JOURNAL OF MATERIALS SCIENCE **34** (1999) 3137 – 3141

# The corrosion of tantalum in oxidizing sub- and supercritical aqueous solutions of HCl, $H_2SO_4$ and $H_3PO_4$

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The corrosion of tantalum was investigated in sub- and supercritical oxidizing solutions of hydrochloric, sulfuric and phosphoric acid at temperatures between 360 and 500 °C. The corrosion rates in HCl and $H_2SO_4$ increased strongly above the critical temperature of water, which was attributed to a phase transformation from vitreous to crystalline $Ta_2O_5$. Corrosion rates in $H_3PO_4$ were low at all temperatures due to the formation of a top phosphate layer. © *1999 Kluwer Academic Publishers*

## 1. Introduction

Organic compounds can be easily oxidized in the Supercritical Water Oxidation process (SCWO) [1]. Due to the low density and dielectric constant of supercritical water ($T_c = 374$ °C; $p_c = 22.1$ MPa), its solvency for both organic compounds and oxygen is high and the conversion of organics into carbon dioxide and water is fast. In the presence of heteroatoms like chlorine, sulfur or phosphorus, the mineral acids HCl, $H_2SO_4$ or $H_3PO_4$, respectively are formed additionally. High-temperature water containing one of these acids and oxygen is extremely corrosive for stainless steels and nickel-chromium alloys [2–9]. The highest corrosion rates were observed at subcritical temperatures and were attributed to transpassive dissolution due to chromate formation. At the same time, nickel or iron cannot form a stable insoluble oxide which could alternatively protect the alloy. At supercritical conditions the acids are not dissociated and ionic corrosion products cannot be dissolved by the solution due to the low polarity of the solvent. Consequently, corrosion drops down to low values.

In a previous paper, we showed that the group Vb-element niobium is corrosion resistant at subcritical temperatures due to the formation of a protecting film of amorphous $Nb_2O_5$ [10]. On the other side, niobium failed at supercritical temperatures. This behaviour was attributed to a phase transformation of the protecting amorphous $Nb_2O_5$ to a crystalline, orthorhombic form of $Nb_2O_5$ which cannot passivate the metal.

Since the common heat and corrosion resistant materials failed under SCWO conditions, research has been done to use valve metals like titanium as liner materials [11]. Titanium outperforms most of the other materials in the subcritical Wet Air Oxidation process (WAO) and showed acceptable corrosion rates in corrosive environments at supercritical temperatures [11, 12].

Tantalum is a valve metal commonly used in chemical applications where corrosion resistance is required [13]. At room temperature, tantalum is protected by a vitreous oxide film that protects the base metal from further oxidation even at high anodic potentials [14, 15]. Consequently, tantalum was proposed as reactor material for SCWO reactors [16].

The literature dealing with the corrosion resistance of tantalum in high-temperature water is controverse. Glasbrenner *et al.* completely dissolved tantalum in supercritical water with 40 ppm oxygen at 500 °C and 26.8 MPa [17]. Hazlebeck *et al.* corroded tantalum in aqueous solutions of 0.7 to 3.5% mixtures of $H_2SO_4$/$H_3PO_4$ and HCl/$H_3PO_4$ with 7% $H_2O_2$ at 28.5 MPa [18]. They reported corrosion rates of $<0.25$ mm/a at 350 °C and 0.25 to 5 mm/a at 550 °C. Vehlow found corrosion rates of up to 4 mm/a in 98% $H_2SO_4$ and HCl at 150 to 270 °C [19]. Lupton *et al.* found tantalum to be suitable up to 210 °C in 98% $H_2SO_4$ [20]. Nagies *et al.* found that tantalum corrodes uniformly in hot salt brines without oxygen at 90 to 200 °C [21]. Bishop found tantalum to be almost perfectly resistant in deareated solutions of HCl, $H_2SO_4$ and $H_3PO_4$ at temperatures up to 250 °C [22].

