Oxidation of High-Chromium Ni–Cr Alloys*

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The oxidation of binary Ni–Cr alloys containing 44 and 50 wt. % Cr has been studied over a range of oxygen partial pressures at temperatures between 800 and 1100°C. The effects of cold work, surface preparation, and distribution of the Cr–rich second phase have been studied. The oxidation behavior is complex and cannot be described by a single model. The oxide grows by short-circuit diffusion as well as bulk transport through Cr₂O₃ scales. The scale-growth mechanism includes extensive metal–oxide separation requiring Cr vapor transport to the scale, compressive stresses within the oxide which result in scale bulging and cracking, and the formation of a second oxide layer which results in voids being incorporated into the scale. Any factor which reduces the oxide grain size, such as cold work, finer distribution of the Cr-rich α phase or reduced oxygen pressure, results in an increased oxidation rate of binary alloys because of an increased number of grain-boundary short-circuit diffusion paths.

KEY WORDS: nickel–chromium alloys; oxidation; high temperature; kinetics; mechanisms.

INTRODUCTION

Alloys which form protective scales of chromium oxide (Cr₂O₃) are generally superior to those which rely on aluminium oxide (Al₂O₃) scales in resisting simultaneous corrosion by sulfur and oxygen, particularly when

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liquid sulfate deposits are present on the alloy surface. The resistance of Ni–Cr alloys to attack by both sulfur dioxide and Na₂SO₄-induced hot corrosion has been shown to increase with increasing Cr concentration, particularly above 30 wt.%. The oxidation behavior of Ni–Cr alloys containing less than 40% Cr has been extensively investigated; however, the oxidation of the single-phase and two-phase alloys containing more than 40% Cr has received little study.

The oxidation rate of Ni–Cr alloys shows a maximum with increasing Cr concentration between 10 and 18% depending on temperature in the range 800 to 1200°C. The increased oxidation rate of nickel with additions of up to 10% Cr is explained in terms of an increased number of cation vacancies in the NiO scale due to doping with Cr ions. The scale on these dilute alloys consists of a layer of NiO with a small amount of Cr in solid solution and a porous inner layer of NiO which contains a dispersion of NiCr₂O₄ particles and is saturated with Cr. An internally oxidized zone containing particles of Cr₂O₃ forms below the scale. Above the Cr concentration giving the maximum rate the oxidation slows with increasing Cr concentration due to the formation of continuous layers of Cr₂O₃ or NiCr₂O₄. According to Giggins and Pettit Ni–Cr alloys containing more than 30% Cr form continuous Cr₂O₃ scales very early during the oxidation process and show oxidation rates comparable to those of pure chromium. External Cr₂O₃ formation on these alloys is accompanied by some internal oxidation of Cr. This can result from a steep Cr concentration profile in the alloy along with a flat oxygen gradient. The authors are not aware of published studies of the oxidation kinetics of alloys containing more than 40% Cr which may contain one or two phases depending on temperature and composition.

The oxidation of Cr₂O₃-forming alloys shows negative departures from parabolic kinetics, particularly at temperatures above 1000°C in flowing gases with high oxygen partial pressures. These departures have been attributed to weight losses resulting from the oxidation of Cr₂O₃ to the volatile species CrO₃. Several mathematical treatments for analyzing experimental rate data obtained under these conditions have been published.

The present paper is a comprehensive presentation of a study of the kinetics and mechanism of oxidation of high-chromium Ni–Cr alloys which

| Table I. Chemistries of Binary Ni–Cr Alloys (wt.%) |
|---|---|---|---|---|---|---|---|
| Alloy | Cr | C | O | S | N | Si | Mn | Fe |
| Ni–44Cr | 43.88 | 0.031 | 0.0378 | 0.005 | N.D. | 0.01 | 0.01 | 0.22 |
| Ni–50Cr | 50.15 | 0.021 | 0.0042 | 0.006 | 0.0099 | 0.01 | 0.01 | 0.22 |