alloy.

This indicates that in the case of the multiphase alloys a little lower-valent dissolution was occuring, but also some undermining was evident. X-ray analysis of the black powder strongly indicates that the powder was titanium metal. High efficiencies at the higher current densities relative to those at the lower current densities are probably associated with a local pH change. A simple test using an indicator showed the electrolyte close to a titanium anode in KBr to be acidic. A similar phenomenon was observed for titanium in NaCl [16]. Furthermore acid generation occurs in an aqueous oxidation scheme of the sort suggested by Chen *et al.* [12]:

$$\begin{aligned} &\mathrm{Ti} + \mathrm{H_2O} \rightarrow \mathrm{TiO} + 2\mathrm{H^+} + 2\mathrm{e} \\ &\mathrm{TiO} + \tfrac{1}{2}\mathrm{H_2O} \rightarrow \tfrac{1}{2}\mathrm{Ti_2O_3} + \mathrm{H^+} + \mathrm{e} \qquad (1) \\ &\tfrac{1}{2}\mathrm{Ti_2O_3} + \tfrac{1}{2}\mathrm{H_2O} \rightarrow \mathrm{TiO_2} + \mathrm{H^+} + \mathrm{e} \end{aligned}$$

or by hydrolysis of the product of direct bromidation [17]:

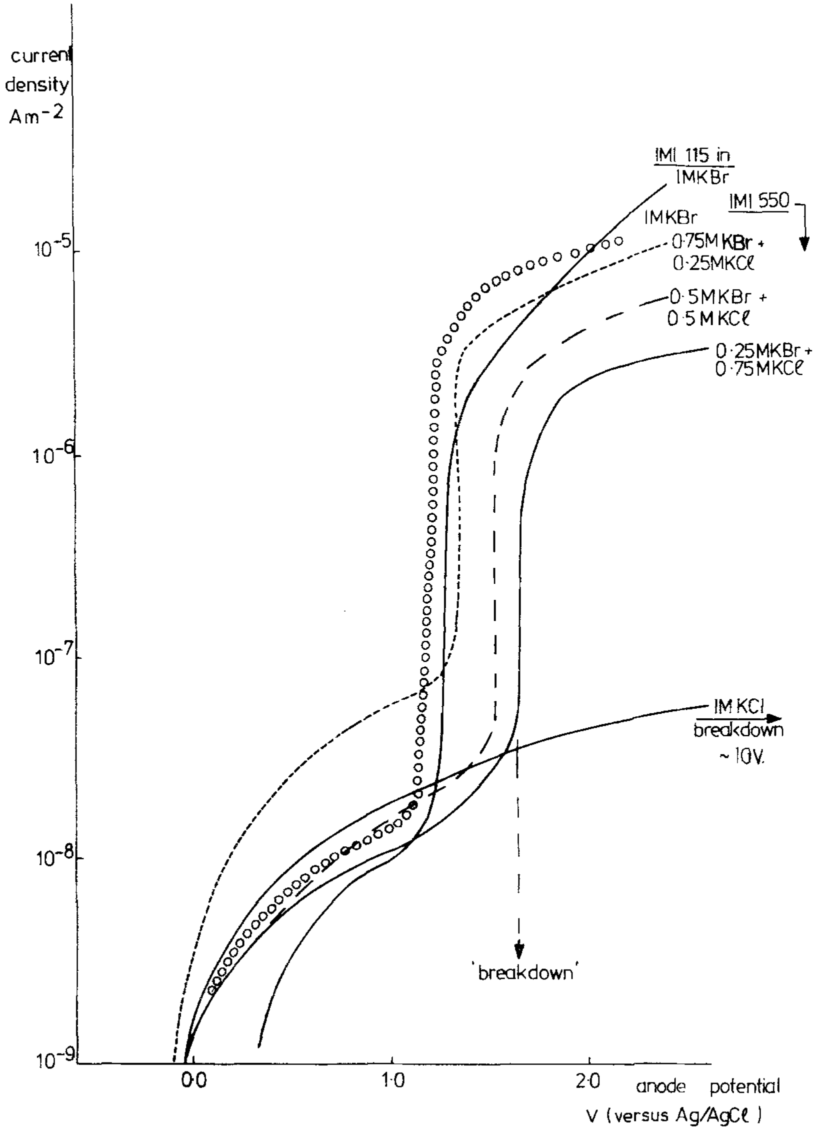

Fig. 4. Polarization plots for titanium.

$$\begin{aligned} &\mathrm{Ti + 4Br^- \rightarrow TiBr_4 + 4e} \\ &\mathrm{TiBr_4 + 2H_2O \rightarrow TiO_2 + 4Br^- + 4H^+}. \end{aligned} \tag{2}$$

