Cobalt-based Superalloys for Applications in Gas Turbines*

D. COUTSOURADIS, A. DAVIN and M. LAMBERIGTS
Centre de Recherches Métallurgiques, Liège (Belgium)
(Received April 11, 1986)

ABSTRACT

Cobalt-based alloys have been in use for several decades in the manufacturing of various components such as vanes or combustion chambers in gas turbines (both the industrial type and aeroengines). They can be implemented as wrought or as precision-cast parts. Their design is aimed primarily at improving elevated temperature strength by use of solid-solution- and carbide-strengthening mechanisms. Such mechanisms must tolerate substantial additions of chromium (above 20 wt.%) in order to obtain a satisfactory oxidation resistance and a good hot corrosion resistance. The design of cobalt superalloys, which is aimed at an enhancement of both their oxidation resistance and their hot corrosion resistance, has received considerable impetus recently, especially since the advent of overlay coating techniques and the extensive studies which have been undertaken to elucidate the hot corrosion mechanisms and the effect of alloying elements. Some of the features of cobalt superalloys mentioned above are reviewed on the basis of work at the Centre de Recherches Métallurgiques and elsewhere.

1. INTRODUCTION

The developments in the physical metallurgy of cobalt- and, in particular, nickel-based superalloys during the last four decades have permitted the design of increasingly efficient gas turbines. These materials have been designed primarily to withstand higher stresses at increasing service temperatures. However, because of the variety of aggressive environments encountered, the attention of materials scientists has also been focused on the problem of degradation from oxidation and hot corrosion. In this case the design trend has been the development of alloys exhibiting a high intrinsic corrosion resistance as well as the development of better coating techniques. The coating process and/or the formation of a layer of corrosion products introduces additional constraints in the design of a particular component because of the surface or interface phenomena and of their evolution during service. The effects of coatings and of the environment on the mechanical properties of the substrate and thus on the performance of the components have become subjects of great interest. The wealth of investigations along these lines, as reported in the proceedings of various conferences, is indicative of the challenge to metallurgists set by new advanced gas turbines or, more generally, by more efficient energy conversion systems using fossil fuels [1-7].

Because of the outstanding strengthening mechanisms of nickel-based alloys, these alloys have been the focal point for the development of improved materials for gas turbines. Cobalt has been a key alloying element in nickel-based superalloys, giving rise to alloying systems of major technological importance, for applications involving elevated temperatures, hot corrosion, wear etc. It is not surprising therefore that the use of cobalt in superalloys was as high as 36% of the total consumption of cobalt in the U.S.A. in 1983 [8].

The purpose of this paper is to review the features of cobalt-based alloys for gas turbine applications both as a substrate and as a coating especially in regard to strengthening and behaviour in aggressive environments.

2. STRENGTHENING MECHANISMS

The effects of cobalt on the mechanical properties of nickel-based alloys have received increased attention in recent years spurred on by the 1978-1980 increase in the world price of cobalt [8-11]. Although the effects are subtle and dependent on the particular alloy considered, it appears that cobalt has a major effect especially on creep strength.

Table 1 shows the composition of current cast or wrought cobalt-based alloys and Table 2 summarizes their main features and assets. The effects of alloying elements on the performance features of cobalt alloys are outlined in Table 3.

In the wrought alloys HA-25 and HA-188 the main strengthening mechanism is solid solution hardening through the addition of chromium, tungsten and nickel. In pure cobalt the stable allotropic modification below 427 °C is the close-packed hexagonal form [12]. Nickel stabilizes the f.c.c. phase whereas chromium and tungsten (or the refractory metals) stabilize the hexagonal form. The resultant solid solution composition controls the stacking fault energy of the alloy and hence the creep strength.

