

## **Selection of an Alloy Composition in the Ternary Co–Cr–Al System for Oxidation Resistance**

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*The system of superimposing oxide maps over the ternary phase diagram in order to select oxidation resistant compositions has been used to select a Co–Cr–Al base alloy. It is suggested that a Co–10Cr–9Al alloy is suitable for the temperatures of 1100–1200°C and may be strengthened by the addition of rare earth oxides for dispersion hardening.*

### **INTRODUCTION**

In the development of superalloys for gas turbine engines, nickel-based alloys have proved to be superior to cobalt-based alloys up to 900°C, owing to their unique  $\gamma'$  strengthening process.<sup>1</sup> For higher temperatures where the  $\gamma'$  precipitates are not stable for long periods, dispersion hardening is required for strengthening purposes, and cobalt-based alloys may prove superior owing to their higher melting points and superior resistance to hot corrosion.<sup>2</sup> For the temperatures between 1000–1200°C, oxidation resistance should be provided by  $\text{Al}_2\text{O}_3$  or spinel scales<sup>3</sup> as  $\text{Cr}_2\text{O}_3$  scales are likely to be volatile, particularly in flowing gas streams.<sup>4</sup> For these reasons an attempt has been made to select an alloy composition in the Co–Cr–Al system, which will preferentially oxidize to  $\text{Al}_2\text{O}_3$  (Group 4).<sup>5</sup>

### **EXPERIMENTAL PROCEDURES AND RESULTS**

From the “oxide map” of the Co–Cr–Al systems,<sup>5</sup> the alloy Co–10 wt. %–Cr–9 wt. %Al was chosen as a suitable ternary composition for the production of a protective scale. Specimens  $0.17 \times 2.0 \times 2.5$  cm were cut from a vacuum-

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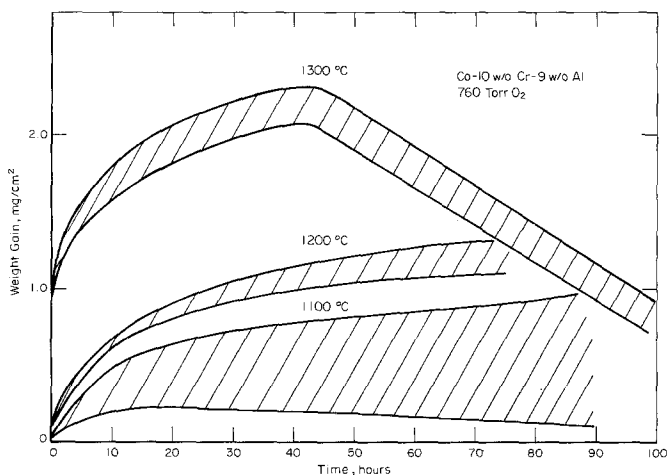


Fig. 1. Weight changes recorded for Co-10 wt.%Cr-9 wt.%Al alloy at 1100, 1200, and 1300°C at 760 Torr O<sub>2</sub> pressure.

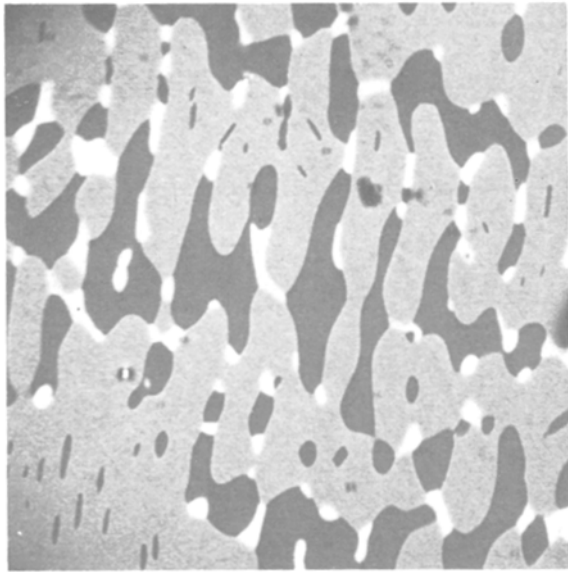
melted, hot-rolled strip. They were prepared and oxidized as previously described<sup>6</sup> and weight changes obtained during oxidation at 1100 to 1300°C in 760 Torr oxygen (Fig. 1). The rate of oxidation was found to be independent of oxygen pressure in the range 10 to 760 Torr. Evaporation of cobalt-bearing compounds was evident from the weight change measurements, and cobalt-bearing deposits could be found on the wall of the reaction chamber. At 1300°C the evaporation rate was high and its overriding effect on weight gain is shown after 40 hr in Fig. 1.

