

## Bromides

Although titanium, like its alloys, is resistant to bromide solutions, there is nevertheless the risk of pitting and stress corrosion cracking. The resistance of titanium can be improved by alloying with palladium, chromium or molybdenum [229].

Alloying additives usually improve the resistance of the protective coatings formed on titanium in halide solutions; the improving effect increases in the series  $V + Al < Mn + Al < Mo < Ni < Pd$ . As is to be expected, the corrosivity of the halides increases from iodide through bromide to chloride, and the pitting corrosion potentials decrease in this direction [230].

Bromide ions in dilute sulfuric acid have an activating effect on passive titanium surfaces, although they have a corrosion-inhibiting effect in higher sulfuric acid concentrations in which titanium is more active [231].

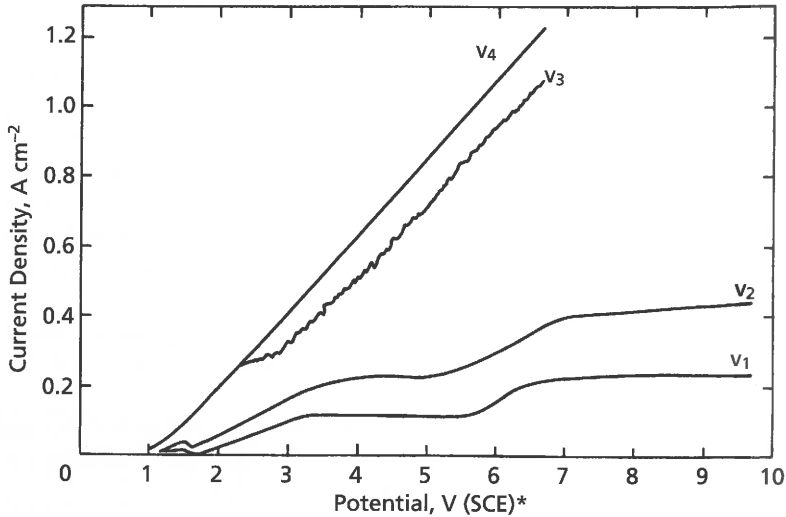
In 2.5 mol/l sulfuric acid the inhibiting effect of inhibitors such as acridine and o-phenanthroline is increased by about 10% by potassium bromide, since the surface coatings produced are only sparingly soluble in the acid [232].

Pitting corrosion of titanium and titanium alloys in halide solutions can be inhibited by anions containing oxygen, e.g. phosphate, provided that the molar concentrations of these anions is equal to or greater than that of the halide ions: for example, titanium in a solution consisting of 1 mol/l sodium phosphate and 1 mol/l sodium bromide was not attacked by pitting corrosion [233].

The influence of flow velocity on pitting corrosion in 1 mol/l potassium bromide solution is shown in Figure 7: according to this, at the low flow velocities, plateaus occur in the current density vs. potential curve, which indicate corrosion points which are not growing further. The pits contain corrosion products which, however are destroyed above a certain potential about  $6 V_{SCE}$  after which the pit continues to grow. At high flow velocities pitting corrosion becomes largely independent of the velocity. In basic bromide solutions 1 mol/l potassium bromide and 1 mol/l potassium hydroxide a white crust of titanium dioxide is produced over the corrosion pits which is destroyed at higher velocities [234].

Such measurements also show that there is a clear relationship between susceptibility to pitting corrosion and bromide concentration: at +1.4 V, for example, no pitting corrosion occurs with bromide concentrations below 0.02 mol/l. The pitting corrosion potential is dependent on the temperature in a complicated way: it falls from 1.7 V at 273 K (0 °C) to 0.9 V at room temperature and then remains constant up to above 373 K (100 °C) [235].

The following pitting corrosion potentials in Table 29 were measured for titanium and various of its alloys at 348 K (75 °C) in 10% oxalic acid to which potassium bromide had been added.



**Figure 7:** Pitting corrosion current density of titanium in 1 mol/l potassium bromide solution as a function of potential and flow velocity  $v$  ( $v_1 < v_4$ ) [234]

Alloy	Pitting corrosion potential $V_{SCE}$
Ti + 0.01 % Fe	0.8
Ti + 0.16 % Pd	1.0
Ti + 15.5 % Mo	2.0
Ti + 6 % Al + 4 % Mo	1.6

**Table 29:** Pitting corrosion potential of Ti and various Ti-alloys in oxalic acid with additions of potassium bromide [236]

It can be seen that the last two alloys listed are significantly less susceptible to pitting corrosion. No pitting corrosion occurs at room temperature [236].

In boiling acetic acid containing 0.03 mol/l sodium bromide the pitting corrosion potential of titanium with 5 % water content is 0.7  $V_{SCE}$ , 1.0  $V_{SCE}$  with 10 % water content. In solutions containing 0.1 to 0.5 % water no pitting corrosion occurs below 1.5 V, although it does occur within 10 minutes above 1.5 V. The corrosion rate of passive titanium in such solutions at 1.5 MPa and 473 K (200 °C) is given in Table 30.