A Mass Spectrometry-Based study on the Effects of H₂ and H₂O on the High-Temperature Oxidation of Ti

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Hydrogen species in the form of hydrogen and water vapor in the atmosphere and/or residual hydrogen dissolved in the metallic matrix may strongly influence the high-temperature oxidation of metallic components. Since most high-temperature industrial processes occur in the presence of water vapor and/or hydrogen, it is essential to understand the more general mechanisms associated with these effects.

Effects of water vapor and hydrogen on high-temperature oxidation may be divided into three main approaches; i) effects on the surface kinetics at the oxide-gas interface, ii) effects on the transport properties across the oxide scale and iii) effects on reactions occurring near the oxide-metal interface. On the basis of i-iii, an ideal model system to study these effects should form an oxide with transport of hydrogen defects and, in addition, the metallic matrix should dissolve hydrogen. It turns out that the Ti-TiO₂ system meets these criteria. In this investigation isotopic labeling and mass spectrometry have been applied to address effects of hydrogen and water vapor on the high-temperature oxidation of Ti.

A schematic illustration of the experimental assembly is presented in Fig. 1. Briefly, it consists of a small (<100mL), closed reaction chamber comprising a highpurity quartz tube, a system which enables introduction of different gasses and gas mixtures, and a quadropole mass spectrometer (MS). The gas is fed from the reaction chamber into the MS through a leak valve. The total pressures in the reaction chamber and in the MS are controlled with precise pressure gauges. Thus the oxidation rate can be measured as the decrease in total pressure in the reaction chamber as a consequence of the consumption of gases during oxidation.

Fig. 2 presents the oxidation kinetics of Ti at 700°C for different gas compositions. The oxidation rate is higher in water vapor than in dry oxygen, whereas a mixture of these yields a complex behavior. For the mixture, the initial part of the oxidation follows essentially the dry behavior after which the oxidation rate increases dramatically. By probing the gas in the reaction chamber with the MS, it is possible to show that, in gross terms, the oxygen associated with O2 is consumed during the first slow part and that oxygen associated with H₂O is consumed during the second period where the oxidation rate is accelerated. However, this does not necessarily give the whole reaction route since water still may be involved in the first period in an intermediate reaction step. Isotopic labeling and mass spectrometry will be applied on examples like in Figs. 2 and 3 to elucidate further the different reaction mechanisms involved in the overall oxidation of Ti and Ti with different amounts of dissolved H₂.



Figure 1. Schematic of the experimental set-up.



Figure 2. Specific weigh gain, w, as a function of time during oxidation of Ti at 700 $^{\circ}$ C in dry oxygen, a mixture of oxygen and water vapor and in pure water vapor



Figure 3. The amount of O in the reaction chamber as a function of time during oxidation of Ti at 700°C in a H_2O - O_2 mixture (same as Fig. 2).