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Current status of Co-Re-based alloys being developed to supplement Ni-based superalloys for ultra-high temperature applications in gas turbines

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Abstract

Although Ni-based superalloys meet the gas turbine needs of today, they are used very close to their melting range. To meet the future demands of gas turbines new materials with higher application temperatures are needed. Addition of Re increases the melting temperature of Co--based alloys and they show promise to supplement Ni-superalloys for ultra high temperature applications. The Co-Re alloy development strategy is first discussed here briefly. Unlike single crystal Ni-superalloys with the γ-γ' structure, the Co-Re alloys have complex microstructure with many different phases present in diverse morphology. MC type carbides are the main hardening precipitate particularly used for high temperature creep resistance. Further, Cr and Si additions in Co-Re alloys provide oxidation resistance. Designing optimal microstructure and ensuring its stability is an essential task of high temperature alloy development. In our alloy development program neutron and synchrotron measurements are extensively used. It allows monitoring the microstructure evolution in-situ at high temperatures and thereby helps in understanding the relatively unexplored Co-Re alloy system. Recent results on the effect of C/Ta ratio on the TaC morphology in Co-Re-based alloys are presented as well.

Key words: Co-base alloy, scanning electron microscopy (SEM), neutron scattering

1. Introduction

In gas turbines, both aero-engines and land based ones, Ni-based superalloys are the dominant material class in the hot section. Internal and film cooling of single crystal turbine blades and the use of thermal barrier coatings (TBC) have made it possible for the turbine gas entry temperature to reach nearly 1500 ℃ in modern turbines [1]. However, the Ni-superalloys which are used close to their melting point ($\sim 0.8\ T_{\mathrm{M}}$) are reaching limits and there is a need for the development of new materials with higher temperature capabilities (Ni-superalloy melting range is $\sim$ 1350 ℃). The choice of alternative material is quite limited with only a few ceramics, intermetallic compounds and refractory metals that can possibly meet the severe demands of the future gas turbines [2]. Although development of these alternate materials is progressing for many years there is no real breakthrough as yet.

At the Technische Universität Braunschweig, Germany, we are also working on this challenge and breaking away from the trend in searching for the alternative material we take a different approach and try to find an alternative metallic alloy to supplement Ni-superalloys. A key criterion for any future high temperature material is to have a very high melting temperature. With this in mind we found the Co-Re based alloys in 2007 [3]. The refractory metal Re and the transition metal Co form an isomorphous binary alloy and very high melting temperatures can be achieved in the Co-Re system. Further alloying additions (e.g. Cr, Si, Ta, Ni, C etc.) are necessary to impart strength and oxidation resistance to the Co-Re-base [4, 5].

The Co-Re alloy development started within a "Forschergruppe" program "FOR727" of the German

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Research Foundation (DFG) entitled "Beyond Ni-base Superalloys" with five German universities, namely, TU Darmstadt, TU Braunschweig, Ruhr-Universität Bochum, Universität Bayreuth and Universität Siegen, participating [6]. The research is now extended and presently continuing as a joint collaboration project between TU Braunschweig and TU Munich funded by the DFG.

The Co-Re alloys are strengthened by a fine dispersion of carbides, particularly MC type TaC and unlike γ-γ' based Ni-superalloys, they have a rather complex microstructure with many different phases present in diverse morphology. In this paper we first discuss our alloy development strategy and then present the current status of the development.