On increasing current density, under otherwise similar conditions, acidity would tend to rise and intermediate steps in the oxidation to be modified:

$$\begin{aligned} &\mathrm{TiO + 2H^+ \rightarrow Ti^{2+} + H_2O} \\ &\mathrm{Ti^{2+} + 3H_2O \rightarrow Ti_2O_3 + 6H^+ + 2e} \end{aligned} \tag{3}$$

which further generates H^+ and ensures that dissolution is self-sustaining at valence 3 as observed by Armstrong and Firman [5] and others. This theory is supported by further work [15], which shows that the efficiency for dissolution of Ti in KBr falls with increase in flow rate. The bromide-ion is undoubtedly involved in the early steps of the dissolution process because of its great effect on the polarization and breakdown behaviour ([6] and Fig. 3). Microprobe analysis [15] shows the reaction product on the surface of dissolved Ti in KBr to be a bromide-containing species. An analogous oxidation scheme to the multistage hydrolysis process can be invoked with the acid interfering in a similar manner to produce dissolution at the lower valencies:

$$\mathrm{Ti + HBr \rightarrow TiBr + H^+ + e}$$

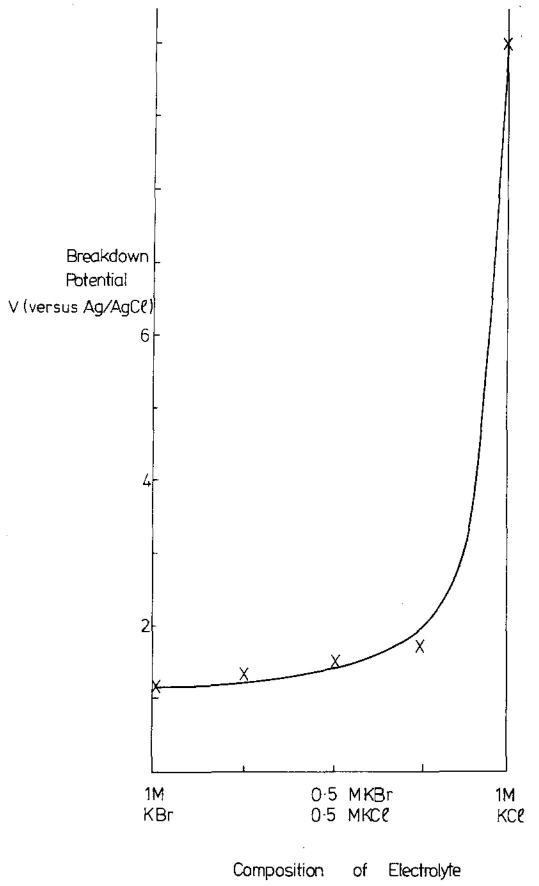

Fig. 5. Breakdown potential on IMI 550.

$$\begin{aligned} &TiBr + HBr \rightarrow TiBr_2 + H^+ + e \\ &TiBr_2 + 2H^+ \rightarrow Ti^{2+} + 2HBr \qquad (4) \\ &Ti^{2+} + 3H_2O \rightarrow Ti_2O_3 + 6H^+ + 2e. \end{aligned}$$

The Ti_2O_3 in both schemes may then be solution-oxidized to TiO_2. Soluble Ti^{3+} species do not appear to be generated as suggested for Ti in H_2SO_4 [2] because (a) the characteristic violet colour of that species was not observed and (b) white solid flakes were seen to fall away from the anode during dissolution. However, these observations are not conclusive because at all but the lowest pH values [1], low valent Ti species in solution would be hydrolysed rapidly to TiO_2.

The reason why efficiencies below 100% are obtained at the lower current densities must be associated with a secondary anodic process. If such a process is occurring, then the surface layers exhibit a degree of electronic conductance and any film is therefore more likely to be crystalline (from a dissolution/precipitation process?) than amorphous. Any such film would tend to be disrupted at the high current density. The marked increase in dissolution current with increase in flow rate for Ti in 3 M KBr [15] would be in agreement with such a mechanism, but this is in contrast to the conclusion of Armstrong *et al.* [2] for Ti in 1 M H_2SO_4.

The principle of adding a film-forming salt to the bromide electrolyte was tested but it is seen from Table 1 that the improvement in the electrolyte properties is only marginal. Inasmuch as chloride is not very aggressive toward titanium, NaCl was regarded as a film-former, as also was KF and Na_2SO_4. Using the segmented-anode cell a direct observation of the effect of the addition of chloride was made and this is presented in Fig. 3. Some slight improvement is apparent, the main improvement being in surface finish, and it is possible that an extension of this approach may lead to improved electrolytes for the dissolution of titanium [15]. It will be noted from Fig. 3 that the weight-loss profile is asymmetric, the stray attack at the outlet being considerably worse than that at the inlet. The reverse is found in the case of mild steel in NaCl where electrolyte depletion or dilution occurs [14]. It is suggested that this is due to the local pH change, described above, causing corrosive conditions at the outlet side of the cell.