In cast cobalt alloys, a carbon content in the range from 0.25 to 1 wt.% also causes carbide strengthening in addition to the solid solution hardening in the matrix. The carbide network formed during solidification is quite stable and is essential for elevated temperature strength. Destruction of the carbide network by hot working, in alloy X-40 and MAR-M 509 for example, increases the intermediate temperature tensile properties but decreases the elevated temperature creep strength [13]. The carbide network at or near grain boundaries prevents grain boundary sliding and provides strengthening in alloys such as MAR-M 509 by carbide fibre reinforcement at the boundary area. Carbides also play an important role in oxidation as will be mentioned in Section 3.

Hardening of cobalt alloys by means of intermetallic phases of the γ' type has been demonstrated in the Co–Cr–Ti and Co–Cr–Ta systems [8, 14]. The instability at high temperatures of the γ' phases formed in these systems prevented them from achieving commercial status. However, the role of intermetallic phases in cobalt alloys is likely to attract attention again because of their occurrence in coating systems and because of the importance of the "free-standing" properties of overlay coatings.

### Table 1
Compositions of cast and wrought cobalt-based alloys

<table>
<thead>
<tr>
<th>Alloy</th>
<th>Amount (wt.% of the following elements)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>C</td>
</tr>
<tr>
<td>X-40</td>
<td>0.5</td>
</tr>
<tr>
<td>X-45</td>
<td>0.75</td>
</tr>
<tr>
<td>FSX-414</td>
<td>0.35</td>
</tr>
<tr>
<td>FSX-418</td>
<td>0.35</td>
</tr>
<tr>
<td>MAR-M 302</td>
<td>0.85</td>
</tr>
<tr>
<td>MAR-M 609</td>
<td>0.60</td>
</tr>
<tr>
<td>WI-52</td>
<td>0.45</td>
</tr>
<tr>
<td>AirResist 13</td>
<td>0.45</td>
</tr>
<tr>
<td>HA-25</td>
<td>0.1</td>
</tr>
</tbody>
</table>

### Table 2
Summary of the properties of cobalt-based alloys

<table>
<thead>
<tr>
<th>Property</th>
<th>Alloy Type</th>
</tr>
</thead>
<tbody>
<tr>
<td>Solid solution strengthening</td>
<td></td>
</tr>
<tr>
<td>Carbide strengthening: eutectic M₇C₃; grain boundary M₇C₃; fine M₂₃C₆; MC carbide (in Ta-containing alloys)</td>
<td></td>
</tr>
<tr>
<td>High creep strength at high temperatures</td>
<td></td>
</tr>
<tr>
<td>High thermal fatigue resistance</td>
<td></td>
</tr>
<tr>
<td>Good oxidation resistance</td>
<td></td>
</tr>
<tr>
<td>Excellent hot corrosion resistance</td>
<td></td>
</tr>
</tbody>
</table>
### TABLE 3

Effect of alloying elements in cobalt-based alloys

<table>
<thead>
<tr>
<th>Element or compound</th>
<th>Effects</th>
</tr>
</thead>
<tbody>
<tr>
<td>Cr</td>
<td>Oxidation and sulfidation resistance Carbide (M(_7)C(<em>3) and M(</em>{23})C(_6)) and intermetallic compound ((\sigma)) former</td>
</tr>
<tr>
<td>C</td>
<td>Carbide former (MC, M(<em>6)C, M(</em>{23})C(_6), M(_7)C(_3))</td>
</tr>
<tr>
<td>Mo, W</td>
<td>Solid solution strengtheners Carbide former (M(_6)C, MC) Intermetallic compound formers (M(_3)X, M(_2)X)</td>
</tr>
<tr>
<td>Al</td>
<td>Oxidation resistance Intermetallic compound former ((\gamma), CoAl)</td>
</tr>
<tr>
<td>Ta, Nb, Ti</td>
<td>Solid solution strengtheners (Ta, Nb) Carbide formers (MC) Intermetallic compound formers ((\gamma), M(_3)X, M(_2)X)</td>
</tr>
<tr>
<td>Ni</td>
<td>Stabilize the f.c.c. matrix Intermetallic compound former ((\gamma), M(_3)X, M(_2)X)</td>
</tr>
<tr>
<td>B, Zr</td>
<td>Increases stress rupture Boride (B) and carbide (ZrC) formers</td>
</tr>
<tr>
<td>Y, La</td>
<td>Increases oxidation resistance</td>
</tr>
<tr>
<td>Stable oxides:</td>
<td>Dispersion hardening ThO(_2), Y(_2)O(_3), Al(_2)O(_3) etc.</td>
</tr>
</tbody>
</table>