2. Alloy development strategy

Co-based alloys are not new and are presently used in gas turbines for static parts up to 1000 ℃. There is even a new development trend in Co-Al-W alloys [7, 8] to produce a γ/γ' structure (fcc/$L1_2$) similar to that in Ni-superalloys to improve strength. However, the development does not promise application at very high temperature and has some of the shortcomings of the γ-γ' Ni-superalloys. It is clear that to develop alloys for very high temperature application one needs an alloy system with relatively high melting point. The refractory metal Re has the third highest melting point (3182 ℃) in the periodic table, after C (3500 ℃) and W (3410 ℃) and therefore is an attractive alloying addition. In fact, the melting point of Re is about twice the melting point of Co (1495 ℃) or Ni (1453 ℃) and therefore provides ample opportunity. Re is added in Ni-based superalloys for this reason as well and has very beneficial effect. However, the solubility of Re in Ni is limited. In contrast, it dissolves readily in Co and a complete miscibility exists in the Co-Re binary system. It is therefore possible to continuously increase the melting temperature of Co alloys with addition of Re, opening up a unique possibility to steadily elevate the melting range in the Co-Re system, changing the character of the material from that of a contemporary Co-based alloy to that of a high temperature material. About 17 % Re (all numbers in composition are in atomic percent unless otherwise mentioned) addition to Co can raise the liquidus temperature from 1495 ℃ in pure Co to $\sim$ 1700 ℃ in the Co-17Re binary alloy. In fact, the Co-Re system offers the possibility to suitably adjust the melting range by the amount of Re addition.

It is clear that along with the high temperature strength, oxidation resistance is an important property for any high temperature alloy. Gorr et al. [9] reported that Co-17Re exhibits very poor oxidation behaviour due to the formation of a porous, non-protective Co-oxide layer, resulting in significant loss of Re due to evaporation of its oxides. Cr promotes the formation of a protective Cr_2O_3 oxide layer in conventional iron, nickel and cobalt alloys and therefore was a logical choice as an alloying addition in Co-Re alloys for the intermediate temperature oxidation resistance. Moreover, like in conventional Co-based superalloys, the addition of chromium to the Co-Re alloy system was expected to improve both the mechanical properties and the oxidation resistance. However, it was found that even addition of 23 % chromium does not provide enough oxidation resistance to the Co-17Re alloy, but actually results in a higher evaporation rate of Re oxides caused by the formation of a more porous $CoCr_2O_4$ spinel phase [9]. A better oxidation resistance was found for alloys with higher chromium content, e.g. Co-17Re-30Cr where a semi-continuous Cr_2O_3 layer was formed underneath the spinel phase [5].

It became quite clear that chromium alone cannot suffice for oxidation protection to high temperatures in Co-Re alloys and therefore a small amount of Si addition in conjunction with Cr was explored. Due to the synergetic effect of Si and Cr, the oxidation resistance of the alloys Co-17Re-23Cr-xSi (x = 1, 2, 3) becomes significantly enhanced [5]. A quasi-continuous chromia layer forms on the alloy Co-17Re-23Cr-3Si surface with subsurface oxidation of the Si to SiO_2 which are dispersed as internal particles [5]. However, in all alloys with up to 3 % Si, a compact and protective SiO_2 oxide layer has never been observed. Considering that higher silicon content may strongly diminish the melting point of the Co-Re alloy, the influence of the Cr content on the oxidation behaviour of the Co-17Re-xCr-2Si system was further studied. Results showed that an increase of the Cr content from 23 to 25 % dramatically enhances the oxidation resistance of the system at 1000 and 1100 ℃, due to the formation of a compact Cr_2O_3 layer [5]. Thus Co-17Re-25Cr-2Si alloy provided good oxidation resistance to 1100 ℃. Further improvement in oxidation resistance to higher temperatures will need other additions, e.g. Al.

An addition of > 20 % Cr to the alloy Co-17Re promotes the formation of the topologically closed packed (tcp) σ phase in Co-Re alloys. The Cr-Re-rich (Cr_2Re_3 type) σ phase has very high strength, but is also brittle and therefore it is generally undesirable in Ni and Fe base alloys. Moreover, in Cr-carbide strengthened alloys it was found that at temperatures above 1000 ℃, where the $Cr_{23}C_6$ type carbides are unstable, the Cr freed from the carbide dissolution combines with Re in the matrix and stabilized σ phase [10]. In the Co-Re-Cr alloys σ phase is mainly present as large (> 10 μm) isolated particles and does not make the alloy inherently brittle. Although cracks easily develop in the σ particles on application of external load, the

cracks do not readily propagate through the ductile Co-Re matrix [11].

