

## The Influence of Hydrofluoric Acid on the Active Behaviour of Titanium

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The active behaviour of titanium in acidic HF-free media has been determined by a number of workers (a review is given by Kelly<sup>1</sup>) and its behaviour can be said to be relatively well understood. It has been known for a long time that HF increases the rate of corrosion and the critical current density needed for passivation of titanium.<sup>2–8</sup> Only one group, Caprani *et al.*, has made a thorough study of the active behaviour of titanium in the presence of HF, using rotating Ti disc electrodes and impedance measurements.<sup>4–9</sup> Caprani *et al.* discovered the diffusion control of HF-consuming metal-ion dissolution at the active titanium surface using rotating titanium disc electrodes,<sup>4</sup> determined the titanium dissolution valence<sup>8</sup> and proposed a complicated titanium dissolution mechanism. In this mechanism the titanium electrode is assumed to be covered by adsorbed reaction intermediates, and it was suggested that  $TiF_2^+$  and  $TiF(HSO_4)^+$  are the final species in ( $H_2SO_4$ , HF) medium.<sup>9</sup> The purposes of the present work were to reexamine the diffusion-limited HF-consuming dissolution of active titanium discovered by Caprani *et al.* and to provide more information on the chemical nature of the titanium ions which pass through the diffusion layer in ( $HCl$ , HF) medium using other and simpler electrochemical methods (stationary polarization and chronopotentiometric measurements).

### Experimental

Stationary polarization and chronopotentiometric measurements have been made with titanium

(99.6 %) sheet electrodes ( $4.5\text{ cm}^2$ ) in a thermostatted ( $25.0 \pm 0.1^\circ\text{C}$ ) three-compartment Pyrex cell with a platinum auxiliary electrode and a thermostatted saturated calomel reference electrode. Before use, the titanium electrode was mechanically polished, cleaned in acetone, etched

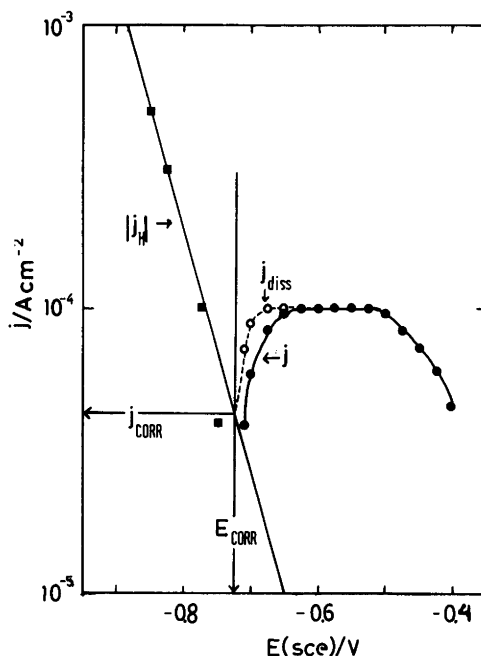


Fig. 1. Stationary polarization curve for titanium electrodes in 1.0 M HCl + 0.001 M HF at  $25^\circ\text{C}$  and without stirring. Open symbols represent true metal dissolution current density.

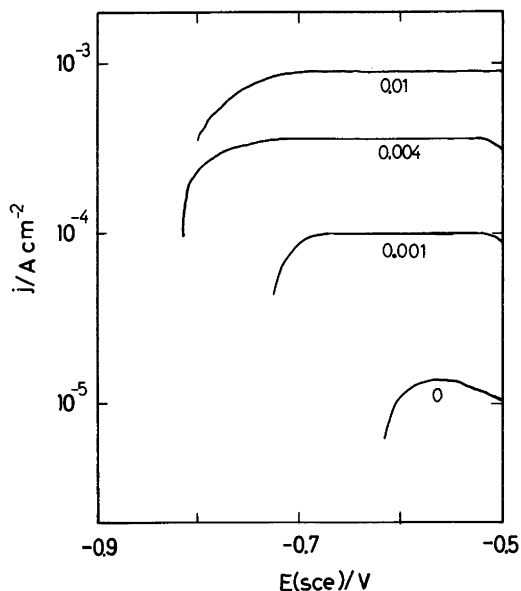


Fig. 2. Stationary Wagner-Traud corrected anodic polarization curves for titanium in 1.0 M HCl +  $x$  M HF at 25°C and without stirring. Values of  $x$  are given under the curves.

for 1 min in aqueous 1 M HF solution and rinsed in twice-distilled water. Test solutions, 1.0 M HCl +  $x$  M HF ( $x = 0-0.1$ ), were made from *pro analysi* HCl and HF with water distilled twice in quartz apparatus. The test solutions were deoxygenated by nitrogen bubbling and were kept under nitrogen atmosphere during measurements. Instruments used were primarily a PAR-173/176 potentiostat/galvanostat, a Cole-Parmer 8371-10 recorder and a Houston 2000 X-Y recorder.

