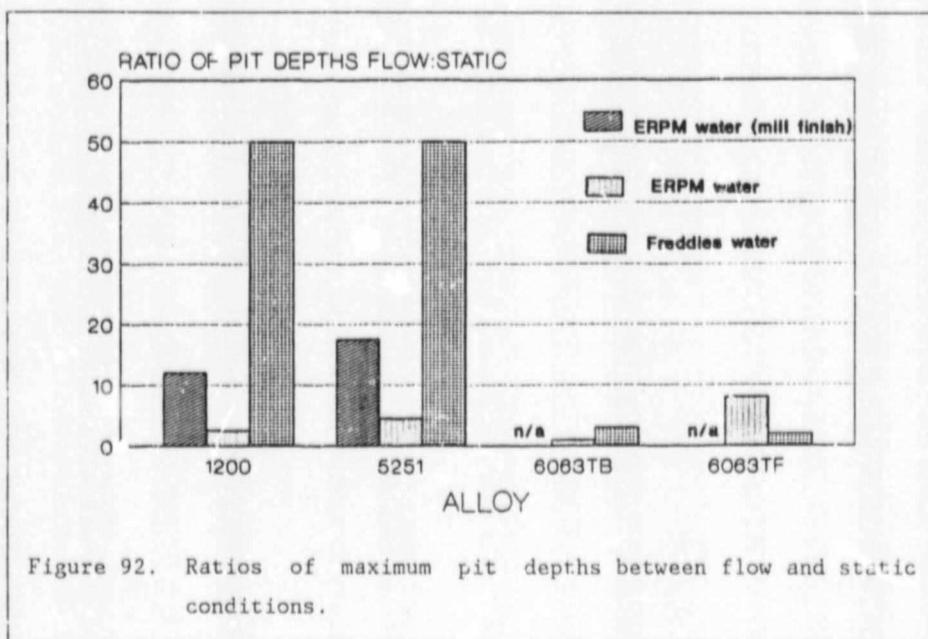


portant with increasing corrosion rates as the reacting specie(s) is/are consumed faster. Without flow, the concentration of the reacting ions may decrease at the metal surface and diffusion polarisation may take place, slowing the corrosion reaction.

A comparison of maximum pit depths under the two conditions was then made, again using ratios between flow and static conditions and the results are depicted in Figure 92.



The ratios for alloys 1200 and 5251 are very large in Freddie's water, since no measurable pits were formed on the static specimens. For the "mill finish" specimens, the large ratios are due to the better than "polished finish" pitting resistance under static conditions and the worse than "polished finish" pitting resistance under flow conditions.

So as flow increased general corrosion rates, flow has also increased the pitting rates of the alloys. This was indicated by cyclic polarisation scans which showed decreases in the passive ranges under flow conditions.

The morphology of pitting changes under flow conditions. Pits tend to elongate in the direction of flow. Figure 93 shows an example of pits linking up and growing laterally in the direction of flow.