A novel strategy was therefore adapted for the Co-Re alloy development in which a new concept of strengthening with the tcp σ phase was used. A fine dispersion of the high strength σ phase could be obtained in Ni containing Co-Re-Cr alloys after suitable heat treatment [12]. Nickel, a fcc stabilizer of the Co matrix (unlike Re and Cr, which are hcp stabilizers) stabilizes a mixed fcc + hcp Co-matrix in the alloy and is apparently responsible for the fine dispersion of the σ phase. The σ phase in this morphology (scale of dispersion: 100 to 200 nm) is likely to be still brittle but is defect free and therefore crack initiation becomes difficult. It was seen that the alloy Co-17Re-23Cr-15Ni with $> 20\,\%$ sigma volume fraction shows significant room temperature ductility ($> 3\,\%$ elongation) [12].

In our alloy development strategy, two separate strengthening paths were followed – i) strengthening by carbides, particularly with MC type carbides and ii) strengthening by σ phase. In both cases, additional strengthening through solid solution effects of Re and strengthening of grain boundaries by B was combined. Long term stability of strengthening phase at high temperatures is an important aspect of study in alloy development. These studies continue and some results for the Ni containing alloys were presented earlier [11]. However, in this paper we will mainly present results from alloys strengthened by TaC precipitation.

At the present development stage, work continues with vacuum arc or induction melted polycrystalline alloys. Although, for application in turbine blade, single crystal or directionally solidified (DS) alloys will be desirable and these technologies will need to be developed in future. Initial exploration with DS casting in Co-Re alloys has shown that there are challenges posed by the allotropic transformation of the Co-matrix (from the high temperature fcc to the low temperature hcp structure). In Co-Re-Cr alloys this transformation is at relatively high temperatures ($> 1200\,$℃) [13] and destroys the directional growth on solidification during further cooling in the casting process.

The ternary alloy Co-17Re-23Cr is a reference experimental alloy of the Co-Re-Cr system. The alloy has attractive strength, but ductility in polycrystalline state is very poor due to grain boundary failure. In general, the grain boundaries of the polycrystalline cast alloy are weak regions and the material fails in a brittle manner by intergranular fracture. Similar problem was known in polycrystalline and directionally solidified Ni-superalloys and was addressed with a small amount of boron addition (0.5 to 1.0 %), which significantly toughened the Ni-alloys [14].

Strengthening of grain boundaries by addition of boron is also quite effective in Co-Re-Cr alloys. Very small amount of B addition (50 to 1000 wt. ppm) to the polycrystalline alloy has a profound effect on both room and high temperature strength and ductility of the Co-17Re-23Cr alloys [15]. In fact, the polycrystalline Co-Re alloys have specific strength comparable to single crystal Ni-superalloy and similar ductility at RT, despite its much higher density (ρ). A comparison of specific strength (UTS/ρ) of the Co-17Re-23Cr + 500B and CMSX4 alloys was presented in Ref [17]. There is evidence of B segregation to the grain boundaries as even the smallest B addition of 50 ppm stabilizes Cr_2B-type borides at grain boundaries [16]. In addition, boron enhances the grain boundary cohesiveness and changes the fracture mode. However, it is apparent that the presence of Cr-borides at grain boundaries may not be the primary reason for the improvement in strength and ductility. Mapping of elemental boron using neutron induced α tracking confirmed segregation of boron atoms to grain boundaries in the Co-17Re-23Cr + B alloys [17]. The nuclear reaction $^{10}B(n,\alpha\gamma)^{7}Li$ is the source of alpha particles. This reaction occurs when neutrons interact with B atoms in the alloys on exposing the sample to the neutron beam. The PGAA instrument at BNC Budapest was used for the boron mapping [17].