## 2. Experimental

Coupons of tantalum ($10 \times 10 \times 1$ mm$^3$; supplied by Goodfellow GmbH) were placed inside a continuous flow reactor with an inner, corrosion resistant tube of alumina ceramic inside a nickel-base alloy pressure tube [23]. The metallic outer tube is only in contact with demineralized water. The experimental set-up is shown in Fig. 1. Oxygen was generated by the catalytical $H_2O_2$ decomposition on platinum in the cold part of the reactor. The concentrations of oxygen and hydrochloric, sulfuric or phosphoric acid together with the experimental conditions and the experimentally determined weight differences are shown in Table I.

After the experiments, the coupons were weighed and then examinated with optical microscopy and

TABLE I Experimental conditions and results

| Acid | [Acid] (mol/kg) | $[O_2]$ (mol/kg) | T (°C) | P (MPa) | Exposure time (h) | weight difference (mg/cm$^2$) |
|---|---|---|---|---|---|---|
| HCl | 0.05 | 2 | 360 | 24 | 55 | +0.12 |
| | 0.2 | 3 | 360 | 25.2 | 100 | +0.24 |
| | 0.1 | 1.5 | 425 | 25.2 | 200 | −5,55 |
| | 0.05 | 0.5 | 440 | 24 | 200 | X |
| | 0.05 | 2 | 500 | 24 | 62 | X |
| $H_2SO_4$ | 0.05 | 2 | 360 | 24 | 49 | +3.77 |
| | 0.2 | 3 | 360 | 25.2 | 88 | +8.78 |
| | 0.1 | 1.5 | 425 | 25.2 | 134 | −40.3 |
| | 0.05 | 0.5 | 440 | 24 | 145 | X |
| | 0.05 | 2 | 500 | 24 | 12 | X |
| $H_3PO_4$ | 0.05 | 2 | 360 | 24 | 91 | +0.41 |
| | 0.1 | 1.5 | 425 | 25.2 | 117 | +1.05 |

X = disintegrated

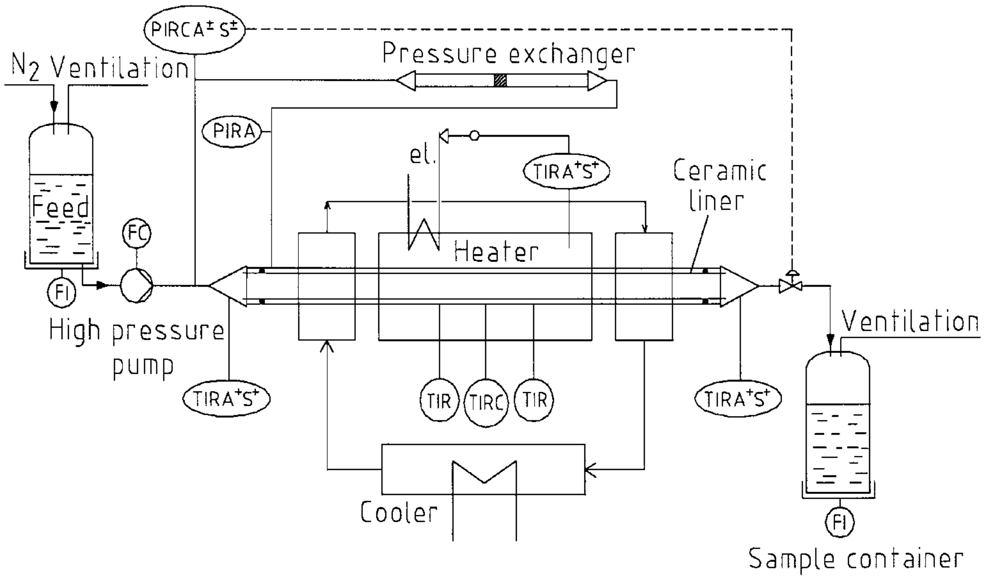

*Figure 1* Experimental set-up.

scanning electron microscopy/energy-dispersive X-ray analysis (SEM-EDX; Leo Gemini 982). Corrosion products were analyzed with SEM-EDX, WD-XRF (Siemens SRS 303), and powder X-ray diffraction analysis (XRD; Siemens D5000) with Cu$K_{\alpha_{1,2}}$ radiation.

