Stability of phases at high temperatures in CoRe based alloys being developed for ultra-high temperature applications

R Gilles a, P Strunz b, D Mukherji c, M Hofmann a, M Hoelzel a and J Roesler c

a Technische Universität München, Forschungsneutronenquelle Heinz Maier-Leibnitz (FRM II) ZWE, Lichtenbergstr. 1, 85747 Garching, Germany

b Nuclear Physics Institute ASCR, CZ-25068 Řež near Prague, Czech Republic

c Technische Universität Braunschweig, Institut für Werkstoffe, Langer Kamp 8, 38106 Braunschweig, Germany

E-mail: ralph.gilles@frm2.tum.de

Abstract

In the development of new high-temperature alloys for gas turbine applications various candidates are under consideration. This contribution deals with a CoRe based alloy strengthened by Cr23C6 type carbide and Cr2Re3 type σ phase precipitations (here designated as CoRe-1 alloy). High-temperature cycling experiments show how the influence of heating, cooling and the hcp<->fcc phase transformation of the Co-matrix on the stability of these phases. Neutron diffraction experiments with high-temperature vacuum furnace show that Cr23C6 carbides starts to dissolve around 1100°C and above 1250°C are almost completely dissolved. On the other hand σ phase is still present at 1300°C. This contribution describes the evolution of the different phases during the heating and cooling cycles which are repeated two times. Further, the influence of boron addition to CoRe-1 alloy was studied for samples in the first heating/cooling cycle. A newly developed tensile rig was also tested up to 980°C to combine in situ loading and heating for the neutron diffraction measurements.

1. Introduction

The Co-Re based alloys, a new class of high temperature alloy with relatively high melting point, were introduced by the Technische Universität Braunschweig, Germany in 2007 [1] to supplement Ni-based superalloys in future gas turbines for application at and above 1200°C. This project is implemented in “Beyond Ni-Base Superalloys” DFG Forschergruppe 727, a German research project. Co-based alloys are already used in gas turbines and achieved sustained success. Their disadvantage is the limited strength and the low service temperature of around 1000°C. To increase application temperatures the melting point of Co-based alloys has to be enhanced. This is achieved by addition of Re (which has the third highest melting point in the periodic table \( T_M = 3182°C \)) to the Co-alloy. In this way, an improvement of the melting point of the alloy by approximately 200°C - in comparison with Ni-based superalloys - is obtained [1].

The microstructure of Co-Re alloys is complex and at RT it has a ε Co (hcp) matrix. CoRe-1 alloy has other phases, particularly Cr23C6 type carbides and Cr2Re3 type σ phase. Massive and blocky Cr-carbides in the form of Cr23C6 are present at the grain boundaries and within the grains and very coarse particles of Cr2Re3 (σ phase) are also present. However, from the strengthening aspect, the most important phase is the fine lamellar form of the Cr23C6 carbides which are homogeneously distributed in the grains [2]. Long term stability of the fine microstructure, particularly at high temperatures in the range of 1000°C to 1300°C, is very critical for the application of the Co-Re alloys.
Previous in-situ investigation at high temperatures by neutron diffraction detected a hcp (ε) to fcc (γ) phase transformation of the Co-matrix in the experimental alloys CoRe-1 (Co-17Re-23Cr-2.6C) and CoRe-2 (Co-17Re-23Cr-1.2Ta-2.6C) [3, 4]. In these alloys the Co-matrix undergoes a phase transformation from hcp (ε) to fcc (γ) phase on heating between 1200°C and 1300°C. Moreover, the phase transformation although reversible exhibits a large hysteresis (around 100°C) in both of the alloys. It was concluded that the hysteresis is a result of the composition interplay between matrix and the minority phases, namely the Cr<sub>23</sub>C<sub>6</sub> and σ phase [3, 4].

As the high temperature microstructure and its stability is of great importance for the application the simpler composition of the CoRe-1 alloy was further examined in more details. As previous neutron diffraction experiments [3, 4] have shown that the amount of σ phase volume increased after the thermal cycle, we monitored the structural evolution very carefully by repeating the thermal cycling to see if the irreversible changes in σ phase after the first cycle affect the transformation in the second cycle. Further, the CoRe alloy development has shown that small addition of boron (which is known to segregate to the grain boundaries) is needed, in order to strengthen the weak grain boundaries in polycrystalline alloys and to mitigate environmental embrittlement [5]. Therefore, an alloy with the same composition like the CoRe-1 but with a further addition of 500 wt. ppm boron (here designated as alloy CoRe-1B) was also studied. Even such small amount of boron has a significant effect on the initial microstructure of the fine Cr-carbide [5].