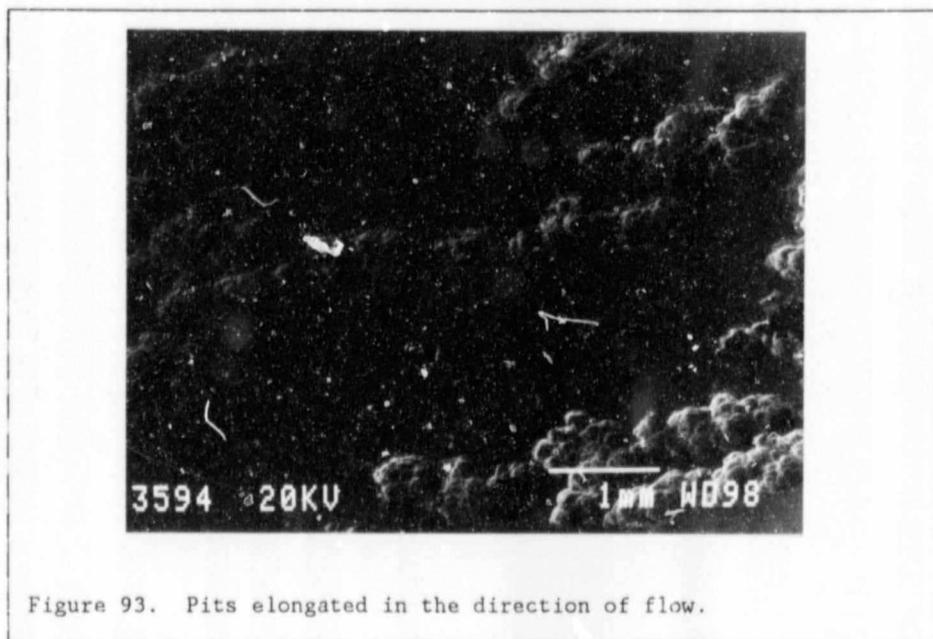


Figure 93. Pits elongated in the direction of flow.

6.8 TEMPERATURE EFFECTS

Van Horn (9) states that although an increase in temperature increases diffusion and ionic activity, other factors make temperature effects difficult to predict. The thickness of the passive barrier layer and the solubility of the bulk film are both temperature dependent (7,8). With a temperature