## 3. Results

### 3.1. Corrosion in hydrochloric acid

At 360 °C, a slight weight gain was observed, increasing with exposure time (Fig. 2) and acid concentration. At 440 °C the sample disintegrated and light brownish corrosion products were formed. They were identified as tantalum pentoxide by SEM-EDX and WD-XRF. The Powder-XRD spectrum only shows the reflections of pure $Ta_2O_5$ (Fig. 3) in agreement with earlier data from the literature [24, 25].

### 3.2. Corrosion in sulfuric acid

The corrosion in sulfuric acid is far more pronounced than in hydrochloric acid. The weight gain increased with temperature (Table I) and exposure time (Fig. 4) at 360 °C. At 425 °C, the weight loss became severe and at temperatures above 440 °C the metal was completely oxidized to orthorhombic $Ta_2O_5$.

### 3.3. Corrosion in phosphoric acid

At 360 °C the weight gain increased again with acid concentration (Table I). At 425 °C the weight gain increased with exposure time (Fig. 5). SEM-EDX analysis showed an elemental composition of 75 at % oxygen, 16.5 at % phosphorus and 8.5 at % tantalum, which is close to the calculated values for $Ta_3(PO_4)_5$ (71.4 at % oxygen, 17.9 at % phosphorus and 10.7 at % tantalum).

## 4. Discussion

In room temperature water, tantalum is protected by a vitreous top layer of $Ta_2O_5$ which protects the metal even at very high anodic potentials [13]. In subcritical solutions the protecting top layer grows with time, as it is also the case for niobium [12]. The anion has a remarkable effect: In sulfate solutions weight gains are by a factor of 10 to 50 higher than in chloride and phosphate solutions. It can be assumed that in sulfate solutions the oxide film loses its protecting properties

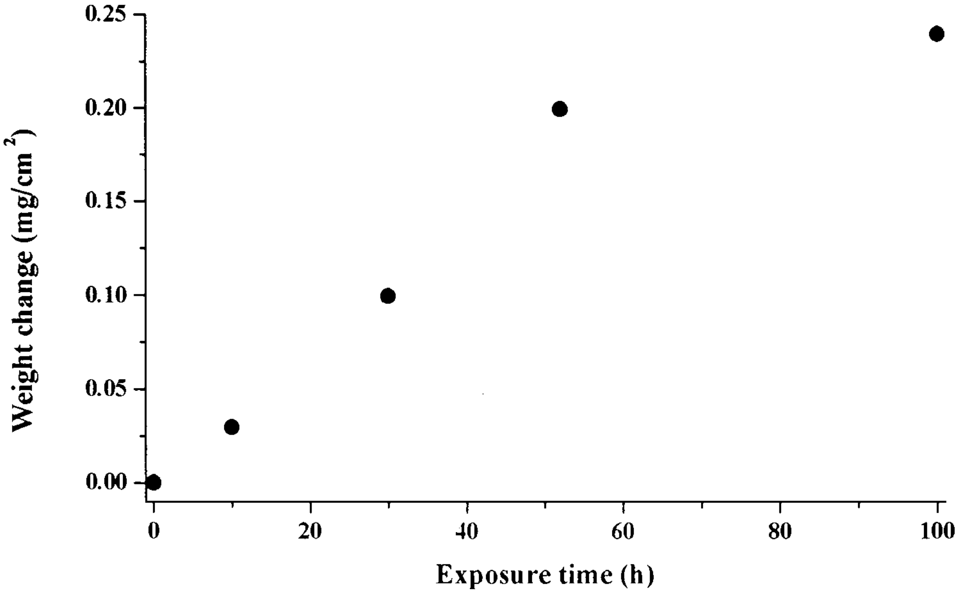

*Figure 2* Weight change of tantalum versus exposure time in an aqueous solution of 0.2 mol/kg HCl and 3 mol/kg $O_2$ at 360 °C and 25.2 MPa.