On cooling, all scales spalled from the specimens, leaving a very thin adherent oxide on the specimen. Both scales were analyzed by X-ray diffraction. The adherent oxide adjacent to the alloy was identified as Al<sub>2</sub>O<sub>3</sub>. The spalled scales were found to be composed primarily of CoAl<sub>2</sub>O<sub>4</sub> spinel with minor amounts of Al<sub>2</sub>O<sub>3</sub>, and traces of another unidentified spinel ( $a_0 = 8.22$ ) and Cr<sub>2</sub>O<sub>3</sub> were also present. The spalling of scales during cooling makes the oxidation resistance of this alloy unsatisfactory.

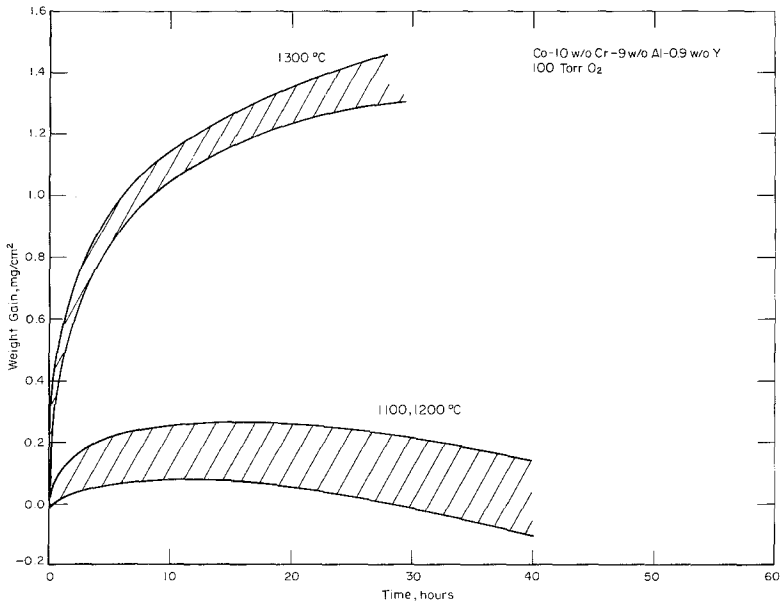
Recently, it has been reported that small additions of yttrium metal promote scale adherence. Hence, some of this element was added to the basic Co-10Cr-9Al alloy by remelting a portion of the original ingot with yttrium. This was performed in an arc furnace in an argon atmosphere. Chemical analysis of the button showed that it contained 9.76 wt.%Cr, 8.67 wt.%Al, 0.9 wt.%Y, and the balance cobalt. Metallographic examination of a section of the button (Fig. 2) showed that far too much yttrium had been added and an intermetallic compound of cobalt and yttrium (bright areas in Fig. 2) was formed. It has since been reported that 0.2-0.3% is sufficient to promote

scale adherence without the precipitation of intermetallic compounds. However, as the oxidation studies do not appear to be greatly affected by variations in yttrium between 0.1% to 0.9%, this alloy was still suitable for the establishment of the effects of yttrium on oxidation.

