The Corrosion Behavior of Fe–Nb–Al Alloys in H₂/H₂O/H₂S Atmospheres

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The corrosion behavior of eight Fe–Nb–Al ternary alloys was studied over the temperature range 700–980°C in H₂/H₂O/H₂S atmospheres. The corrosion kinetics followed the parabolic rate law for all alloys at all temperatures. The corrosion rates were reduced with increasing Nb content for Fe–xNb–3Al alloys, the most pronounced reduction occurred as the Nb content increased from 30 to 40 wt.%. The corrosion rate of Fe–30Nb decreased by six orders of magnitude at 700°C and by five orders of magnitude at 800°C or above by the addition of 10 wt. % aluminum. The scales formed on low-Al alloys (≤3 wt. % Al) were duplex, consisting of an outer layer of iron sulfide (with Al dissolved near the outer-/inner-layer interface) and an inner complex layer of FeₓNb₂S₄ (FeNb₂S₄ or FeNb₃S₆), FeS, Nb₃S₄ (only detected for Nb contents of 30 wt. % or higher) and uncorroded Fe₂Nb. No oxides were detected on the low-Al alloys after corrosion at any temperature. Platinum markers were found to be located at the interface between the inner and outer scales for the low-Al alloys, suggesting that the outer scale grew by the outward transport of cations (Fe and Al) and the inner scale grew by the inward transport of sulfur. The scales formed on high-Al alloys (≥5 wt. % Al) were complex, consisting primarily of Nb₃S₄, Al₂O₃ and (Fe, Al)ₓNb₂S₄, and minor amounts of (Fe, Al)S and uncorroded intermetallics (FeAl and Fe₂Nb). The formation of Nb₂S₄ and Al₂O₃ blocked the transport of iron through the inner scale, resulting in the significant reduction of the corrosion rates.

KEY WORDS: corrosion; Fe–Nb–Al alloys; (Fe, Al)ₓNb₂S₄; Nb₃S₄; Al₂O₃.

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INTRODUCTION

Most metals and alloys are not thermodynamically stable in air at elevated temperatures, due to corrosion which converts metals into their stable oxide. In past decades, numerous research studies on the high-temperature oxidation on structural materials, such as Fe-, Ni- and Co-base alloys, have been performed. These alloys, developed for good oxidation resistance by adding adequate amounts of Al, Cr and Si, are generally classified as alumina, chromia and silica formers, depending upon which oxide forms after steady-state conditions have been achieved.\(^1,2\) These oxides grow at an extremely slow rate on the alloy surface, acting as a protective barrier to separate the reactants. As a result, the alloys can be used for various applications in high-temperature, oxidizing environments.

However, several important applications in technical processes, such as coal gasification and/or oil refining, involve multi oxidants, containing significantly high partial pressures of sulfur (\(\sim 10^{-5}\) atm) and relatively low partial pressures of oxygen (\(< 10^{-20}\) atm). Therefore, the predominant corrosion problem is sulfidation.

In fact, the highly defective nature of sulfides leads to the growth of less-protective layers, as compared to that of oxides. In addition, the low eutectic temperatures (\(T_{\text{eutectic}}\)) in these metal/sulfide systems exacerbates the sulfidation problem (e.g., \(T_{\text{eutectic}} = 880^\circ\text{C}\) for cobalt/cobalt sulfide, \(985^\circ\text{C}\) for iron/iron sulfide, and \(645^\circ\text{C}\) for nickel/nickel sulfide). Thus, the sulfidation rates of these base metals are generally 4–6 orders of magnitude greater than their oxidation rates.

It has been reported that alloys developed for good oxidation resistance, such as the alloys described above, usually have poor sulfidation resistance. On the contrary, some refractory metals, such as Mo, Nb, and W exhibit very low sulfidation rates.\(^3,4\) In fact, the sulfidation rates of Mo and Nb have the same magnitude as the oxidation rate of Cr at the same temperatures, as shown in Fig. 1. The corrosion behavior of the base metals (Fe, Ni, and Co) with additions of either Mo or Nb in \(\text{H}_2/\text{H}_2\text{O}/\text{H}_2\text{S}\) mixed-gas environments has been studied in this laboratory.\(^5-10\) It has been shown that a certain reduction in the corrosion rates of the base metals could be achieved by alloying them with either Mo or Nb (up to 40 wt.% additions), even if the corrosion rates were still significantly higher than those of pure Mo or Nb. In the case of Fe–Nb,\(^5\) the scales formed on the alloys were duplex, consisting of an outer layer of iron sulfide and an inner complex layer of \(\text{Fe}_2\text{Nb}_2\text{S}_4\) (\(\text{FeNb}_2\text{S}_4\) or \(\text{FeNb}_3\text{S}_6\)) ternary sulfides, \(\text{FeS}\), and uncorroded \(\text{Fe}_2\text{Nb}\). The formation of iron sulfide is continuously favored due to rapid iron diffusion through the non-protective layer structure of the double sulfides. As a result, the corrosion rates of Fe–40Nb are not as low as the corrosion rates of pure Nb.