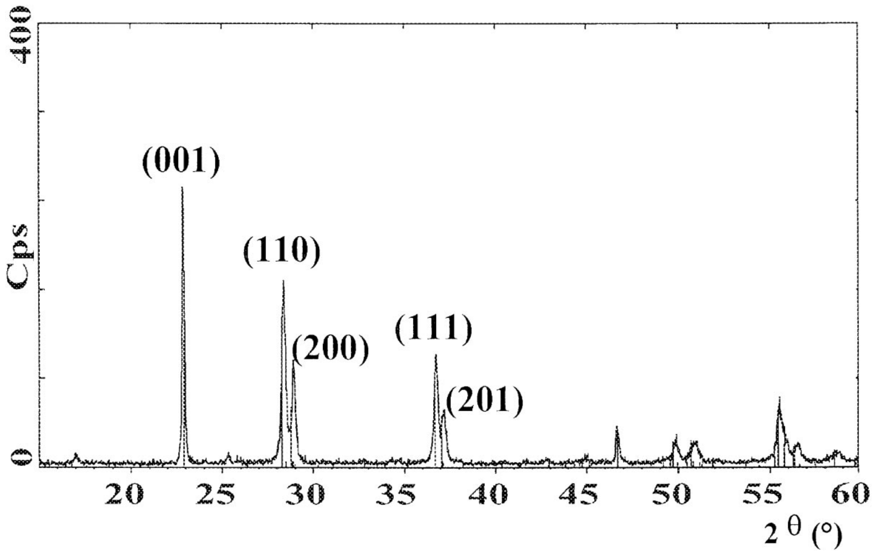

*Figure 3* Powder-XRD spectrum and hkl-indices of orthorhombic $Ta_2O_5$-corrosion products found at supercritical temperatures; reference lines after Roth et al. [24].

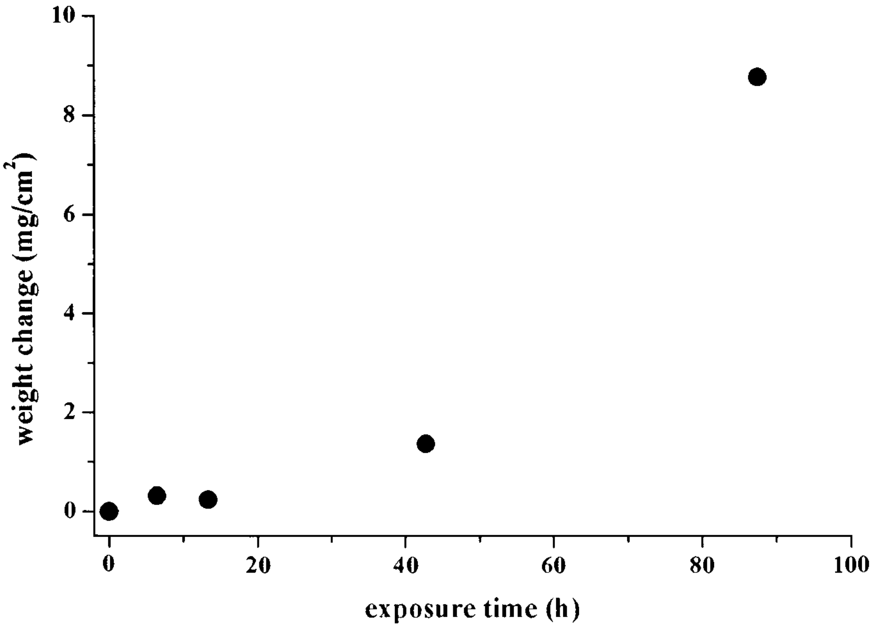

*Figure 4* Weight change of tantalum versus exposure time in an aqueous solution of 0.2 mol/kg $H_2SO_4$ and 3 mol/kg $O_2$ at 360 °C and 25.2 MPa.

