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High temperature sulfidation of pack-tantalized iron

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Abstract. — The tantalization of iron in a pack containing Ta, CrF_2 and alumina leads to a duplex coating containing $\text{TaFe} + \text{TaFe}_2$ in the internal part and nearly pure Ta containing iron in the external part. The kinetics of tantalization are parabolic due to the limitation by a gas phase diffusional mechanism. Tantalized iron samples were submitted to flowing $\text{Ar-H}_2\text{S}$ mixtures at temperatures between 500 and 700 °C and the kinetics followed continuously with a magnetic suspension balance. Due to the very low sulfidation rates, great care was taken to the amount of residual H_2O in the sulfidizing gas. The formed product was always FeS, with no evidence of Ta sulfide(s). This compound was shown to grow by outward transport of Fe from the bulk through the Ta-rich external layer of the coating. The kinetics exhibit a first decreasing rate period followed by a constant rate regime. A model of diffusion-reaction explains correctly the experimental results. The decreasing rate period corresponds to transitory effects leading to steady state boundary condition where the rate law becomes linear. Calculated curves fit correctly the experimental results and reaction and diffusion data are derived.

1. Introduction.

Degradation of metals and alloys by high temperature oxidation is easily reduced by application of appropriate coatings containing either chromium, aluminium or silicon. In the case of purely sulfidizing atmospheres, the problem is more severe and no satisfactory solution has emerged. Systematic experiments by Mrowec showed that refractory metals exhibit very low sulfidation rates and can become good candidates for coating application [1, 2]. The present work describes the use of tantalum in a diffusion coating deposited on iron substrate by pack cementation and subsequently submitted to H_2S corrosion. Contrary to other refractory metals, tantalum sulfidation was seldom studied and very few references are available [3]. The present work is therefore also a contribution to tantalum reactivity knowledge.

2. Elaboration of the coatings.

Iron samples ($15 \times 15 \times 1.5$ mm) were tantalized during 50 h at 1050 °C in a pack containing 40 wt% Ta, 50 wt% Al_2O_3 and 10 wt% CrF_2 as an activator. In such conditions, tantalization takes place parabolically with a rate constant $K_p = 2.5 \times 10^{-7} \text{ kg}^2 \text{ m}^{-4} \text{ s}^{-1}$.

The tantalized samples exhibited a two layers structure (Fig. 1):

- an external layer ($\sim 10 \mu\text{m}$ thick) consisting of nearly pure tantalum (with little Fe and Cr in solid solution);
- an internal layer ($\sim 40 \mu\text{m}$ thick) exhibiting a biphased morphology ($\text{TaFe} + \text{TaFe}_2$).

Fig. 1. — Cross section of an iron sample tantalized at 1050 °C during 50 hours.

The overall growing rate was shown to be controlled by a mixed regime involving slow gas phase diffusion and interface reaction [4].

3. Sulfidation of tantalized specimens.

3.1 EXPERIMENTAL. — Isothermal sulfidation kinetics were followed during 50 h in a dynamic (0.5 cm s^{-1}) Ar - 5% H_2S mixture at atmospheric pressure (50 hPa H_2S) in order to evacuate hydrogen produced by the reaction. A magnetic suspension balance (Sartorius) was used. The temperature was varied between 500 and 700 °C. Under 500 °C, weight gains were very low; above 700 °C massive sulfur deposits on the magnet and suspension hook led to non valid measurements.

Great care was taken to the residual water vapor in the gas. With no precautions, corrosion of pure tantalum and tantalized iron by Ar- H_2S led to the rapid formation of Ta_2O_5 . A 50 cm long fresh P_2O_5 trap was therefore used for all experiments and allowed to suppress any oxide formation.

3.2 KINETICS. — Kinetic curves obtained for sulfidation of superficially tantalized iron are reported in figure 2 and compared with sulfidation of pure iron and pure tantalum. It may be observed that tantalization inhibits markedly (about ten times) the sulfidation of iron, but cannot reduce it to that of pure tantalum. The rate law exhibits a first decreasing period (5 to 6 hours long) before remaining linear. Careful examinations of the first period showed that the initial rate has a finite value. The activation energy derived for the linear part of the kinetic curves was found to be 44 kJ mol^{-1} .

Fig. 2.

Fig. 2. — Kinetic curves of sulfidation at different temperatures by H_2S of tantalized iron. Comparison with iron and tantalum sulfidation.

Fig. 3. — Surface view of a tantalized specimen sulfidized at 500 °C during 55 hours.

Fig. 3.

3.3 FORMED PRODUCTS AND MORPHOLOGY OF THE SCALES. — For all the duration and temperature ranges explored, only FeS was observed without any trace of tantalum sulfide(s). Iron sulfide appeared as large crystals, scattered on the surface for the lowest temperatures, closely joined for the highest (Figs. 3, 4).

Cross-section examinations showed that the coating was not modified during sulfidation. In particular, the thickness of the external Ta-rich layer remained constant (Fig. 5).

