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To cite this article: D Mukherji and J Rösler 2010 J. Phys.: Conf. Ser. 240 012066

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Co-Re-based alloys for high temperature applications: Design considerations and strengthening mechanisms

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Abstract. Cobalt-Rhenium base alloys are being developed for applications at temperatures beyond Ni-base superalloys. The high melting refractory element Re readily dissolves in Co and thereby changes the character of a Co-based alloy to a high melting point material. So far Co-Re system has not been investigated from the point of view of strengthening and oxidation and therefore different possibilities of strengthening mechanisms have been explored for our alloy development. Cr, a common element for oxidation resistance in many systems, is added along with Si in Co-Re alloys to improve oxidation behaviour at high temperatures.

1. Introduction
Ni-base superalloys are the dominant material class for gas turbine applications. However, the temperature capability of superalloys is limited by the possibility to raise further their melting point (which is around 1300° – 1400°C). There is an urgent need for the development of alloys for temperatures beyond the application range of Ni-superalloys. New Co-Re-based alloys are being developed at the Technische Universität of Braunschweig for applications aimed at +100°C metal temperature above Ni-base superalloys to meet this need. Addition of refractory metal Re, which has complete miscibility in the Co-Re system, considerably increases the melting temperature of Co-Re alloys. This opens a unique possibility, as it allows to steadily elevate the melting range in Co-alloys, changing the character of the material from that of a contemporary Co-based alloy to that of a high melting point material. This gives a good chance to tune the properties and find a suitable balance between the need for toughness and ductility on the one hand and strength at temperatures beyond the capability of Ni-based superalloys on the other hand.

Higher application temperatures however, also impose severe demand on the high temperature oxidation behaviour of alloys, which is generally met in Ni-superalloys. Oxidation resistance along with high temperature strength is therefore important in our alloy development consideration. The Co-Re system has been explored very little so far, in fact from strengthening and oxidation point of view not at all. Cr which promotes the formation of a protective Cr₂O₃ oxide layer in conventional iron, nickel and cobalt alloys is a logical choice as alloying addition to Co-Re alloys. It is however clear that chromium alone will not suffice for oxidation protection at very high temperatures. In this paper we present the alloy development strategy and the design considerations we adapted.

2. Alloy development strategy
Co-based alloys are presently used in gas turbines for static parts up to 1000°C. In contrast to the conventional cast Co-base superalloys, where the matrix phase has a face centred cubic (fcc) structure, Re addition stabilizes the hexagonal close packed (hcp) phase as the matrix in the new Co-Re alloys. This demands a new strategy in alloy development for the Co-Re alloys. Moreover, the Co-Re is a little studied alloy system and we therefore explored different strengthening possibilities for the alloy development. Primary aim was to explore different strengthening mechanisms in the Co-Re system exploiting the following possibilities:
• Precipitation hardening: Carbides precipitates (M23C6 and MC type)
• Solid-solution hardening: by Re atoms
• Second phase (composite) hardening: σ phase (Cr-Re rich TCP phase)
• Grain boundary strengthening: by B and Zr atoms addition

Thermodynamic calculations formed the basis for choosing the alloy compositions. Thermocalc [1] was used to determine the stability of phases in the multi-component Co-Re-base alloys. This information was used to fix the composition of the experimental alloys studied.

As mentioned, along with high temperature strength, oxidation resistance is an important parameter in the alloy development. We felt the necessity to study these two aspects of the alloy development separately, from a more fundamental point to understand the physical basics and mechanisms. The knowledge gained formed the basis for the development of technical alloys.

2.1. Microstructure, strength and ductility
The atom size of Re is ~10% larger than Co atom and it provides significant matrix strengthening (figure 1) by solid solutioning, in addition to increasing the alloys’ melting temperature. Re in amounts of 17 to 30 at.% is added in the experimental alloys. Further, Cr and Ta are added in combination with C to derive precipitation strengthening through carbides. Microstructures of the CoRe1 (Co-17Re-23Cr-2.6C) and CoRe2 (Co-17Re-23Cr-1.2Ta-2.6C) alloys after solution heat treatment at 1450°C are shown in figure 2. In addition to the massive Cr23C6-type carbides (several micrometers in size) at the grain boundaries and within the grains reported in [2, 3], the matrix also contains lamellar Cr23C6-type carbides in the form of thin plates (~40 nm thick and inter-plate distance between 200 to 500 nm), oriented in parallel (figure 2 Left). In CoRe2 alloy, additionally, a very fine dispersion of TaC-type MC carbide forms (figure 2 Right). These carbide particles are extremely fine and are homogeneously dispersed between the plate-like M23C6 type Cr-carbides. The microstructure of the heat treated Co-Re alloys show that the alloys are strengthened by M23C6 and MC carbides in different morphologies and on varying length scales.