## Results

Fig. 1 shows an example of a polarization curve (anodic and cathodic). The titanium electrode was conditioned at open circuit in the test solution for 1 h before potentiostatic polarization measurements were performed, and 5 min stabilization was allowed for stationary conditions to be attained.

Cathodic polarization measurements gave Tafel plots with a slope of  $-120$  mV/decade for the test solutions employed in this work. In order to determine the titanium dissolution rate correctly it is necessary to correct for the hydrogen evo-

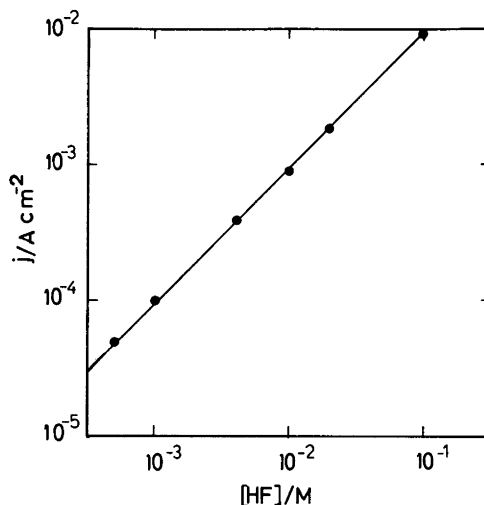


Fig. 3. The potential-independent current plotted against the HF concentration to which it applies, temp. 25°C and without stirring.

lution reaction, as shown in Fig. 1 (Wagner-Traud correction,  $j_{\text{diss}} = j + |j_{\text{H}}|$ ). Fig. 2 shows examples of such Wagner-Traud corrected anodic polarization curves, and it can be seen that the titanium dissolution current density possesses a potential-independent range and that this current

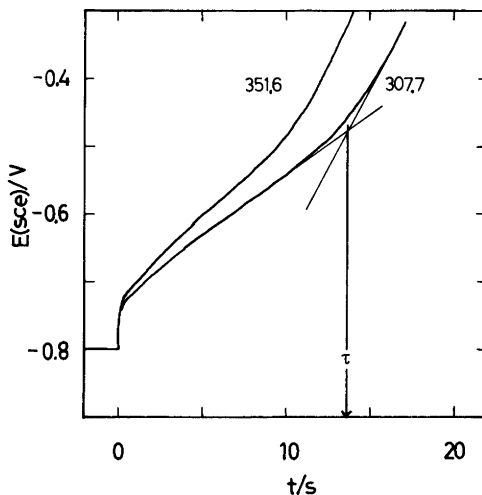


Fig. 4. Chronopotentiometric curves for titanium in 1.0 M HCl + 0.001 M HF at 25°C and without stirring. Values of the impressed current density ( $\mu\text{A cm}^{-2}$ ) are given beside the curves.

Table 1. Data from chronopotentiometric curves.

$j/\mu\text{A cm}^{-2}$	$\tau/\text{s}$	$j\sqrt{\tau}/\mu\text{A cm}^{-2} \text{s}^{0.5}$	$x$
220.0	25.5	1111	0.98
263.7	18.0	1118	0.97
307.7	13.4	1126	0.97
351.6	10.6	1144	0.95

density increases with increasing HF concentration.

The latter is better seen in Fig. 3, in which the potential-independent current is log-log plotted against the HF concentration. A line has been drawn with unit slope and seems well obeyed.

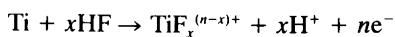
Stirring (by nitrogen bubbling) increases the titanium dissolution rate and displaces the corrosion potential in the negative direction.

Fig. 4 shows examples of chronopotentiometric curves. The titanium electrode was conditioned at open circuit in the test solution for 1 h and then stabilized at  $-87.9 \mu\text{A cm}^{-2}$  for 5 min before measurements were performed. In order to minimize HF concentration gradients, the titanium electrode was stabilized at  $-87.9 \mu\text{A cm}^{-2}$  for 5 min between each measurement. From the chronopotentiometric curves, the transition time ( $\tau$ ) was determined as shown for one of the curves in Fig. 4, and is given in Table 1.

