The High-Temperature Oxidation Resistance of Co-Al Alloys*

G. N. Irving,† J. Stringer,† and D. P. Whittle†

Received January 8, 1975—Revised April 8, 1975

Most Ni- and Co-base alloys used for high-temperature service rely on the production of a compact, stable \( \text{Cr}_2\text{O}_3 \) scale for their oxidation resistance. However, as operating temperatures have risen above 900–950°C, the loss of \( \text{Cr}_2\text{O}_3 \) as the volatile \( \text{CrO}_3 \) has led to an inadequate life span of these alloys, particularly in rapidly flowing, turbulent gas streams. As a result of this, it has been necessary to examine the possibility of using \( \text{Al}_2\text{O}_3 \) as the protective scale. \( \text{Al}_2\text{O}_3 \) has a lower growth rate than \( \text{Cr}_2\text{O}_3 \), it is nonvolatile, and, unlike \( \text{Cr} \)-containing systems, it is less likely to form compound oxides such as spinels. In this study, the amount of Al which must be present in the Co-Al system to form a continuous layer of \( \text{Al}_2\text{O}_3 \) in the temperature range 800–1000°C has been determined. The quantity was found to rise from about 7–10 wt.% at 800°C to 10–13 wt.% at 900°C and 13 wt.% at 1000°C. Notice has also been taken of the abilities of the alumina-forming alloys to re-form a protective oxide in the event of spalling, blistering, or any other disruptions of the scale, and some “cyclic-oxidation” checks have been conducted on the Co13Al alloy at 900 and 1000°C.

KEY WORDS: cobalt; cobalt–aluminum alloys; oxidation; thermal cycling.

INTRODUCTION

Most Ni- and Co-base alloys used for high-temperature service rely on the production of a compact, stable \( \text{Cr}_2\text{O}_3 \) scale for their oxidation resistance. However, as operating temperatures have risen above 900–950°C, the

*This work has been partly supported by the Science Research Council and one of us (G.N.I.) wishes to thank them for the award of a Science Research Council Research Studentship.
†Department of Metallurgy and Materials Science, University of Liverpool, Liverpool, England.
loss of $\text{Cr}_2\text{O}_3$ as the volatile $\text{CrO}_3$ (Ref. 2) has led to an inadequate life span of these alloys, particularly in rapidly flowing, turbulent gas streams. As a result of this it has become necessary to examine the possibility of using $\text{Al}_2\text{O}_3$ as the protective scale. $\text{Al}_2\text{O}_3$ has a lower growth rate than $\text{Cr}_2\text{O}_3$, and is nonvolatile, and, unlike Cr-containing systems, it is less likely to form compound oxides such as spinels, the role of which has long been the subject of debate.\textsuperscript{3,4}

\[
\text{CoO} + \text{Cr}_2\text{O}_3 = \text{CoCr}_2\text{O}_4 \quad \Delta G^o = -11.2 \pm 0.6 \text{ kcal at } 1350^\circ\text{C} \quad (1)
\]

\[
\text{CoO} + \text{Al}_2\text{O}_3 = \text{CoAl}_2\text{O}_4 \quad \Delta G^o = -6.3 \pm 0.4 \text{ kcal at } 1350^\circ\text{C} \quad (2)
\]

The production of $\text{Al}_2\text{O}_3$ in the superalloys may be achieved by cladding alloys of the CoCrAlY type or by pack alumining the surface of the alloy.

In general, dilute alloys will not form a complete layer of the oxide of the addition, even though this may be the more stable product. However, as the concentration is increased a point will be reached at which a complete layer of the more stable product will be achieved, although this may be preceded by a prolonged period of nonsteady-state conditions. Wagner\textsuperscript{6} suggests that the critical concentration of the more reactive element, $N_B$, is given by

\[
N_B = \left(\frac{V}{Z_B M_O}\right)\left[\frac{\pi k_p^{1/2}}{D}\right]
\]

where $V$ is the molar volume of the alloy, $Z_B$ is the valence of the B atom, $M_O$ is the atomic weight of oxygen, $D$ is the diffusion coefficient of B in the alloy, and $k_p$ is the parabolic rate constant for the growth of the oxide of B on the alloy. Using the values of $D$ for the Co–Al and Ni–Al systems, at 1000°C, calculated by Green and Whittle\textsuperscript{7} and the $k_p$ value from Pettit's\textsuperscript{8} work on the Ni–Al system, $N_B$ can be estimated to be 0.025 for the Co–Al system and 0.008 for the Ni–Al system. In fact, the growth rate of $\text{Al}_2\text{O}_3$ is so slow that the calculation gives a wholly misleading result, since the practical oxidation behavior is determined by the initial nonsteady-state period.

Pettit\textsuperscript{8} has found that the oxidation behavior of Ni–Al alloys containing up to 25 wt. % Al in the temperature range 900–1300°C could be divided into three types of behavior:

I. In dilute alloys the Al oxidized internally giving an insufficient mole fraction of $\text{Al}_2\text{O}_3$ to cause the transition from internal to external oxidation. This results in a duplex scale of an outer layer of NiO and an inner layer of $\text{Al}_2\text{O}_3$ and NiAl\textsubscript{2}O\textsubscript{4} particles in a NiO matrix.