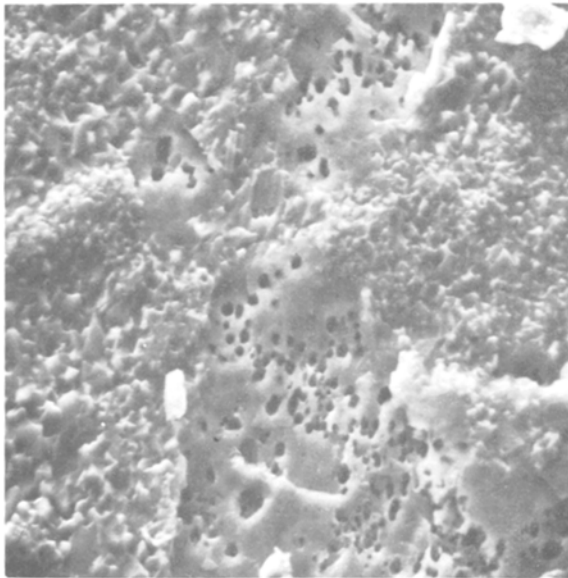
Specimens  $0.3 \times 0.1 \times 2.5$  cm were cut from the button without further processing, metallographically polished and oxidized in the same manner as the previous specimens. The kinetic data obtained at 1100°C, 1200°C, and 1300°C at 100 Torr  $O_2$  pressure are shown in Fig. 3. At 1100°C there was a slight loss in weight after the initial increase followed by a weight gain after 60 hr. The surface of the scale was ultramarine blue and adhered to the alloy surface. Some evaporation from the surface of the scale had obviously taken place, as is shown in Fig. 4. x-Ray diffraction analyses of scales taken from the specimen showed that the scale was predominantly composed of  $CoAl_2O_4$ ,  $Al_2O_3$ , with only a trace of  $Cr_2O_3$ . A section through the scale (Fig. 5) shows that it consists of two distinct layers, and microprobe analysis confirmed that the outer blue layer was  $CoAl_2O_4$  and the inner layer  $Al_2O_3$ . Yttrium was not detected in either oxide and no chromium was detected in the outer spinel layer. There was also some evidence of cobalt losses at the outer surface of the spinel layer.



**Fig. 2.** Microstructure of the Co-10wt. %Cr-9 wt. %Al-1 wt. %Y alloy before oxidation showing the  $\alpha + \beta$  phases together with the  $Co_3Y$  intermetallic phase ( $\times 500$  S.E.M.).



**Fig. 3.** Weight changes recorded for Co-10 wt.%Cr-9 wt.%Al-1 wt.%Y at 1100, 1200, and 1300°C at 100 Torr O<sub>2</sub> pressure.



**Fig. 4.** Photomicrograph of the surface of a Co-Cr-Al-Y alloy after oxidation at 1200°C for 40 hr at 100 Torr oxygen pressure showing on the center of the micrograph an area from which evaporation has taken place ( $\times 1000$  S.E.M.).