The Co-Re alloys were never before considered for any structural application and the literature on the Co-Re system is scanty as it had been seldom investigated in the past. Particularly mechanical property data are completely missing. Few studies that exist mainly relate to crystallographic investigations and phase diagrams. Exploiting Co-Re-Cr alloys for structural application is therefore a challenge and needs fundamental approach and basic understandings. Moreover, TaC which is the main strengthening phase is a strongly nonstoichiometric interstitial compound and exists over a wide composition range in the binary Ta-C system. Although it is stable at very high temperatures ($> 3800\,$℃) in the binary alloy, its behaviour when confined in the Co-Re-Cr system is unknown. So far, the investigations on TaC in Co-Re alloys were limited to the complex composition only – i.e. Co-17Re-23Cr-1.2Ta-2.6C. However, it is apparent from the binary Ta-C phase diagram that the TaC phase exists over a wide composition range ($y = 0.6$–1, where y is the C/Ta ratio), therefore presently we are studying simpler alloys (without Cr addition) with different C/Ta ratios in order to understand the behaviour of TaC. Other Ta_xC_y-type phases (e.g. zeta-Ta_4C_3, alpha-Ta_2C) may form in some of these alloys, particularly in the carbon-lean compositions. As Cr also has strong affinity for carbon, alloys containing Cr may form Cr-carbides. Therefore, to avoid any interference with the TaC phase, the alloys being investigated presently are deliberately kept free of Cr. The effect of small amount of Cr addition on the TaC phase is also investigated within the DFG project.

Often a strong criticism against the use of Co-

-Re alloys in gas turbine is the high cost of Re. It is true that large amount of Re addition not only makes the alloy heavier but also costlier compared to Ni-superalloys. However, to understand why Co-Re alloys are still attractive, especially if they can deliver a significant improvement in temperature capability, one needs to consider the following: A typical Ni-superalloy single crystal blade in land based turbine weighs ∼ 5 kg and costs around 15 to 20 thousand €, in which the alloy cost is only ∼ 1000 €. The manufacturing cost of the complex investment cast blades and coating is far greater than the material cost for these components. Therefore, even if the Co-Re alloy costs significantly more, the higher temperature capability will offset the material cost. Secondly, as the specific strengths of Co-Re alloys and Ni-superalloys are comparable, the actual weight of the Co-Re alloy is likely to be lower. Thirdly, latest generation of single crystal Ni-superalloys already uses significant amount of Re in them.

3. Results and discussion

As discussed above, the melting temperature of the alloy is the critical parameter and therefore it was determined with careful thermal analysis. The technique of Differential Scanning Calorimetry (DSC) was selected for the study of Co-Re-Cr alloys. When using DSC to find the transition temperatures, specific heat or enthalpy, it is necessary to choose a constant heating and/or cooling rate for measurement and any calibration is valid only for this particular heating/cooling rate. When different ramp rates are used, different transition temperatures are mostly observed. However, this can be corrected by testing several heating/cooling rates and then extrapolating to the zero ramp rate [18]. This procedure was followed to get the solidus and liquidus temperatures in Co-Re alloys from measurements done with heating/cooling rates of 5, 10 and 20 K min^{-1} (Fig. 1). Typical result for the reference Co-17Re-23Cr alloy is shown in Fig. 1a,b. Since boron particularly is a melting temperature depressant the effect of its addition was checked and the results are shown in Fig. 1c. When the amount of B addition is small (50–500 ppm), it does not have a significant influence on the melting temperature (Fig. 1c).

The microstructures of two Co-Re alloys strengthened by TaC, one with and the other without Cr addition are compared in Fig. 2. As Cr also has a strong affinity for carbon and forms carbides it is likely that the Cr addition will affect the formation of TaC. Keeping this in mind it is clearly important to study the TaC precipitation and how its morphology develops in alloys without Cr. On the other hand Cr is an essential addition to Co-Re alloys for oxidation resistance,