3.4 DISCUSSION. — Experimental observations that tantalum sulfide(s) did not form during sulfidation are not in agreement with thermodynamics. Indeed the sulfur (S_2) pressures in equilibrium with TaS_2 and FeS at 500 °C are in the order 10^{-20} and 10^{-10} bar respectively. TaS_2 is therefore the most thermodynamically stable sulfide, but its rate of formation is infinitely low. FeS forms at a rate depending on iron concentration at the Ta/FeS interface. This concentration decreases continuously due to the slow diffusion rate of Fe in the Ta layer and tends to a lower limit when stationary conditions are achieved. Such a mixed kinetic regime can be described as presented in figure 6, using the expressions of the iron diffusion flux:

$$J_{Fe} = D \frac{(C_i^o - C_e)}{y} \quad (1)$$

Fig. 4.

Fig. 5.

Fig. 4. — Surface view of a tantalized specimen sulfidized at 650 °C during 45 hours.
Fig. 5. — Cross section of a tantalized specimen sulfidized at 650 °C during 50 hours.

Fig. 6. — Schematic representation of the tantalized specimen during sulfidation (actual scale not respected).

and of the interface reaction rate:

$$V = k C_e \quad (2)$$

(with J_{Fe} : iron flux in the external tantalum layer of the coating, y : thickness of this layer, C_i^o : equilibrium Fe concentration at the interface between the two layers of the coating, C_e : Fe concentration at the Ta/FeS interface, D : Fe diffusion coefficient in the Ta layer, V : rate of sulfidation of iron, k : interfacial rate constant).

At the Ta/FeS interface, the mass balance imposes:

$$\frac{dC_e}{dt} = \left(\frac{dC_e}{dt} \right)_{\text{diffusion}} - \left(\frac{dC_e}{dt} \right)_{\text{reaction}} \quad (3)$$

It is therefore easily understood why the rate law is firstly decreasing due to an initial reaction rate higher than the diffusion flux. During this transitory period, C_e decreases continuously. When C_e achieves a stationary value where reaction rate and diffusion flux are equal, the rate law becomes linear.

Introducing the thickness " a " of the reactive interface [5], C_e can be calculated from:

$$\frac{dC_e}{dt} = \frac{D}{a} \frac{C_e - C_i}{y} - \frac{k}{a} C_e \quad (4)$$

leading to:

$$C_e = \frac{kyC_i^o}{D + ky} \exp\left(-\frac{D + ky}{ay}t\right) + \frac{DC_i^o}{D + ky} \quad (5)$$

It can be verified that $C_e = C_i^o$ for $t = 0$ and that C_e decreases continuously with time, tending to:

$$C_{e\text{limit}} = \frac{DC_i^o}{D + ky} \quad (6)$$

The reaction rate is:

$$\frac{1}{dt} d\left(\frac{\Delta m}{A}\right) = k M_S C_e \quad (7)$$

(with $\frac{\Delta m}{A}$: weight gain per unit area, M_S : atomic mass of sulfur), leading, by integration, to:

$$\frac{\Delta m}{A} = a M_S \left(\frac{ky}{D + ky}\right)^2 C_i^o \left[1 - \exp\left(-\frac{D + ky}{ay}t\right)\right] + \frac{k M_S D C_i^o}{D + ky} t \quad (8)$$

Fig. 7. — Comparison between the calculated curve and the experimental points for the sulfidation at 650 °C of tantalized iron.

Figure 7 shows that this theoretical equation fits well the experimental results. From the measured values of:

- the initial rate: $\frac{1}{dt} d \left(\frac{\Delta m}{A} \right)_0 = M_s k C_i^o$
- the rate in stationary conditions: $\frac{1}{dt} d \left(\frac{\Delta m}{A} \right)_{\text{stat.}} = \frac{M_s k C_i^o}{D + ky}$
- the ordinate at the origin: $\left(\frac{\Delta m}{A} \right)_0 = M_s a C_i^o \left(\frac{ky}{D + ky} \right),$

average values of a , D and k can be derived in the 500-700 °C temperature range. These values lie in the following intervals:

a : 7×10^{-12} to 3.5×10^{-11} m; D : 2×10^{-15} to 9×10^{-15} m² s⁻¹; k : 1×10^{-10} to 7×10^{-9} m · s⁻¹.

Calculated values of k cannot be discussed, but the realistic values obtained for a and D may be a positive argument for the validity of the model.

4. Conclusions.

Superficial tantalization affords an important inhibition of iron sulfidation in H₂S at 500-700 °C. The tantalum-rich solid solution containing a little iron and chromium acts as a diffusion barrier for iron atoms which are therefore slowly converted into FeS. The sulfidation rate is initially decreasing during the establishment of an iron gradient within the diffusion

layer (transitory period). When steady-state boundary conditions are achieved, the rate becomes constant. A mixed regime, involving two limiting steps leads to calculated curves fitting well the experimental results. The physical parameters derived from this model were shown to be realistic.

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