An additional general feature of cobalt alloys is their wear resistance used not only in a number of commercial Co–Cr–W–C alloys but also in cobalt-based alloys for gas turbines [8]. Wear resistance is controlled, among other factors, by the work-hardening behaviour of cobalt-based solid solutions and their tendency to transform from an f.c.c. to an h.c.p. structure [12].

3. OXIDATION AND HOT CORROSION BEHAVIOUR

The effect of cobalt on the oxidation resistance and hot corrosion resistance of nickel alloys should be expected to be neutral because of the predominant effect of other alloying elements. However, in the alloys Waspaloy and Udimet 700, the reduction of cobalt increased the oxidation resistance at temperatures above 900 °C. In these alloys the chromium-to-aluminium ratio (on an atomic basis) is higher than unity so that the oxides formed consist of Cr\(_2\)O\(_3\) or MCr\(_2\)O\(_4\) spinels and NiO. The latter leads to excessive spalling and rapid failure. Cobalt seems to enhance an earlier formation of NiO and thus increased attack. In the alloy MAR-M 247 in which the chromium-to-aluminium ratio is less than unity, it was found that cobalt did not affect the oxidation behaviour. In this case the oxide layers consisted of Al\(_2\)O\(_3\) or MA1\(_2\)O\(_4\) spinel and subsequent formation of NiO [11]. The hot corrosion behaviour at 900 °C of Udimet 700 and MAR-M 247 was improved by reducing their cobalt content but the mechanism for this effect was not further analysed [11].

It is apparent that in nickel alloys the principal rationale for adding cobalt is based on mechanical properties or phase stability rather than on oxidation resistance or hot corrosion resistance. These properties are controlled by the overall design of the alloy in which other elements such as chromium and aluminium play the overwhelming role.

Examination of the compositions of cobalt alloys in Table 1 shows that for most of these alloys the major alloying elements used for control of oxidation and hot corrosion behaviour is chromium. Apparently, only one alloy, namely AlResist 13, was designed bearing in mind improvement of the oxidation resistance through additions of aluminium [15].

As far as oxidation behaviour is concerned, Fig. 1 shows the self-diffusion of cations in various oxides [10], which is related to the parabolic rate constant for the growth of various oxide barriers [16]. This figure supports the observation of lower oxidation rates for pure nickel compared with that for cobalt and the fact that Co–Cr alloys are equivalent or even slightly more oxidation resistant than Ni–Cr alloys under conditions leading to the formation of Cr\(_2\)O\(_3\) or MCr\(_2\)O\(_4\) spinel barriers. The low self-diffusion coefficients of silicon and aluminium in their oxides justify the interest in forming SiO\(_2\) or Al\(_2\)O\(_3\) scales. SiO\(_2\) barriers are of current interest in coatings whereas Al\(_2\)O\(_3\) scales are at present impor-
tant in all nickel-based superalloys and in virtually all coating systems.

It should be recalled here that pure CoO is a metal-deficient semiconductor (p type) and that small additions of the higher valency element chromium increase the oxidation rate [16, 17]. Nickel behaves similarly [18]. It is only for chromium contents higher than 4-5 wt.% that the oxidation resistance is improved though the formation of continuous films of Cr$_2$O$_3$ or of MCr$_2$O$_4$ spinels.

Aluminium additions also enhance the oxidation resistance of cobalt and nickel through the formation of Al$_2$O$_3$ or MAI$_2$O$_4$. As stated before, aluminium additions are not frequent in commercial cobalt alloys but are always present in the M-Cr-Al type of coatings.

