The High-Temperature Corrosion of Fe–Nb Alloys in a H₂/H₂O/H₂S Gas Mixture

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The corrosion of Fe–Nb alloys containing up to 40 wt.% Nb has been studied over the temperature range 600–980°C in a mixed gas of constant composition having sulfur and oxygen pressures ranging from 10⁻⁸ to 10⁻⁴ atm. and from 10⁻²⁷ to 10⁻¹⁸ atm., respectively. All alloys were two-phase, consisting of an Fe-rich solid solution and an intermetallic compound, Fe₂Nb. The scales formed on the Fe–Nb alloys were duplex, consisting of an outer layer of iron sulfide (FeS) and an inner complex layer of FeₓNb₁₋ₓS₂ (FeNb₂S₄ or FeNb₃S₆), FeS and unreacted Fe₂Nb. No oxides were detected at any temperature. The addition of Nb reduced the corrosion rate. The corrosion kinetics of Fe–Nb alloys followed the parabolic rate law, regardless of alloy composition and temperature. Platinum markers, attached to the original alloy surfaces, were always located at the interface between the inner and outer scales.

KEY WORDS: sulfdation; Fe–Nb alloys; FeₓNb₁₋ₓS₂; corrosion kinetics.

INTRODUCTION

Fe-, Ni-, and Co-base alloys are common and versatile engineering materials used in many corrosive, high-temperature environments such as those involved in coal gasification and oil-refining processes. When the alloys are exposed to mixed-gas environments containing high sulfur and low oxygen partial pressures, the predominant corrosion problem is sulfidation. In fact, the highly defective nature of sulfides leads to the growth of less-protective
layers. Furthermore, the low eutectic temperatures in these metal/sulfide systems exacerbates the sulfidation problem. The sulfidation rates of these base metals are generally many orders of magnitude greater than their oxidation rates.

Alloys having good oxidation resistance, such as those containing additions of Cr, Si, and Al, generally have poor sulfidation resistance.\(^2\) However, some of the refractory metals such as Nb, Mo, and W exhibit excellent sulfidation resistance at elevated temperatures.\(^3\) During recent years, considerable research on high-temperature sulfidation of numerous metals has been developed and summarized by Mrowec and Przybylski\(^3,4\) and by Strafford.\(^5\) Niobium was reported to have the best sulfidation resistance. Recently, the sulfidation behavior of the base metals (Fe, Co, and Ni) with additions of either Mo or Nb in sulfur vapor has been studied in this laboratory.\(^6,11\) It was shown that a significant reduction in the sulfidation rates of the base metals could be achieved by alloying them with either Mo or Nb, even though the sulfidation rates were still significantly higher than those of pure Mo or pure Nb.

It was of interest to extend the previous work to examine the corrosion behavior of the same materials in practical environments containing two oxidants, sulfur, and oxygen. The purpose of the work presented here is to investigate the effect of Nb on the corrosion kinetics and the reaction mechanism of Fe in a gas mixture of H\(_2\)/H\(_2\)O/H\(_2\)S. The investigation of the role of Nb on Co\(^12\) and Ni-base\(^13\) alloys in the same mixed gas is currently being studied in this laboratory.

**EXPERIMENTAL PROCEDURES**

The starting materials were 99.98% Fe lumps and 99.8% Nb turnings (AESAR Chemical Co.). Pure Fe samples were directly selected from the lumps and fine-polished down to 6 \(\mu\)m diamond paste. The alloys and pure Nb were fabricated into 60-g buttons by arc-melting on a water-cooled copper hearth. Ti turnings were melted initially to getter the argon atmosphere. The buttons were flipped over and remelted at least six times to ensure alloy homogeneity. The as-cast samples were cut in half, and then annealed in vacuum at 1000°C for 24 hr as well as at 900°C for another 24 hr. The annealed samples were sliced into about 1-mm thick coupons using a low-speed diamond saw (ISOMET). A suspension hole was drilled through each coupon by a spark-cutter. These coupons were first ground with 600 SiC paper and then polished to a 6- \(\mu\)m finish. The specimens were ultrasonically cleaned with either acetone or methanol. The average weight and surface area of the specimens were generally around 0.6 g and 2.5 cm\(^2\), respectively. Typical optical micrographs of annealed Fe–10Nb, Fe–20Nb, Fe–30Nb, and