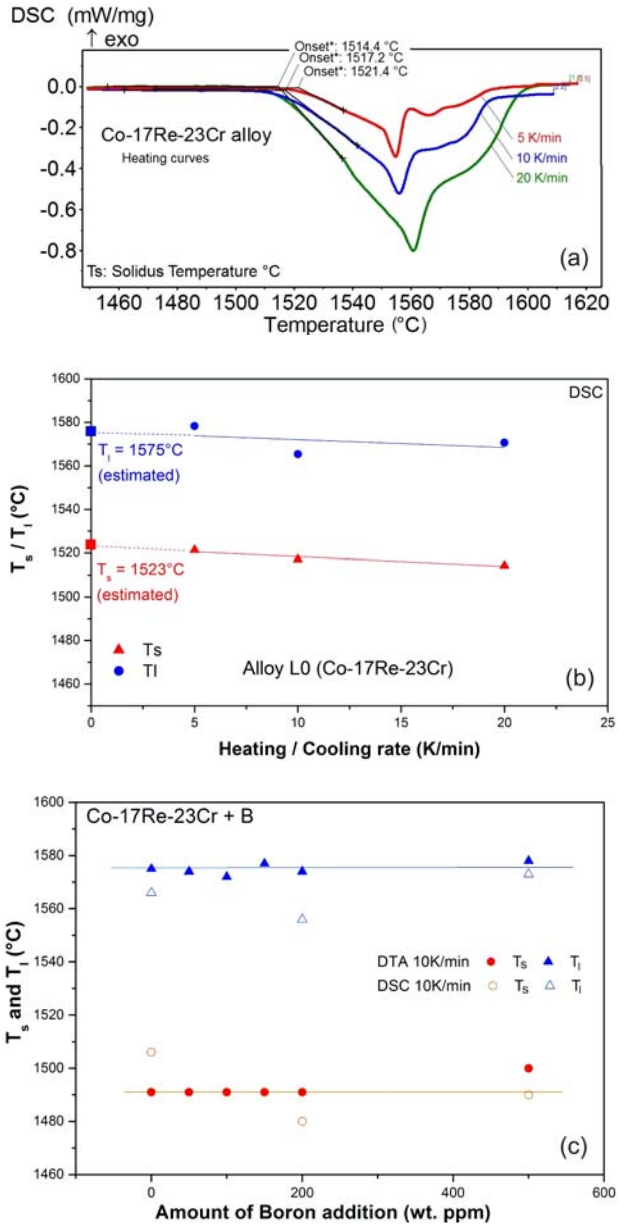

Fig. 1. DSC results of melting temperature measurement in Co-17Re-23Cr + B alloys. (a) Typical example of measurements at different heating/cooling rates, (b) estimated T_s and T_l by extrapolation to zero heating/cooling rates, (c) effect of boron addition on the melting temperature (DTA = Differential Thermal Analysis).

and its influence on carbide formation also needs to be checked.

From Fig. 2 it is clear that Cr not only has an influence on the carbide phases but it also controls other phase formation and strongly influences the alloy microstructure in general. For example, the Chinese Script (CS) type Ta carbides and the large σ phase particles which are present at the grain boundaries in the Co-17Re-23Cr-1.2Ta-2.6C alloy (Fig. 2a) are absent in the Co-17Re-1.2Ta-1.2C alloy (Fig. 2b)

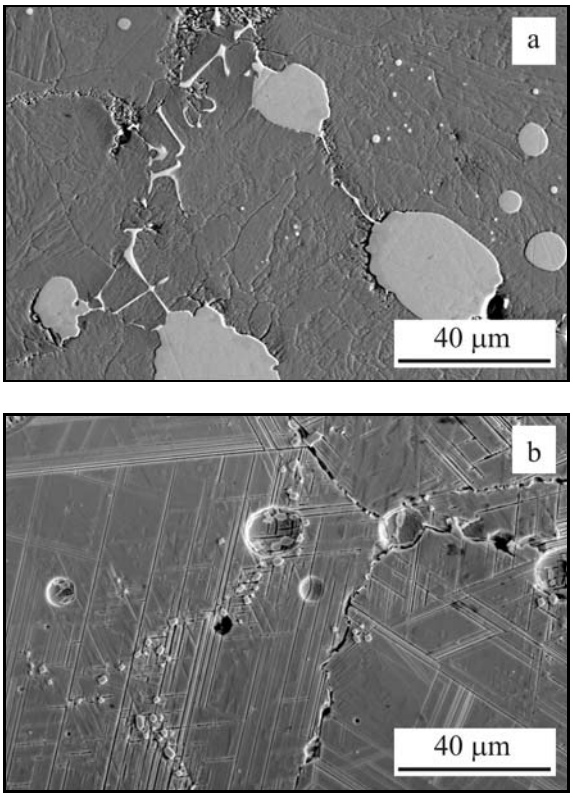

Fig. 2. Low magnification SEM images of (a) Co-17Re-23Cr-1.2Ta-2.6C and (b) Co-17Re-1.2Ta-1.2C alloys after ST heat treatment.