Simultaneous additions of chromium and aluminium enhance the oxidation resistance of cobalt through the formation of an inner Al$_2$O$_3$ layer adjacent to the metal and an outer layer of Cr$_2$O$_3$ [18]. The formation of a stable Al$_2$O$_3$ layer occurs only if the aluminium content exceeds a minimum value below which internal oxidation is observed.

Tantalum additions improve the oxidation resistance of Co-Cr alloys. The addition of tantalum to Co-30Cr alloy (where the content is in approximate weight per cent) increases the oxidation resistance and also suppresses the breakaway phenomenon occurring at temperatures higher than 1150 °C. During the oxidation process, tantalum becomes enriched in the chromium-rich oxide layer adjacent to the metal while it is absent from the CoO external layer [18]. In commercial alloys the good oxidation behaviour of the alloys MAR-M 509 and MAR-M 302 compared with that of WI-52 has been attributed to their tantalum contents [19].

Molybdenum and niobium additions to Co-Cr alloys have a deleterious effect on their oxidation resistance. This is especially evident in Co-30Cr alloy where an addition of 3 wt.% Mo results in an accelerated attack at temperatures equal to or higher than 1200 °C [20]. The deleterious effect of molybdenum is due to the formation of the low melting point oxide CoMoO$_4$. Tungsten additions to Co-10Cr or Co-30Cr alloys were shown to be slightly beneficial or neutral. Although molybdenum is not currently used as an alloying element in cobalt-based superalloys, tungsten is used for solid-solution- and carbide-strengthening purposes and as such does not contribute much to the oxidation resistance.

Niobium is not a common alloying element in most of the current cobalt superalloys except in the alloy WI-52.

Rare earth additions in small amounts are known to enhance adherence of oxidation scales in superalloys especially under cyclic conditions. In fact, additions of cerium or yttrium to Co-10Cr and Co-30Cr alloys were shown to be neutral under conditions which did not involve any cycling during oxidation [21]. None the less the reason for the addition of rare earths, such as lanthanum in HA-188 or yttrium in FSX-418, to alloys is so that their effects in preventing oxide spallation can be utilized.

The sulphidation behaviour of cobalt in sulphur vapour or in H$_2$S [22] obeys a parabolic law, the rate-controlling step being the outward diffusion of the cobalt ions. The reaction rates are appreciably lower than those determined for nickel or iron. The addition of chromium leads to a drastic decrease in the sulphidation rate in H$_2$S. From a large number of addition elements, only aluminium was shown to improve the sulphidation kinetics of Co-Cr alloys in H$_2$S.
The role of chromium in combating severe sulphidation has been evidenced also in Ni–Cr alloys in which the corrosion rate for chromium contents lower than 35 wt.% is appreciably higher than in Co–Cr alloys of the same chromium content; for a chromium content of 35 wt.% and higher the corrosion rates of the two systems are similar [22]. This behaviour is often ascribed to the fact that the nickel–Ni₃S₂ eutectic melts as 645 °C whereas the cobalt–Co₄S₃ eutectic melts at 880 °C. Although such a simple explanation may be valid under pure sulphidation conditions, it is apparent that it does not take into account the complex phenomena occurring in hot corrosion [23]. In general, commercial cobalt alloys contain chromium content levels of 20–30 wt.% whereas nickel alloys have only moderate levels, generally lower than 15 wt.%. Alloys FSX-414 and FSX-418 were specifically designed with high chromium levels to withstand sulphidation.

As regards hot corrosion, it is beyond the scope of this paper to proceed to any extent with a review of the subject which is the object of considerable research work. From the three main theories, i.e. sulphidation, fluxing and pseudoscale formation, it appears that the fluxing theory accounts best for the corrosion pattern observed in actual service [16]. Type I corrosion can be distinguished as occurring at high temperatures and is characterized by outer porous oxide layers with an intermediate layer of mixed unreacted metal and oxide, beneath which internal sulphidation occurs. Type I corrosion is further subdivided into acidic and basic fluxing, depending on the composition of the atmosphere and the reactions taking place in the layer of molten Na₂SO₄ base salts.