## Discussion

HF clearly accelerates the corrosion of active titanium in acidic solution. HF seems to induce some fast and transport-limited process of HF-consuming metal-ion dissolution at the active titanium surface. This is indicated both by the fact that stirring increases the titanium dissolution rate and by the occurrence of a limiting current plateau (Fig. 2) which is proportional to the concentration of HF (Fig. 3). This agrees well with the linear  $j^{-1} - \omega^{-0.5}$  curves found by Caprani *et al.* using rotating Ti disc electrodes<sup>4</sup> (linear  $j^{-1} - \omega^{-0.5}$  curves indicate first-order dependence of  $j$  on [HF]).

Assuming the overall anodic dissolution reaction at the titanium electrode to be represented by the equation



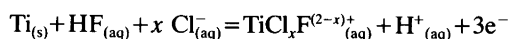
and the approximate Nernst diffusion layer treatment to be applicable, the limiting current is given by the expression

$$j_{\text{lim}} = (n/x)FD[\text{HF}]/\delta.$$

With  $n = 3^8$  and  $D = 1.8 \cdot 10^{-5} \text{ cm}^2 \text{ s}^{-1}$ <sup>10</sup> one obtains  $x = 0.055/\delta$  ( $\delta$  in cm). The diffusion thickness,  $\delta$ , is not known accurately but is often observed to be equal to 0.05 cm for unstirred solutions.<sup>11</sup> Provided  $\delta = 0.05$  cm,  $x$  seems to be equal to 1. In order to determine  $x$  with greater accuracy, chronopotentiometric measurements were performed. Assuming Sands equation is valid,  $x$  is given by the expression

$$j\sqrt{\tau} = 0.5(n/x)F[\text{HF}]\sqrt{(\pi D)}.$$

With  $D = 1.8 \cdot 10^{-5} \text{ cm}^2 \text{ s}^{-1}$  and  $n = 3$  one obtains  $x = 0.97 \approx 1$ , which is the same value for  $x$  as determined from the limiting current. In previous work, the major species formed in chloride solutions, in HF alone and in ( $\text{H}_2\text{SO}_4$ , HF) mixtures were found to be  $\text{TiCl}_2^{2+}$ ,<sup>12-14</sup>  $\text{TiF}_2^{+9}$  and a mixture of  $\text{Ti}(\text{HSO}_4)^+$  and of  $\text{TiF}_2^{+9}$ , respectively. Although the present measurements rule out  $\text{TiF}_2^{+9}$  as final species, this does not necessarily exclude the possibility of participation of  $\text{Cl}^-$  ions in the dissolution reaction. The overall anodic dissolution reaction at the titanium electrode is therefore represented by



where the most probable values of  $x$  are 0 and 1. The value of  $x$  should be sought established in future studies.

## References

- Kelly, E. J. In: Bockris, J. O'M., Conway, B. E. and White, R. E., Eds., *Modern Aspects of Electrochemistry*, Plenum, New York and London 1982, Vol. 14, Chap. 2.
- Mandry, M. J. and Rosenblatt, G. J. *Electrochem. Soc. 119* (1972) 29.
- Kelly, J. J. *Electrochim. Acta* 24 (1979) 1273.
- Caprani, A. and Epelboin, I. *C.R. Seances Acad. Sci., Ser. C* 269 (1969) 1087.
- Caprani, A. and Epelboin, I. *J. Electroanal. Chem.* 29 (1971) 335.
- Caprani, A., Epelboin, I. and Morel, P. *J. Electroanal. Chem.* 43 (1973) App. 2.

7. Caprani, A. *J. Chim. Phys. Phys.-Chim. Biol.* 72 (1975) 171.
8. Caprani, A. and Morel, P. *J. Chim. Phys. Phys.-Chim. Biol.* 72 (1975) 183.
9. Caprani, A. and Morel, P. *J. Less-Common Met.* 56 (1977) 223.
10. Noulty, R. A. and Leaist, D. G. *Electrochim. Acta* 30 (1985) 1095.
11. Bockris, J. O'M. and Drazig, D. G. *Electro-chemical Science*, Taylor and Francis, London 1972.
12. Frayret, J. P., Pointeau, R. and Caprani, A. *Electrochim. Acta* 26 (1981) 1783.
13. Frayret, J. P. and Caprani, A. *Electrochim. Acta* 26 (1981) 1789.
14. Frayret, J. P. and Caprani, A. *Electrochim. Acta* 27 (1982) 391.

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