rise the barrier film and bulk film thicken, but their solubilities also increase and the bulk film becomes more permeable. Although limited corrosion rate measurements were taken over a range of temperatures, they did appear to indicate that the corrosion rate vs temperature

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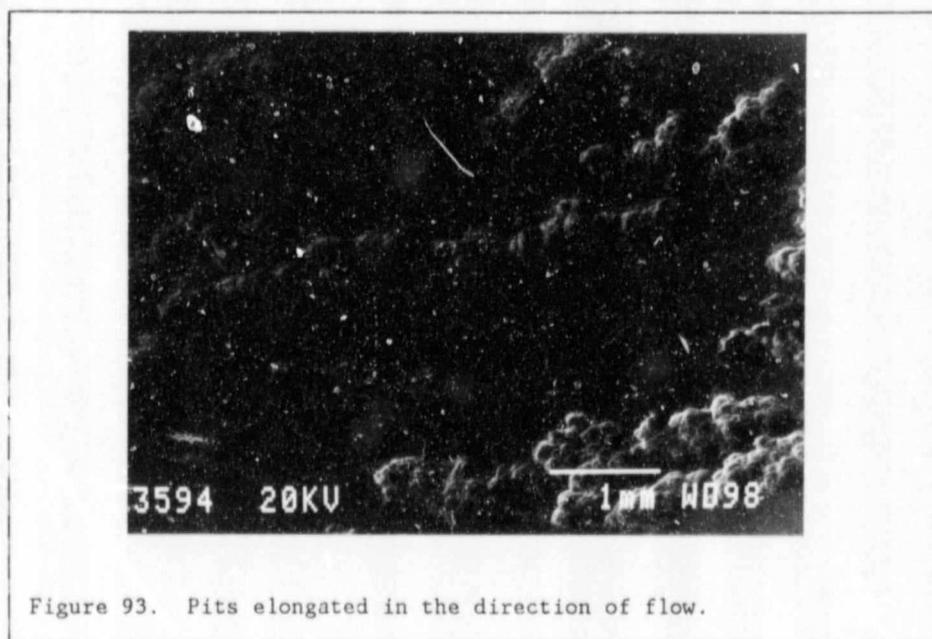
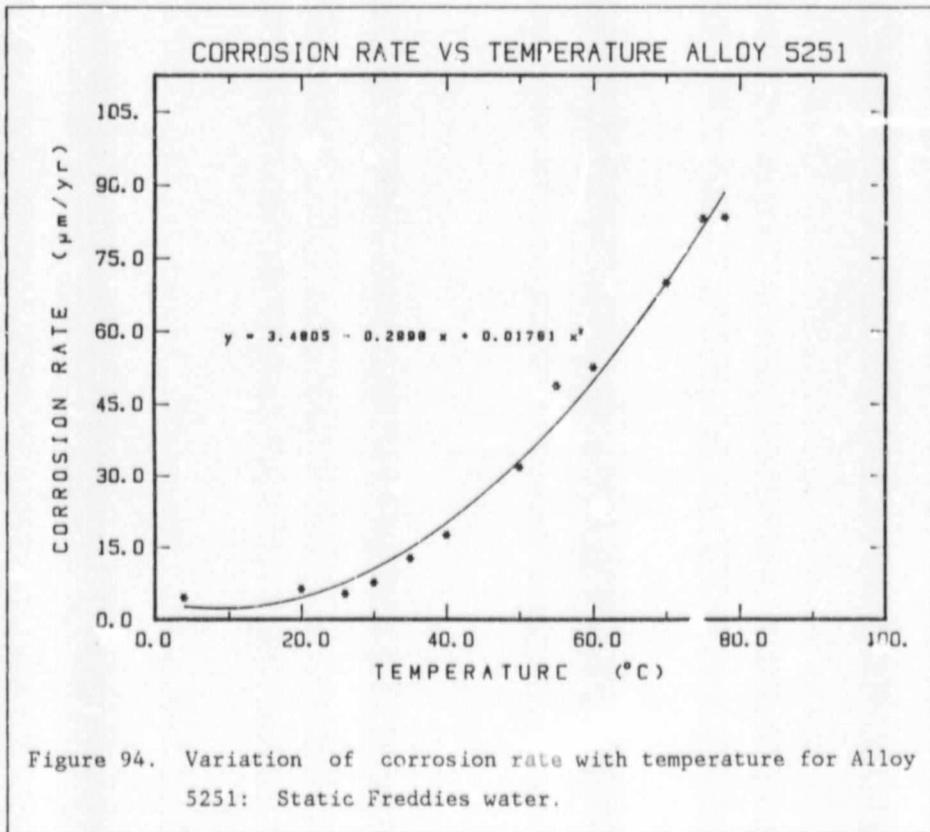