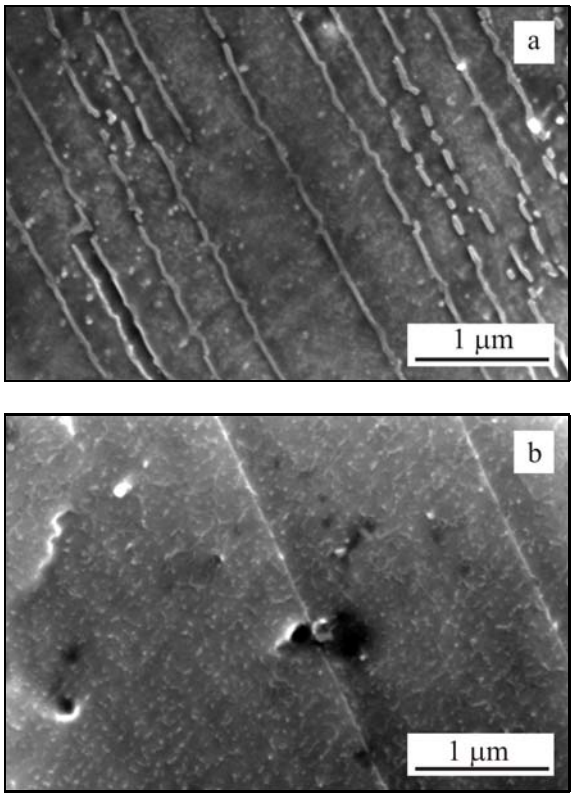

Fig. 3. High magnification SEM images of (a) Co-17Re-23Cr-1.2Ta-2.6C and (b) Co-17Re-1.2Ta-1.2C alloys after ST heat treatment. Beam deceleration mode with effective landing voltage of 1 kV was used in imaging to resolve the very fine precipitate morphologies.

after the same heat treatment (ST = 1350 ℃/5 h + 1400 ℃/5 h + 1450 ℃/5 h + Argon quenched). Moreover, the Co-matrix is heavily twinned in Fig. 2b while a fine substructure of lamellar $Cr_{23}C_6$ carbide is present in Fig. 2a.

The TaC morphologies are quite different in the two alloys. Instead of the CS-type TaC phase in the Cr containing alloy, large cuboidal TaC particles are present at or near the grain boundaries in the alloy without Cr. The fine TaC precipitates are also present in both the alloys and can be seen in Fig. 3. Here again the morphology of the fine TaC precipitates and their distribution are different in the two alloys.

In Fig. 3a (Co-17Re-23Cr-1.2Ta-2.6C alloy) the lamellar $Cr_{23}C_6$ carbides are better resolved and it is seen that the fine TaC precipitates lie between the Cr-carbide lamellae. The mean thickness of the $Cr_{23}C_6$ lamellae and the mean diameter of the fine TaC precipitates were determined from small angle neutron scattering (SANS) measurements as 50 nm [19]. Fine TaC precipitates are also seen in the Co-17Re-1.2Ta-1.2C alloy, however, due to the absence of Cr no lamellar structure is found in Fig. 3b. Also the TaC precipitates are much finer in the alloy without Cr. The precipitate size was estimated by SANS and found to be below 10 nm in the Co-17Re-1.2Ta-1.2C alloy. Both the SEM micrographs in Fig. 3 were imaged with the beam deceleration (BD) mode with electron acceleration voltage of 5 kV and specimen bias of 4 kV and thus an effective landing voltage of only 1 kV. This imaging mode improves image resolution and allows to better resolve the fine precipitate structures.