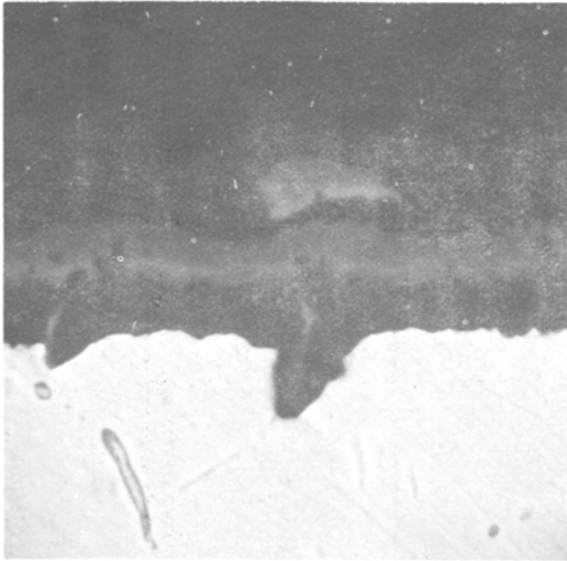


Fig. 5. Photomicrograph of a section through a specimen of Co-Cr-Al-Y alloy oxidized at 1100°C at 100 Torr oxygen pressure for 40 hr showing the outer  $\text{CoAl}_2\text{O}_4$  spinel and inner  $\text{Al}_2\text{O}_3$  layer. The area of deeper penetration is associated with the presence of a grain boundary  $\text{Co}_3\text{Y}$  intermetallic ( $\times 2000$  S.E.M.).

At 1200°C the specimen again showed small weight gains and within the error of the experiments they were similar to those obtained at 1100°C. At 1300°C the weight gain had markedly increased but, as with all specimens, the weight gain was approximately half that obtained with the alloy without the yttrium addition. The scale morphology was not dependent on the temperature and oxygen pressure of oxidation.

In order to examine the effect of the aluminum addition on the melting point of the alloy, the melting point was measured and showed that this composition melted at  $1485 \pm 5^\circ\text{C}$ ; thus lowering the melting point only  $15^\circ\text{C}$  below that of pure cobalt.

Thermal cycling experiments were carried out in air at 1100°C on both yttrium-containing and yttrium-free alloys. The first cooling took place after 50 hr, and the specimens were held at room temperature for about 5 min in each hour.

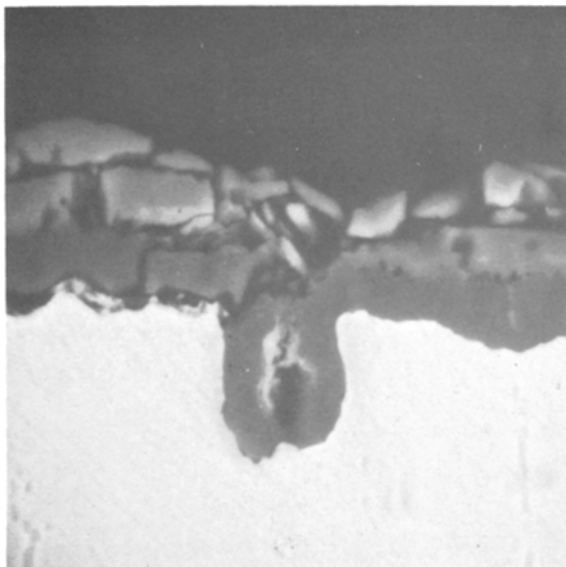
Spalling occurred each time the yttrium-free alloy was cooled, and the nature of the spalled scale changed with each cycle. The first layer was a  $\text{CoAl}_2\text{O}_4$  scale, which fell off in one flake. Some alumina was also found in the scale as well as some chromium-containing spinel. The weight gains observed during the subsequent oxidation were relatively small, but the spalled scale

contained a considerable quantity of CoO and a Co (CrAl)<sub>2</sub>O<sub>4</sub> spinel, with only traces of alumina. On cooling, these scales again spalled and subsequent oxidation runs were accompanied by an increase in oxidation rate, while the spalled scale consisted mainly of CoO and the mixed spinel.

The yttrium-containing alloy did not spall during cycling and the weight changes were relatively unaffected by the cooling and reheating procedures, but the spinel layer was shattered by this procedure (Fig. 6). This layer was easily scraped off, leaving the Al<sub>2</sub>O<sub>3</sub> scale adherent to the alloy. A specimen from which the outer CoAl<sub>2</sub>O<sub>4</sub> layer was carefully removed was reoxidized, and no appreciable weight gain was observed; furthermore, the CoAl<sub>2</sub>O<sub>4</sub> outer layer did not re-form.