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relationship between 4 and 78°C for alloy 5251 in Freddie's water is of a quadratic form (Figure 94). The overall trend is thus an increase in corrosion rate with temperature. This is mainly due to the decreasing solubility of oxygen in water and the increase in reaction rates with increasing temperature. The solubility of the oxide film increases with temperature, but at the same time its thickness increases.



Godard et al (7) noted in their corrosion studies of aluminium alloy 1100 in a mildly corrosive water, up to 70°C, that pitting rates went through a maximum around 40°C.

The corrosion behaviour of these aluminium alloys does vary with temperature and more extensive tests in the range 5-60°C are necessary to define

the behaviour. The behaviour of the different alloys will not necessarily be the same since the stability of their passive films are different.

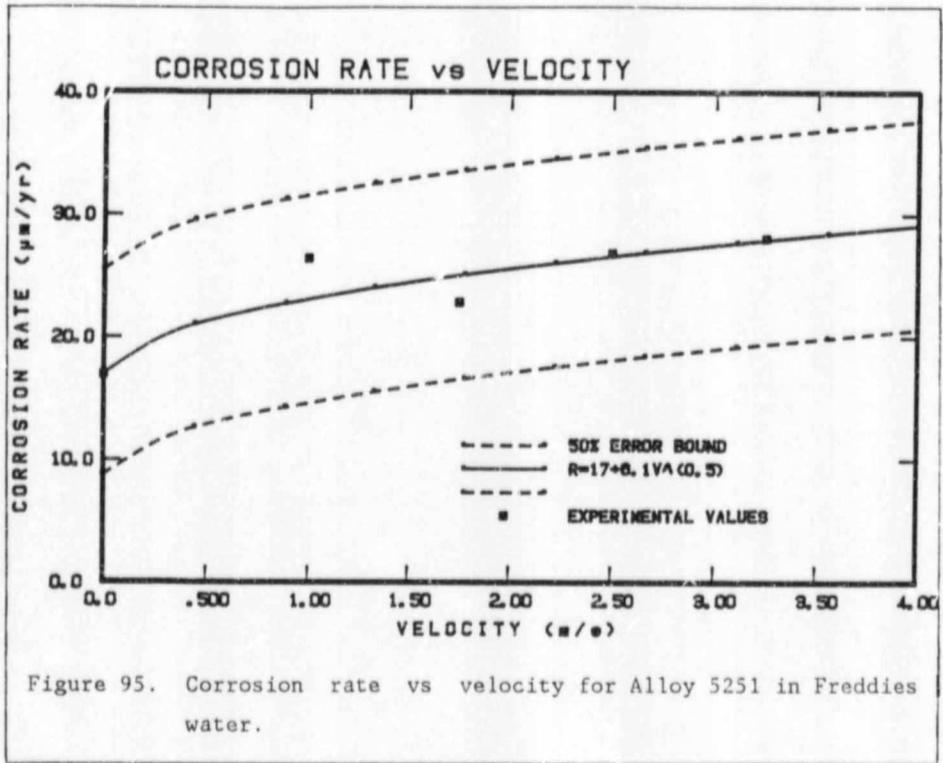
6.9 FLOW VELOCITY EFFECTS

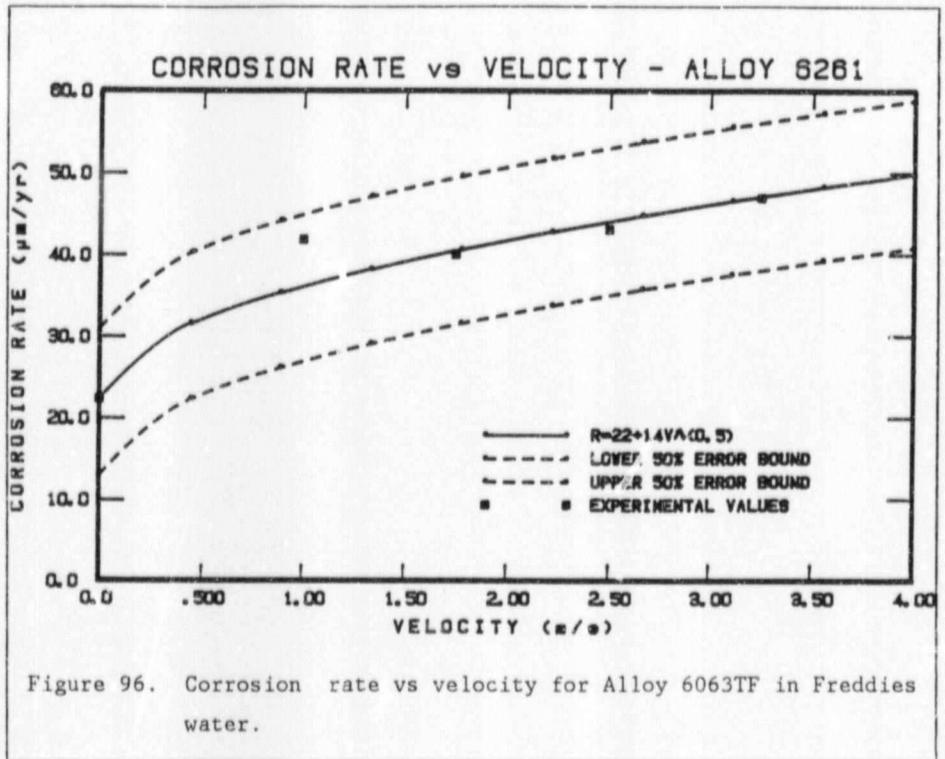
6.9.1 CORROSION RATES AND VELOCITY

Various authors (7,9) have found that in general, corrosion rates of aluminium alloys in water increase with the square root of velocity. From the limited tests conducted at various velocities for two alloys, relationships of the form:-

$$f = kv^{1/2} + c \quad (k \text{ and } c \text{ are constants})$$

were fitted through the data as shown in Figures 95 and 96. By considering possible errors as being of the order of 50% (in fact possibly 100% with electrochemical testing) all data fell within this range.