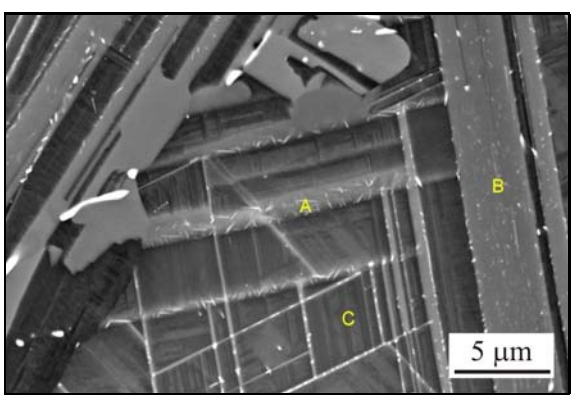

Fig. 4. SEM images of Co-17Re-1.2Ta-1.2C alloy after ST + 900 ℃/24 h/WQ. The three different regions marked A, B and C have different TaC morphologies.

The TaC morphology in the Co-17Re-1.2Ta-1.2C

alloy changes to a great extent when the ST sample is further exposed at 900 ℃. The SEM image at Fig. 4 shows that TaC precipitates are somewhat coarser after the 900 ℃/24 h/WQ heat treatment. In general, the twinned microstructure shows distinct regions with different TaC morphologies. Some regions show elongated needle or plate like TaC precipitates which are coarse (marked A in Fig. 4). In other regions (marked B) TaC remains globular and fine. A third region (marked C) shows a seemingly precipitate free structure with cross twins but examination at very high magnification showed that these regions also have very fine precipitates. In the relatively low magnification image of Fig. 4 the precipitates are too fine to resolve. In addition, elemental mapping by energy dispersive X-ray spectroscopy (EDS mapping) showed that the region C also has a higher Co and lower Re than the rest of the matrix. A detailed analysis of the structure will be presented in a separate publication [20] where the microstructure of different alloys with varying C/Ta ratio will be discussed.

Pure cobalt undergoes an allotropic transformation (low temperature phase ε is hcp and high temperature phase γ is fcc) at 417 ℃ by a diffusionless martensitic mechanism. This transformation is often incomplete because of the very low stacking fault energy of Co and causes the formation of stacking faults and twins in the cubic high-temperature γ phase, which remains in metastable form at room temperature [21]. Alloying additions of Re, Ta and Cr (hcp stabilizers) increase the transformation temperature and in the alloys investigated it can vary widely depending on the composition. The fcc to hcp transformation is a simple structural change and can be accomplished by the passage of Shockley partial dislocation on alternate {111} planes. The resulting {111} interfaces between the transformed and untransformed regions are coherent in nature. In the microstructure shown in Fig. 4, the TaC precipitation appears to be more predominant at the interfaces.

The allotropic transformation in some Co-Re alloys is mapped in Fig. 5 from in-situ neutron diffraction measurement and shows that the alloy composition and the phases present have a strong influence on the Co phase transition. Figure 5 also shows that the transformation has a broad hysteresis and it does not occur at the same temperature range on heating and cooling. The transition in the alloy without Cr, i.e. Co-17Re-1.2Ta-1.2C has not yet been measured but there is microstructural indication that it starts below 1000 ℃. However, the binary Co-Re phase diagram shows the transition temperature for Co-17Re alloy is at around 1200 ℃. This is also marked in Fig. 5. The Co-matrix allotropic transformation is an important parameter for the Co-Re alloys and can be a cause of structural instability at the application temperatures. On the other hand it may be used for microstructure

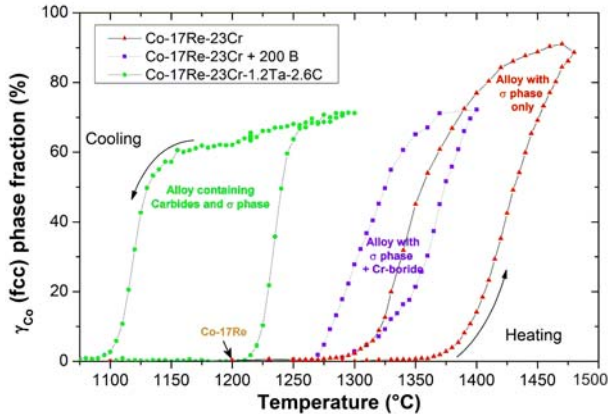

Fig. 5. Allotropic transformation of Co-matrix in various Co-Re alloys shows hysteresis as determined by in-situ neutron diffraction measurements.

tailoring, e.g. creating a mixed fcc + hcp matrix or in influencing the fine precipitate dispersion.