![Figure 1. Hardness measurements in binary / multi-component Co-base alloys, with varying Re content.](image)

In figure 1 it is also seen that the hardness increases much more in the ternary alloys containing Cr compared to the Co-Re binary alloys. This is because Cr also stabilizes the Cr-Re-rich σ phase which has very high hardness (microhardness > 800 HV). Further, when C is added to the Co-Re-Cr alloy (i.e. alloy CoRe1), lamellar carbides are present in the matrix in place of the σ phase, which also significantly increase the matrix hardness. This was clearly demonstrated by comparing microhardness values measured in differently heat treated CoRe1 alloy - when the lamellar carbides are present and absent in the matrix.

Generally, the topologically close packed σ phase is very hard and brittle. This is seen in figure 3 (Left), where the Co-Re alloy containing a significant volume fraction of the σ phase shows that cracks develop in the σ particles (bright phase) due to the hardness indentation. However, the surrounding matrix shows considerable plasticity (slip lines) and no cracks, thereby clearly indicating that in Co-Re alloys the presence of σ phase does not render the material inherently brittle. This gives
us the possibility to consider a second phase (composite) hardening mechanism using the $\sigma$ phase. In order to utilize this hardening concept, it is however, necessary to optimize the $\sigma$ phase morphology and distribution.

An addition of 15 to 25 at.% Ni to Co-17Re-23Cr refines the $\sigma$ particles (~ 500 nm), which are also sometimes present as thin lamellae (~ 200 nm thick). The $\sigma$ phase is very homogenously dispersed. Furthermore, in this size scale the $\sigma$ phase is no longer brittle (figure 3 Right). This is a potential microstructure for high temperature creep strengthening. The stability of $\sigma$ phase was tested at high temperatures up to 1300°C.

In any polycrystalline cast alloy, grain boundary cohesion is an important issue. In the case of Co-Re alloys, it was found that the grain boundaries are rather weak. Bend tests at room temperature showed e.g. that the Reference alloy (Co-17Re-23Cr) failed with brittle inter-granular fracture (figure 4 Left). To address this issue B and Zr was added in ppm levels up to 2000 ppm (by wt.) to the Reference alloy. The room temperature bend-test results in alloys containing B and Zr are shown in figure 4 (Right). The results show that B and Zr addition is effective in addressing the grain boundary cohesion issue. In fact, an addition of only 200 ppm B not only results in a significant increase in ductility, but the flow stress of the alloy is almost doubled (at RT). This trend is maintained also at high temperatures. Apparently, Zr also affects at high temperatures.

2.2. Oxidation behaviour

Oxidation mechanisms and scale formation is well understood in Co-Cr binary system [4] however, how Re addition affects the oxidation in Co-Cr alloys was not known and recently we investigated this [5, 6]. Generally, Re has a minor but negative effect and acts in two ways. Firstly, in combination with Cr, Re stabilizes the $\sigma$ phase, which has an inferior oxidation behaviour compared to Co(Re) solid solution. Secondly, the element Re itself oxidizes readily forming volatile Re$_2$O$_7$, which is lost from
the base metal. Knowing that chromium alone can not provide the needed oxidation protection, addition of Si (1-3 at.%) to the Co-17Re-Cr-base was investigated, where the Cr content was also varied between 23 and 30 at.%. Si addition showed promising results and matched the oxidation behaviour of the conventional Co-base alloy X40.

Addition of Al in Co-Re-Cr-Si alloy can also be helpful, as at high temperatures the presence of Si and Al, can assist in the formation of a more protective SiO₂ and Al₂O₃-oxide scales. Additionally, combination of B with Si will also be explored, which is expected to form a glassy protective layer and thereby prevent oxidation.

**Figure 4.** (Left) RT bend test results: Fracture surface in Co-17Re-23Cr alloy shows inter-granular fracture. (Right) Bend test results at RT.

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**Fig. 5:** Oxidation behaviour of Co-17Re-30Cr-2Si alloy at 1000°C compared to Co-base alloy X40.

**Acknowledgements**

We thank Ms Kruger and Prof. Heilmaier (TU Darmstadt) for the bend tests and Ms Gorr and Prof. Christ (Universität Siegen) for the oxidation tests. The financial support of Deutsche Forschungsgemeinschaft for the research group 727 “Beyond Ni-base Superalloys” is gratefully acknowledged.

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