The Corrosion Behavior of Co–Mo Alloys in \( \text{H}_2-\text{H}_2\text{O-} \text{H}_2\text{S} \) Environments

C. C. Shing,* D. L. Douglass,* and F. Gesmundo†

Received August 30, 1991; revised October 21, 1991

The corrosion behavior of Co alloyed with up to 40 wt.\% Mo alloys was studied in \( \text{H}_2-\text{H}_2\text{O-} \text{H}_2\text{S} \) gas mixtures over the temperature range between 600°C and 900°C. The parabolic rate constants for corrosion decreased with increasing amounts of Mo. The compositions of all gas atmospheres fall in the sulfide(s) stability region of the ternary M–O–S phase diagrams at all temperatures investigated. All the corrosion scales were composed of sulfides, while no oxide was detected. The sulfide scales formed were duplex at all temperatures except at 900°C. The outer layer consisted primarily of cobalt sulfide, while the inner layer was complex and heterophase, the phases formed being highly composition dependent. \( \text{MoS}_2 \) predominated in the inner layer for all alloys. However, a metallic Mo layer was formed in the innermost layer of Co–40Mo. Activation energies were different for all alloys, increasing with increasing Mo content. Identical kinetics were observed for Co–30Mo corroded at 700–800°C. A Chevre phase \( \text{Co}_{1.62}\text{Mo}_6\text{S}_8 \) was present in scales formed on the samples exhibiting the temperature-independent kinetics. A possible model in which \( \text{Co}_{1.62}\text{Mo}_6\text{S}_8 \) forms preferentially in \( \text{H}_2 \)-containing mixed gas is suggested. Alloys corroded at 900°C formed a lamellar-structure scale which contained Co and \( \text{CoMo}_2\text{S}_4 \) layers perpendicular to the alloy surface. A eutectoid decomposition of an unknown Co–Mo sulfide may be responsible for the presence of the lamellar structure.

KEY WORDS: mixed gas; \( \text{Co}_{1.62}\text{Mo}_6\text{S}_8 \); lamellae; multilayered scale; sulfidation.

INTRODUCTION

The corrosion of conventional high-temperature alloys exposed to multi-oxidant environments is of considerable importance in many technical
processes, such as the petrochemical industry, the conversion of fossil fuels, and coal gasification. The gaseous atmospheres in a typical coal-gasification system possess low oxygen activities along with relatively high activities of sulfur, carbon, and nitrogen. It is well known that sulfidation causes the degradation of alloys much more rapidly than oxidation. At present, most high-temperature alloys contain sufficient amounts of Cr or Al to form compact, protective oxide scales. In practice, the degree of protection provided by an oxide scale depends on the stability of the constituent oxides with respect to the atmosphere and on the rapidity of sulfur diffusion through the scale. The protective aluminum or chromium oxides constitute efficient barriers to corrosion in oxygen-rich atmospheres, but the breakdown of these scales occurs eventually in sulfur-containing environments.

Numerous investigators have studied the effect of refractory-metal additions on the sulfidation behavior of the common base metals, Fe, Co, and Ni. The results have clearly demonstrated that beneficial effects do occur. Gleeson et al. have found that Mo contents up to 40% in Co–Mo alloys resulted in a progressive decrease of the sulfidation rate in 0.01 atm. of pure sulfur. The simultaneous sulfidation and oxidation of cobalt in SO2 or SO2/argon mixtures has also been studied extensively. In general, the scales consisted of a duplex oxide-sulfide mixture at low temperatures, while an innermost sulfide layer and an outermost oxide layer formed at high temperatures. The scale morphology changed with the SO2 pressure. Linear kinetics and breakaway kinetics were observed at 900°C where liquid sulfide formation occurred. Very slow reaction rates were found when a stable, single-phase oxide layer formed.

The aim of the present study was to investigate the effect of Mo on the corrosion behavior of Co in a mixed-oxidant gas. Corrosion tests were carried out in a H2–H2O–H2S gas mixture. The composition of the mixed gas used in this study corresponds to an oxygen pressure of 10−20 atm. and a sulfur pressure of 10−5 atm. at 850°C. This particular gas composition contains lower oxygen and higher sulfur pressures than those of a typical coal-gasification atmosphere. This combination generally leads to much more severe material degradation than oxidation or corrosion in other mixed oxidizing environments. The same gas composition was employed throughout the experiments regardless of the various test temperatures.

EXPERIMENTAL PROCEDURES

The alloys studied were Co–10, 20, 30, and 40 wt.% Mo. The starting materials were at least 99.8% pure. The alloys were arc-melted under a titanium-gettered atmosphere of high-purity argon to produce buttons. The buttons were flipped over and remelted at least five times in order to ensure