6.10 PERFORMANCE RATING OF THE ALUMINIUM ALLOYS

To gain an overall performance rating for the alloys for the whole test programme, their positions (1st, 2nd, etc) in each test were tabulated (Tables 6.20 and 6.21). The positions were then added and divided by the number of tests. The results from two waters were then added together for each alloy and the smallest number was the best rating and so on. The ratings obtained are fairly subjective as perhaps weighting factors could be applied to individual test results and for example Alclad and alloy 1200 were very close to each other. However, even if adjacent alloys may in some places have interchangeable positions in the rating order, the overall trend does give a good indication of the relative performance of these alloys.

Table 6.20 Performance positions in each test in ERPM water.

Alloy	Alclad	1200	5251	6063TB	6063TF	7017
<u>Flow</u>						
Corr.Rate						
E.C.	n/a	3	2	4	1	6
Imm.	6	2	3	4	1	5
Pass.Rg.	n/a	2	3	1	4	6
P.D.ave.	1	3	2	5	4	n/a
P.D.max.	1	3	2	4	4	n/a
Str.loss	1	3	2	6	3	5
<u>Static</u>						
Corr.Rate						
E.C.	n/a	2	n/a	1	3	5
Imm.	5	2	4	3	1	6
Pass.Rg.	n/a	4	1	2	3	5
P.D.ave.	4	3	1	5	2	n/a
P.D.max.	4	3	1	5	2	n/a
Str.loss	1	6	3	3	5	2
TOTAL	23	36	24	43	33	40
<u>TOTAL</u>						
No.Tests	2,88	3,00	2,18	3,58	2,75	5,00
RATING	3	4	1	5	2	6

Table 6.21 Performance positions in each test in Freddie's water.

Alloy	Alclad	1200	5251	6063TB	6063TF	7017
<u>Flow</u>						
Corr. Rate						
E.C.	n/a	3	1	2	4	5
Imm.	5	3	1	4	2	n/a
Pass. Rg.	n/a	4	1	2	3	5
P.D. ave.	1	4	2	5	3	n/a
P.D. max.	1	2	4	5	3	n/a
Str. loss	1	5	3	4	2	n/a
<u>Static</u>						
Corr. Rate						
E.C.	n/a	2	3	1	4	5
Imm.	5	1	4	3	2	6
Pass. Rg.	n/a	1	4	3	2	5
P.D. ave.	3	1	1	5	4	6
P.D. max.	3	1	1	4	4	6
Str. loss	1	5	6	3	2	4
TOTAL	30	32	31	41	35	42
<u>TOTAL</u>						
NO. TESTS	2,50	2,67	2,58	3,42	2,92	5,25
RATING	1	3	2	5	4	6

Table 6.22 Performance totals and overall ratings of aluminium alloys.

Alloy	Total 1	Total 2	TOTAL	Overall Position
Alclad	2,88	2,50	5,38	2
1200	3,00	2,67	5,67	3
5251	2,18	2,58	4,76	1
6063TB	3,58	3,42	7,00	5
6063TF	2,75	2,92	5,67	3
7017	5,00	5,25	10,25	6

The alloys in order of overall performance best to worst:-

5251 > Alclad > 1200 > 6063TF > 6063TB > 7017.

Alclad performs well only as long as the cladding is intact. However once this has been removed it will behave according to the base metal used. It is also important to note that with the cladding layer present, the Alclad specimens perform best overall with regards to pitting.