### DISCUSSION

The oxide map previously developed<sup>5</sup> was used to select a ternary composition in this Co-Cr-Al system which would prove to be oxidation resistant at the temperature for which the map was drawn. It was assumed that at these temperatures a Cr<sub>2</sub>O<sub>3</sub> scale would prove to be unsatisfactory due to CrO<sub>3</sub> evaporation.<sup>4</sup> The composition therefore was aimed at selectively producing CoAl<sub>2</sub>O<sub>4</sub> spinel or Al<sub>2</sub>O<sub>3</sub> scale.



**Fig. 6.** Photomicrograph of a section through a Co-Cr-Al-Y alloy oxidized at 1100°C at 100 Torr oxygen pressure showing the shattering of the outer spinel layer caused by thermal cycling ( $\times 2000$  S.E.M.).

The results show that for this composition both  $\text{Al}_2\text{O}_3$  and the  $\text{CoAl}_2\text{O}_4$  spinel were formed. It appeared, however, that the spinel formation is a secondary reaction superimposed on the rate-controlling process of  $\text{Al}_2\text{O}_3$  formation. Evidence to support the conclusion that the  $\text{Al}_2\text{O}_3$  layer controls the oxidation process is that where the outer spinel layer was removed from the oxidized yttrium-bearing alloy, subsequent oxidation rate was not altered and the spinel did not re-form. The increased oxidation rate of the yttrium-free alloy after cycling can be explained by the fact that after spalling some areas of the surface of the alloy are left scale free.  $\text{Al}_2\text{O}_3$  was identified in the spalled scale and over some areas of the specimen surface. Where the  $\text{Al}_2\text{O}_3$  was removed, cobalt was oxidized in the aluminum-depleted surface. The overall oxidation rate was limited by the partial exposure of the surface and the presence of the spinel-forming elements aluminum and chromium. After spalling, the mode of oxidation is one described<sup>5</sup> as Group 2 oxidation.

The formation of the outer  $\text{CoAl}_2\text{O}_4$  layer during the first oxidation cycle is probably the result of a reaction between  $\text{CoO}$  and  $\text{Al}_2\text{O}_3$ ; the  $\text{CoO}$  being formed during the initial stages before a continuous  $\text{Al}_2\text{O}_3$  layer fully covered the surface. It is unlikely that cobalt diffused through the  $\text{Al}_2\text{O}_3$  to form the spinel as there was no spinel formed on the cycled Co–Cr–Al–Y specimen from which the spinel had been removed.

There are some indications that the yttrium-bearing alloys oxidize at a slower rate than the yttrium-free alloys; however, these data are not conclusive and may be affected by the presence of evaporation. Furthermore, this improvement is only marginal. The most beneficial effect of yttrium is the imparting of adherence to the scales. The mechanism by which this is achieved is not yet understood. From thermodynamic considerations it would be expected that yttrium will internally oxidize, forming under the  $\text{Al}_2\text{O}_3$  layer a dispersion of  $\text{Y}_2\text{O}_3$ . This has not been observed experimentally, but it could be due to the fineness of the particles.

If much internal oxidation occurs, it is possible that adherence may be imparted by a dispersion of  $\text{Y}_2\text{O}_3$  in the alloy, thus providing both adherence and dispersion strengthening. It may be noted in this context that chromium scales formed on thoria-dispersed alloys have improved adherence properties relative to the unthoriated alloy.<sup>4</sup>

## CONCLUSIONS

In designing cobalt alloys for high temperature usage, it is necessary to first select a basic composition that is oxidation resistant. In this case, the Co–10Cr–9Al ternary would appear to be suitable. The main strengthening mechanism for alloys in the temperature range 1000–1200°C seems to be dispersion hardening and in view of the need to add rare earth metals to

promote scale adherence, it would seem that the addition of a dispersion of rare earth oxide to this basic composition would be an excellent basis on which to develop a cobalt alloy operable at temperatures from 1000 to 1200°C.

### ACKNOWLEDGMENTS

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