Type II corrosion occurs at lower temperatures and is a special case of acidic fluxing. It is characterized by the formation of mixed oxide–sulphide scales and by pitting.

Under hot corrosion conditions, simulated in a burner rig, again chromium is the main element providing enhanced resistance for cobalt alloys. The corrosion rate was higher at 800 °C than at 900 °C while at 1000 °C the corrosion rate is similar to that observed in oxidation. Also, chromium, aluminium, tantalum and yttrium were shown to exert a slight beneficial effect. In contrast, molybdenum and tungsten have a deleterious effect [18, 21].

Evidence of low temperature hot corrosion attack on a Co–Cr–Al–Y coating at temperatures below the melting point of Na₂SO₄ (884 °C) prompted a detailed investigation of Co–Cr, Co–Al and Co–Cr–Al alloys [24] subjected to SO₂–SO₃ atmospheres after coating with Na₂SO₄ at 650 and 750 °C. Co–Cr alloys suffered pitting attack which was more severe for Co–30Cr than for Co–20Cr. Co–Al alloys suffered broad frontal attack rather than pitting. The mechanism proposed for this attack [25] involves the formation of the low melting (melting point, 565 °C) Na₂SO₄–CoSO₄ eutectic. On the basis of data on cobalt-free nickel alloys, it was conjectured that these alloys would be less prone to this type of attack because the Na₂SO₄–NiSO₄ eutectic melts at a higher temperature (670 °C). Furthermore the Co³⁺–Co²⁺ exchange reaction proposed for cobalt transport would be inoperative in nickel-based alloys because, reportedly, there are no known Ni³⁺ compounds.

Although the temperature range is not the same, the improvement in the hot corrosion resistance of Udimet 700 and MAR-M 247 when their cobalt content was reduced [11] might be related to the mechanism proposed above.

The formation of the deleterious Na₂SO₄–CoSO₄ eutectic was shown to be prevented by formation of Cr₂O₃ or CoCr₂O₄ in Co–Cr alloys containing high contents of chromium (30–40 wt.%) [26]. Co–40Cr alloys with additions of silicon, yttrium or hafnium were said to exhibit at 750 °C a resistance an order of magnitude superior to those of the Co–20 and 30Cr–6–12Al–Y alloys and, at higher temperatures, a resistance which is equivalent to or slightly inferior than those of Co–Cr–Al–Y alloys [26].

4. COATINGS

Coating technology, although limited for a long time to essentially aluminizing by various chemical vapour deposition and pack cementation processes, has evolved during the last decade or so into a new area since the advent of overlay coating techniques. Among these, physical vapour deposition (PVD) (electron beam evaporation) and plasma spraying (especially low pressure plasma spraying (LPPS)) have already achieved or are likely
to reach industrial prominence. In these developments, cobalt-based alloys play an important role.

Aluminized coatings were applied with minor modification of the technique to both nickel-based and cobalt-based alloys although, for the latter, low activity (high temperature) processes are preferred [27]. As regards the aluminizing of nickel-based alloys, it has been shown [28] that cobalt in the alloy helps in the development of a pore-free coating at the chromium-rich interface between the substrate and the coating. The same favourable effect was shown to be obtained if prior to aluminization of a cobalt-free alloy a thin cobalt coating (2–25 μm) was deposited by PVD or sputtering. This technique proved helpful in aluminizing TD-NiCr by prior PVD deposition of an Ni-10Co-20Cr alloy. Alloy development for overlay coatings is active because the independence from the substrate allows more freedom for alloy selection.