6.11 THE EFFECT OF COMPOSITION AND MICROSTRUCTURE

Alloy 5251 performed best overall in terms of corrosion resistance. It is a non heat-treatable Al-Mg alloy containing between 1,7 and 2,4% Mg. The solid solution is anodic to pure aluminium and the second phase particles that come out of solution are anodic to even the solid solution. The silicon present tends to increase the solution potential to nearer that of pure aluminium. If proper control ensures extensive random precipitation, then there is little or no selective attack at grain boundaries as was true for the specimens used in this work.

The Alclad 3004 rated second overall in the testing. This was mainly due to the excellent resistance to pits growing deeper than the cladding layer. Once pits reached the base material, the cladding cathodically protected the substrate. This protection continued even when only very small areas of the cladding remained. In terms of general corrosion there were very high rates with this material since the corrosion rate of the cladding was accelerated by galvanic effects due to its coupling with the cathodic base metal.

Alloy 1200 which is a commercial purity aluminium, with a minimum of 99% Al, rated third overall in corrosion performance. Many alloying elements impair corrosion resistance so "pure" Al was expected to perform better than most alloys. The second phases and precipitates are often anodic to the primary phase or solid solution and so are points of preferential attack. The alloying elements may also introduce inhomogeneities to the oxide film and so decrease its efficacy as a barrier to further oxidation.

Alloy 6063 is a heat-treatable Al-Mg-Si alloy. It contains Mg and Si in solid solution in the proportion 2:1 because this has virtually the same electrochemical potential as pure aluminium. Mg on its own in solid solution makes the potential more anodic and Si moves the potential in the cathodic direction. This overall effect of these two alloying elements is shown in that the electrochemical potential of this alloy is almost the same in all different tempers.

However, some of the particles formed by precipitation out of solid solution after solution heat-treatment may not be exactly Mg_2Si - if this is so they will have a different potential to the solid solution. This was seen in the way that these particles were preferentially attacked, especially those that had formed at the grain boundaries.

The 6063TF i.e. the artificially aged temper, performed better overall than the 6063TB (naturally aged). The 6063TF had noticeably higher yield and tensile strengths - UTS values of ± 185 and ± 130 MPa for 6063TF and 6063TB respectively. Natural aging tends to cause hardening by the formation of zone structures within the solid solution, while artificial aging induces an extensive general precipitation within the grains (9).

The more extensive and dispersed precipitation formed with artificial aging tends to lower any solution potential differences between the grains and the boundary areas.

Alloy 7017 was markedly inferior in corrosion resistance to any of the other aluminium alloys. This alloy is of the medium-high strength Al-Zn-Mg type. It has 0,35% Cr, which improves resistance to stress corrosion cracking. The ratio Mg : Si is between 4 and 6 so that anodic potential shift effect of the Mg is not counteracted effectively by the Si. Zn strongly decreases the electrode potential. For example, in a solution of 53g/l of NaCl, 99,95% Al has a potential of -0,85V vs SCE, while Al+4Zn has a potential of -1,05V vs SCE. With Mg in the ratio of Mg : 2Zn added, the potential decreases to -1,07V. This is the approximate ratio in this particular alloy. Thus this alloy is anodic to almost all other aluminium alloys. In the aggressive waters used in these tests, the protective oxide layer was weak, as could be seen by the way that the alloy underwent exfoliation and general corrosion rather than pitting. Aluminium alloys tend to decrease in corrosion resistance with an increase in strength viz. with an increase in alloying elements.

7.0 CONCLUSIONS AND RECOMMENDATIONS

7.1 CONCLUSIONS

Equipment suitable for electrochemical and total immersion corrosion testing under both flow and static conditions was designed and constructed. The total immersion test section of the flow loop was not ideal as regards correct modelling of hydrodynamic parameters, but with only flat specimens machined from sheet available, this was the only practical choice. In the constructed loop total immersion tests could be carried out under flow conditions at a controlled flow rate and temperature.