Polarization plots for the dissolution of titanium (IMI 115) and two phase IMI 550 in 1 M KBr are shown in Fig. 4. The effect on the polarization of IMI 550 of the addition to KBr of chloride was studied. It is seen that in all cases, electrochemical machining occurs by transpassive dissolution. In this case the zones of the Hoar plot [13] are such that a passage from passivation to active dissolution occurred with rise in potential. The breakdown potential rises with the additions of chloride; breakdown in 1 M KCl does not occur below ~ 10 V (Ag/AgCl). Fig. 5 shows the breakdown potential plotted against the proportion of KCl in the electrolyte. A significant point for electrochemical machining, arising from Figs. 4 and 5, is the one relating costs. The plots show that cheap chloride-based electrolytes may be used but that anode voltage requirements may be considerably lowered by the inclusion of only small amounts of the relatively expensive bromide. After various stages of the polarization in KBr the anode was studied under an optical microscope and it was observed that around the point of 'breakdown' discrete pits occurred on the surface. These pits grew and increased somewhat in number until, in the limiting current region of the polarization plot, the pits had agglomerated to leave only small isolated patches, and sometimes no zones, of the original surface. The machined surface shows the etching reminiscent of active dissolution. These observations suggest that no dissolution-controlling film forms, but rather, once the original passive (oxide?) film has been ruptured that active dissolution occurs, the only control being the limiting current brought about by diffusion limits at high rates. If film control is required to bring about polishing [18], then the observed polarization curves would suggest that true polishing is not occurring and this is in agreement with the surfaces obtained. Additions of chloride may have some effect in this respect commensurate with the improvement in surface finish observed, but this is not obvious from the character of the polarization curve nor from the effect on stray current attack. Attempts were not made to analyse the anolyte thoroughly and in this respect spectrophotometric work could make a contribution. However, it must be concluded that the anodic dissolution occurs via a mixture of both lower-valent and 4-valent kinetics, possibly by way of the mechanism of Chen *et al.* [12] (although Fig. 4 does not suggest a multistage reaction) but more likely involving a simple Br^- adsorption/desorption reaction with interference from H^+. The effect of mixing Cl^- and Br^- is that competition occurs for adsorption sites and inhibits the dissolution, possible because of the formation of an insoluble titanium oxychloride [19]. Complications arise with multiphase alloys due to severe grain undermining.

Acknowledgements

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References

[1] M. Pourbaix, 'Atlas of electrochemical equilibria in aqueous solutions', Pergamon Press, Oxford (1966).
[2] R. D. Armstrong, J. A. Harrison, H. R. Thirsk and R. Whitfield, *J. Electrochem. Soc.* **117** (1970) 1003.
[3] J. C. Griess, *Corrosion* **24** (1968) 96.
[4] R. D. Cowling and H. E. Hinterman, *J. Electrochem. Soc.* **117** (1970) 1447 and *ibid* **118** (1971) 1912.
[5] R. D. Armstrong and R. E. Firman, *J. Electroanal. Chem.* **34** (1972) 391.
[6] J. B. Cotton and I. Dugdale, *Corr. Sci.* **4** (1964) 397.
[7] M. Stern and H. Wissenberg, *J. Electrochem. Soc.* **106** (1959) 755.
[8] N. D. Tomashov, *Corr. Sci.* **4** (1964) 315.
[9] M. Levy, *Corrosion* **23** (1967) 236.
[10] M. Levy and G. N. Sklover, *J. Electrochem. Soc.* **116** (1969) 323.
[11] J. M. Peters and J. R. Meyers, *Corrosion* **23** (1967) 326.
[12] C. M. Chen, F. H. Beck and M. G. Fontana, *ibid* **26** (1970) 135.
[13] J. Bannard, *J. Appl. Electrochem.* **4** (1974) 229.
[14] J. Bannard, To be published.
[15] M. F. Abd Rabbo and P. J. Boden, To be published.
[16] R. W. Powers and J. F. Wilfore in 'Fundamentals of Electrochemical Machining', Electrochem. Soc. 1971.
[17] R. F. Rolsten, *J. Appl. Chem.* **18** (1968) 292.
[18] T. P. Hoar, D. C. Mears and G. P. Rothwell, *Corr. Sci.* **5** (1965) 279.
[19] M. F. Abd Rabbo and P. J. Boden, Proc. NACE Conf., Williamsburg (Dec. 1971).