Microscopic observation shows that very fine precipitates are present in Co-Re alloys, which are ideal hardening phase. To characterize the fine Ta and Cr carbides, particularly those having size below 100 nm, in-situ SANS measurements were performed at room temperature (RT) and at high temperatures. Typical results obtained from the alloy Co-17Re-23Cr--1.2Ta-2.6C are presented in Fig. 6. SANS is an ideal tool for monitoring precipitate morphology evolution in these fine scales and therefore provides information regarding the stability of the hardening precipitates. Figure 6a shows scattering from the fine TaC particles in the alloy. Their globular/cuboidal morphology allows them to be distinguished from the lamellar $Cr_{23}C_6$ carbides. Also the large probe volume in SANS provides good statistics for the particle size distribution (PSD). The PSD for the fine TaC precipitates at RT and high temperatures are presented in Fig. 6b. Coarsening of TaC precipitates during holding at 1200 ℃ is clear but the particle size remains very fine.

3. Current development status

Co-Re alloys show promise. However, much more research is needed before they can be tested for any technical application. Precipitation hardening by carbides, particularly the fine dispersion of TaC is found to be stable up to temperatures above 1200 ℃. Although the precipitates coarsen on long exposures, they remain still fine enough to be an effective barrier for dislocation and interact with dislocations during creep exposure. However, the oxidation resistance is only effective to 1100 ℃ and much work is needed to improve this critical property. Work is already planned

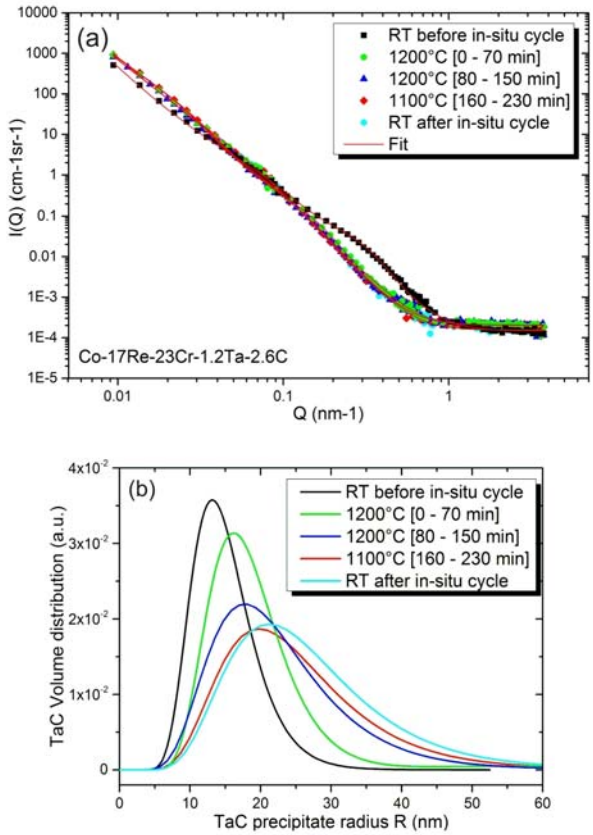

Fig. 6. Measurement of TaC precipitate morphology evolution at high temperatures. (a) Experimental and fitted SANS data, (b) corresponding TaC particle size distributions at different temperatures.

for alloys with Ni additions, where preliminary studies suggest possible scope for improvements.

For turbine blade applications, single crystal cast blades of complex geometry will be needed. In this area of investment casting work is still to be initiated. Some trials on directional solidification studies showed there are formidable challenges to be overcome in this area. So far the reason for the observed difficulties is not clear but it is supposed that the allotropic phase transformation in the Co-matrix, which occurs at relatively high temperature in Co-Re system, is a possible cause as it destroys the initial cast microstructure.

So far limited evaluation of mechanical property in Co-Re alloys shows their potential. However, extensive testing both at RT and high temperatures is still needed. Long term mechanical behaviour, both creep as well as fatigue properties are critical for gas turbine components and these also need to be tested.

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