HIGH TEMPERATURE SULPHIDATION OF NIOBIUM

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The sulphidation behaviour of pure niobium in H_2S–H_2 gas mixtures, $10^{-3} \leq p(S_2) \leq 5$ Pa, was investigated at 1073–1273 K. It has been found that over the whole temperature and pressure range studied, the sulphidation reaction follows a parabolic rate law, being diffusion controlled. The calculated parabolic rate constant k_p was in the range of $8.1 \cdot 10^{-12}$—$3.6 \cdot 10^{-10}$ [$g^2cm^{-4}s^{-1}$], the pressure exponent $1/n$ was about 1/4, the activation energy E_a ~ 89 [kJ/mole]. X–ray diffraction studies of the sulphide scales have shown that they were mixtures of the following sulphide phases: 2H-NbS_2, 3R-NbS_2, Nb_3S_4, *hex.*$Nb_{1-x}S$ and *orth.*$Nb_{1-x}S$. Morphological observations have revealed that the sulphide scales formed on niobium were compact and adherent to the substrate. Their thickness varied between about 9 and 30 μm, depending on temperature, sulphur pressure and sulphidation time (ranging from 20 to 80 hours). The sulphide layers were characterised by columnar plate-like grains growing perpendicularly to the surface of metallic core. The texture analysis, based on measurements of the pole distributions of $(00.2)_{Nb3S4}$ and $\{101\}_{NbS2}$ crystallographic planes, have shown the preferred orientation of (00.2) plane in Nb_3S_4 to the metallic core. The intensity of the $(00.2)_{Nb3S4}$ reflection (intensity about 70 000 of impulses) was several orders of magnitude greater than those of other reflections. The {101} plane is preferentially oriented in the compound 3R–NbS_2. High intensities of the $(00.2)_{Nb3S4}$ and $\{101\}_{NbS2}$ reflections showed the following crystallographic relation: $(00.2)_{Nb3S4} \parallel \{101\}_{NbS2} \parallel$ metal surface, which means that *c* axis in the crystallographic structure of the scale is parallel to the surface of the metallic core. Microstructure, chemical composition and crystallography of the sulphide scale were also studied by conventional transmission electron microscopy (TEM), energy dispersive X–ray spectroscopy (EDS) and selected area diffraction (SAD) using a Philips CM20TWIN equipped with a Link eXL energy dispersive spectroscopy system. It has been found that columnar grains of the outer layer of the scale (NbS_2) exhibit lamellar structure characterized by a large number of twinnings. The width of NbS_2 lamellae was about 0.01 to 0.05 μm. SAD investigations have confirmed strong orientation of these defects along the *c* axis of the NbS_2 structure. The common feature of the twinnings was high density of dislocations which can be regarded as short–circuit diffusion paths. TEM observations of the scale inner layer close to the metal substrate (Nb_3S_4 and NbS) have shown the scale in this region to be built of columnar grains of 0.3 μm - 1μm width and are 1 - 3 μm thick. Grains of this layer were almost dislocations free. Marker masurements using gold have demonstrated that the inner scale layer (Nb_3S_4 and NbS) grows by inward diffusion of sulphur and the outer layer (NbS_2) mainly by outward diffusion of niobium.