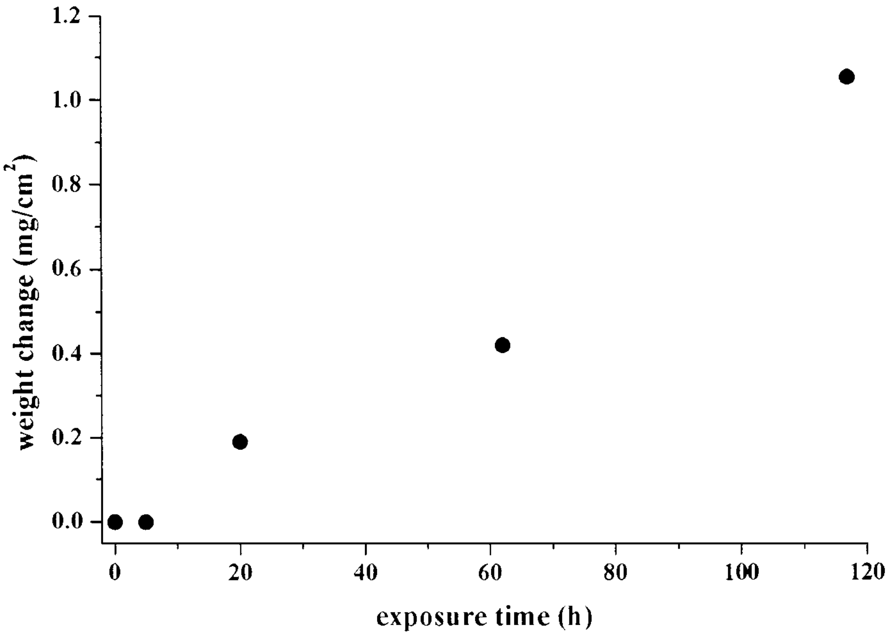

*Figure 5* Weight change of tantalum versus exposure time in an aqueous solution of 0.1 mol/kg $H_3PO_4$ and 1.5 mol/kg $O_2$ at 425 °C and 25.2 MPa.

and therefore leads to a faster oxidation of the underlying metal. In supercritical chloride and sulfate containing aqueous solutions, complete metal oxidation to insoluble $Ta_2O_5$ was found. $Ta_2O_5$ is reported to be nearly insoluble in supercritical solutions [26]. Powder XRD-analysis showed that crystalline orthorhombic $Ta_2O_5$ was formed at temperatures of 440 and 500 °C. At $T = 360$ °C, an amorphous structure was found. Orthorhombic $Ta_2O_5$ is reported to be the stable phase below 1000 °C [24, 25]. The crystalline structure cannot protect the underlying metal from oxidation in contrast to the well-protecting amorphous oxide layer formed at lower temperatures. Gramberg *et al.* reported that the conversion of the amorphous into the crystalline phase takes place at temperatures of 190 to 250 °C [13]. The neighbouring group Vb-element Niobium showed a similar behaviour with low corrosion rates in subcritical and complete disintegration in supercritical oxidizing solutions [10]. In contrast, phosphoric acid caused a slight weight gain and no disintegration occured. This can be explained by an insoluble tantalum phosphate layer that protects the metal from further oxidation. A similar effect was described by Cragnolino for phosphate layers on stainless steels and nickel-base alloys in high-temperature water, that form insoluble corrosion products that plug pores or other imperfections of the passive film [27]. The reason for the extremly high corrosion rates of tantalum at temperatures above 425 °C therefore is the phase transformation into a crystalline oxide with less protecting properties. Consequently, the underlying metal can be oxidized rapidly by the strongly oxidizing solution.

## 5. Summary

The corrosion of tantalum was investigated in oxidizing aqueous solutions of hydrochloric, sulfuric and phosphoric acid at temperatures between 360 and 500 °C and pressures up to 25.2 MPa. The corrosion rates in HCl and $H_2SO_4$ were low at 360 °C and unacceptably high at supercritical temperatures. This behaviour can be explained by a phase transformation of the protecting oxide layer from vitreous to crystalline $Ta_2O_5$. Corrosion rates in $H_3PO_4$ were low at all temperatures due to the formation of a top phosphate layer. Tantalum can be used as a reactor material for high temperature applications up to 360 °C, even in acidic environments. At higher temperatures, tantalum is not applicable in strongly oxidizing environments.

## Acknowledgement

The authors thank W. Habicht, M. Schacht, K. Weiss and J. Göttlicher for supporting this work.

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*Received 29 July*
*and accepted 23 December 1998*