7.1.1 ERPM HERCULES' SHAFT WATER

7.1.1.1 Electrochemical tests

Spontaneous passivation of all alloys, with the exception of 7017 occurred in this water under both flow and static conditions. Corrosion rates were low, varying from 7 - 29 $\mu\text{m}/\text{yr}$ under static conditions, and increasing to 20 - 50 $\mu\text{m}/\text{yr}$ as measured by electrochemical techniques under flow conditions. Alloy 7017 corroded at very high rates of 274 and 99 $\mu\text{m}/\text{yr}$ respectively. 3CR12 and 316L stainless steel tested for comparison purposes, underwent corrosion at rates from 0 - 12 $\mu\text{m}/\text{yr}$.

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Flow as opposed to static test conditions increased the corrosion rates and the passive ranges, but aluminium alloys had very limited, if any, regions of perfect passivation. These ranges were not sufficient for the safe operation of these alloys in this environment and pitting corrosion would be expected to take place.

7.1.1.2 Total immersion testing

Flow increased both general corrosion rates, and also the number and depth of pits formed. There was no real difference observed between pitting rates on the upper and lower surfaces of specimens. Maximum pit depths varied from 0,31 - 0,52mm under flow, to 0,02 - 0,52mm under static conditions. The corrosion products formed were dense and strongly adherent under flow conditions. "Mill finish" specimens exhibited better behaviour than polished specimens under static conditions, but were similar to polished specimens under flow conditions.

This was probably due to the fact that under static conditions, the thicker oxide film already present on the "mill finish" specimens gave better protection than that on the polished material. Under the more aggressive flow conditions, the films on both the "mill finish" and polished specimens would grow faster, because of the increased mass transport to the metal surface. Since the maximum film thickness is a function of temperature, eventually both types of specimens will have the same film thickness on their surfaces. Thus because of the rapid film growth under flow conditions, the equilibrium thickness would soon be reached, and the specimens would show similar corrosion behaviour. The deeper scratches on the "mill finish" specimens tended to act as initiation sites for pits.

7.1.1.3 Tensile strength

Strength reductions varied from effectively zero for Alclad to 18%, with greater losses taking place with specimens exposed under flow conditions.

7.1.2 FREDDIES NO. 5 SHAFT WATER

7.1.2.1 Electrochemical corrosion testing

All alloys, with the exception of 7017 showed spontaneous passivation, but had small passive ranges and limited if any, perfect passive ranges. E_p values were at active potentials (typically -500mV vs SCE). As expected from comparison of the two water analyses, the passive ranges were smaller than in ERPM water.

Corrosion rates were in the ranges 20 - 40 μ m/yr and 12 - 22 μ m/yr for flow and static conditions respectively. Alloy 7017 had corrosion rates of 173 and 230 μ m/yr in these conditions. It was the only alloy that appeared to show "better" behaviour under flow conditions, although this difference is within experimental error. 3CR12 and the stainless steels showed very small perfectly passive ranges (\pm 300mV) under flow conditions i.e. they behaved worse under flow conditions - a reversal of the behaviour in ERPM water.

De-aeration causes a decrease in corrosion potential and an increase in corrosion rates of around 100%. However, the perfectly passive ranges increased for both the Al alloys and the stainless steels. De-aeration decreases the oxygen concentration thus slowing the cathodic reaction rate and so E_{corr} is depressed. The maintenance of a continuous protective

oxide film depends on an adequate supply of oxygen, without which general corrosion will increase.

7.1.2.2 Total immersion tests

Corrosion rates were high under flow conditions (204 - 506 $\mu\text{m}/\text{yr}$), while in static water they were only 40 - 60 $\mu\text{m}/\text{yr}$. Pitting was far more severe under flow and was worse than in ERPM water. Pits tended to elongate in the direction of flow and many initiated at sites of mechanical damage on the specimen surfaces.