When using the PVD technique, an obvious limitation is the inability to incorporate low vapour pressure elements into the coating from the melt. Thus, although tantalum appeared to be beneficial to the hot corrosion of Co-Cr alloys as mentioned above, complex Co-Cr-Al-Ta-Y alloys could not be vacuum vaporized because tantalum remained in the melt. Yttrium, however, was shown to reach the exact desired content in the coating (about 0.2 wt.%) by using an alloy containing 18 wt.% Y on the top of the rod electrode [29]. Further studies [30] showed that, by adapting the composition of the top button melt in the PVD coating, it was possible to reach the required levels in the coating for elements such as silicon, titanium and zirconium, in addition to yttrium. Figure 2 shows the relationship between the molten metal composition and the vapour composition for these elements.

Active elements such as yttrium in Co-Cr-Al alloys are known to exert a beneficial effect on the scale adherence by several mechanisms [17] among which is the formation of pegs at the oxide-substrate interface. Thus, in a study of Co–Cr–Al–X coatings produced by PVD, it was shown that titanium and silicon did not result in the formation of pegs [31] although these elements were shown on cast M-Cr-Al-Y alloys to promote the formation of tenacious Al₂O₃ scales showing little spalling [32]. The addition of zirconium, hafnium and yttrium to Co-Cr-Al-Y coatings was shown to result after oxidation in the formation of pegs of different types [31]. Furthermore, it was shown that pegs grow along the α–β interfaces in the coating and that anchoring through the pegs is effective in the highly textured PVD coatings but less so in coatings produced by LPPS [33].

In the development of overlay coatings, hot corrosion or oxidation resistance has been naturally the prime criterion. Very soon, however, it was recognized that the mechanical properties of M-Cr-Al-Y coatings and especially ductility were important for the overall
performance of the substrate-coating system. Furthermore, the influence of the coating on the mechanical properties of the substrate material is being studied extensively [2, 27].

As an illustration of these, Fig. 3 shows the effect of temperature on the strain to cracking of a Co–29Cr–6Al–0.1Y coating on IN-738 obtained by LPPS; this alloy had a ductile-to-brittle transition temperature at about 650 °C [34].

Figure 4 shows the “free-standing” mechanical properties of the same coating as a function of temperature. It may be seen that the γ′-β (CoAl) fine structure coating develops quite a high strength at low temperatures and that at temperatures around 1000 °C it exhibits an almost superplastic behaviour because of its fine structure [34].

There is no doubt that future work on the development of coating systems will take into account the importance of their mechanical properties with the objective of maximizing the corrosion resistance of the coating, while matching its mechanical properties to those of the substrate and providing adherent substrate-coating and coating-scale interfaces.

Overlay coatings of the M–Cr–Al–Y type are being extensively considered as intermediate layers for thermal barrier coatings. Also, overlay coatings have been studied in combination with aluminizing. For example, the application by sputtering of a Co–Cr–Al–Y layer on top of an aluminized coating improved the hot corrosion resistance of the system considerably [29]. Figure 5 shows the microstructure of such a composite coating.
Further applications of alloys initially developed as coatings include their use as brazing alloys. For example the S-57 alloy (Co-25Cr-10Ni-5Ta-3Al-0.5Y) has been modified with additions of silicon or boron and is now available as a brazing alloy [35] used in various applications including repair by diffusion-brazing techniques of damaged gas turbine components [36].

ACKNOWLEDGMENT

The research was carried out under the auspices of Institut pour l’Encouragement de la Recherche Scientifique dans l’Industrie et l’Agriculture.

REFERENCES

8 J. D. Donaldson and S. J. Clark, Cobalt in Superalloys, Cobalt Development Institute, London, 1985.
12 W. Betteridge, Cobalt and its Alloys, Ellis Horwood, Chichester, West Sussex, 1982.
16 P. C. Patnaik, High temperature oxidation and hot corrosion of nickel and cobalt based superalloys, Rep. WRC 25075, October 1985 (National Research Council, Ottawa, Canada, Grant NPE-AN-33).
19 A. Beltran, Cobalt, 46 (1971) 8-14.
29 A. Davin and D. Coutouradis, Hot corrosion
resistant coating prepared by sputtering, Proc. 8th Int. Conf. on Vacuum Metallurgy, September 30-October 4, 1985, Linz.