Tensile testing

Alciad specimens suffered no real strength loss, whilst the rest of the aluminium alloys underwent reductions of 6-14% and 3-10% for flowing and static water respectively.

7.1.2.3 Microscopy

As expected, cladding is effective in preventing pit penetration of the substrate by virtue of conferred cathodic protection. Pitting morphology varies from alloy to alloy and also according to the test conditions viz. whether in static or flowing water. Selective attack of grain boundary precipitates took place in alloys 6063TB and 6063TF in these environments, while alloy 7017 underwent exfoliation corrosion. Pitting frequently initiated at sites of mechanical damage such as surface scratches, especially in the tests carried out in the flow loop.

7.1.2.4 EDAX analysis

The main elements identified in corrosion products were Al, S, Si, Zn, with minor elements Co, Ni, Cl, Cu, Mg, Mn, Ca and Ti. Higher levels of copper were found in the corrosion products formed in flowing water. This will of course produce accelerated corrosion by micro-cathode formation on the aluminium alloy surface. The relatively high levels of sulphur may have originated from microbial activity, along with the high levels of sulphates in these waters.

7.1.2.5 Electrochemical vs Total Immersion testing

The ratios of corrosion rates obtained in these different tests varied between 8-22 and 0,2-4,3 for flowing and static water respectively. The higher ratio in flowing water is partially due to the difference in the flow characteristics over immersion and electrochemical test specimens. This difference is due to the use of flat coupons set in the centre of the flow in the total immersion tests whilst in the electrochemical tests, the specimens were set flush in the wall of the test section. This resulted in higher net water velocities and shear stresses on the surfaces of the coupons.

7.1.2.6 Flow vs static conditions

Corrosion rates increase with flow velocity. The increase appears to be proportional to the square root of the velocity. Pitting may be up to 17x worse under flow conditions than in static water in these environments, as measured both by numbers of pits and their depths.

Flow appears to be beneficial with regards to pitting in less aggressive solutions (like the ERPM water) and detrimental in more aggressive solutions.

7.1.2.7 Temperature effects

The limited work carried out showed that the overall trend was for general corrosion rates to increase according to a quadratic type relationship with temperature. It must be noted that these rates have little bearing on pitting rates.

7.1.2.8 Rating of alloys

Taking all conditions into consideration, an overall performance rating would be as follows:-

5251 > Alclad 3004 > 1200 > 6063TF > 6063TB > 7017

Alloy 5251 was placed first due to its resistance to pitting and low general corrosion rates. The cladding layer prevented pits from growing into the 3004 substrate, however the general corrosion rates of the cladding were high. Alloy 1200 had the next best performance as could be expected, since it is a commercial purity aluminium and generally speaking, the higher the purity the better the corrosion resistance. The difference in the two tempers of alloy 6063 was concluded to be because the artificial aging process tends to produce a finer and more dispersed precipitate than natural aging does. Alloy 7017 is significantly anodic

to the other alloys due to the Zn and Mg alloying elements and appears to have a less protective oxide film as can be seen in the high general corrosion rates noted with this alloy.

7.1.2.9 Suitability of alloys for use

In flowing and static ERPM and static Freddie's water, all the alloys with the exception of 7017 gave low general corrosion rates. However pitting is a serious problem with all the alloys, especially under flow conditions. The absence of perfect passivity in the electrochemical tests confirms this. Perforation due to pitting is likely to be the failure mode of components fabricated from these alloys. Alclad alloys provide the best resistance to pitting provided that the cladding layer is intact.

Overall, these alloys are not suitable for use in these environments without some extra protection.

7.2 RECOMMENDATIONS

In order to improve the correlation between electrochemical and immersion test results in the flow loop, tubular specimens should be used (assuming the test materials are available in this form and a size suitable for insertion into the loop). The corrosion behaviour at temperatures below 40°C under flow conditions should be studied, but this will involve the installation of cooling facilities in the flow loop. The influence of temperature on corrosion should be investigated more extensively.

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