Moreover, the evolution of the microstructure at high temperatures up to 980°C under an applied uniaxial load was studied by means of a deformation rig on the Stress Spec instrument at FRM II. The results from the first test of the rig are presented.

2. Experimental

A sample of alloy CoRe-1 which already underwent a thermal cycling as in reference [4] was subjected to a second identical thermal cycling. It was intended to study the structural stability and equilibration during and after the second cycle. In addition a boron-containing alloy CoRe-1B (Co-17Re-23Cr-2.6C + 500 wt. ppm B) was subjected to a single thermal cycle for determination of the influence of boron on high temperature microstructure of CoRe-1 alloy.

The alloys CoRe-1 and CoRe-1B were melted in a vacuum arc furnace and cast into square rods in a solid Cu mould. After a heat treatment of the bars between 1350°C and 1450°C for a total time of 15 hours to homogenize them, the samples were water quenched. Cylinders of around 6 mm diameter and 30 mm length were cut for neutron diffraction measurements.

A Zeiss scanning electron microscope (SEM) Leo 1550 (FEG) was used to study the microstructure of the alloys. Microstructural images were recorded with standard and in-lens secondary electron (SE) detectors as well as with back scatter electron (BSE) detector at high resolution and fine particles in the sizes of 20 to 50 nm could be easily resolved. While BSE images were recorded using an accelerating voltage of 15kV, SE and in-lens SE images were taken with only 5 kV. The Z (atomic number) contrast from heavy elements like Re in the BSE images allows to distinguish the phases from their grey level.

In-situ neutron diffraction measurements at RT and in the high temperature region between 1100°C and 1300°C were performed at FRM II, Garching, Germany to study the microstructural stability of experimental Co-Re alloys. With a high temperature furnace in situ heating/cooling in 5°C steps (reached in 5 seconds) were effected to carry out measurements during a 10 minute hold at a given temperature. Using an area detector, with a sufficient angular region where all strong scattering Bragg reflections are present, measurements were performed at the Stress-Spec [6] instrument with a wavelength of 0.16225 nm. Further, high resolution measurements at RT were done at SPODI instrument [7, 8] using a wide angular region with 80 He<sup>2</sup> tube detector bank and a wavelength of 0.15482 nm.

At Stress-Spec, we adjust the same temperature program for the first and the second thermal cycle of CoRe-1 alloy. The sample with boron (CoRe-1B) was examined at the high temperature diffractometer SPODI. We followed basically the same thermal cycle as previously with the CoRe-1 sample without

---

1 All compositions in this paper are expressed in atomic percentage (at. %) except for the boron additive which is always given as wt. ppm.
The evolution of main phases (hcp, fcc) as well as of the strengthening phases (Cr$_{23}$C$_6$ and σ phase) during the thermal cycle RT – 1300°C – RT was studied in this way and compared to the previously measured phase evolution in CoRe-1 alloy.

As a first test of a new tensile rig to combine loading and heating in situ during the neutron diffraction measurement, tensile samples of CoRe-1 with 40 mm gauge length and diameter of 6 mm were prepared. These cylinders were connected with a M8 thread to the grips of the tensile rig. Slow increase of the load (1N/sec) allowed easy acquisition of diffraction patterns in the 2Θ range of 42° up to 56° with a 2 dimensional area detector at Stress-Spec instrument. The experiments were carried out at three different temperatures, namely T = 538°C, 800°C and 980°C.

3. Results and Discussion

The microstructure of the CoRe-1 and CoRe-1B alloys are shown in Figure 1. The low magnification of SEM images (Fig. 1a and c) shows the coarse microstructures in both alloys. The CoRe-1 alloy has Cr-carbides at the grain boundaries and also blocky Cr-carbides within the grains. The CoRe-1B alloy shows instead the presence of coarse (> 20 µm) σ phase particles within the grains (Fig. 1a and c). In addition the fine structure of lamellar Cr$_{23}$C$_6$ carbide is seen in both alloys in the higher magnification SEM images (Fig. 1b and d).

The neutron diffractograms were recorded during temperature increase (RT-1300°C) and temperature decrease (1300°C-RT) with various temperature steps (denser around the transformation temperatures). Usually, a selected angular region in 2Θ (43°-70°) where the large peaks of important phases are present was chosen at Stress-Spec, whereas the full angular region (38°-104°) was measured only at defined temperatures.

![Fig. 1: SEM micrographs of CoRe-1 alloy (a and b) and CoRe-1B (c and d) in standard heat treatment condition. The CoRe-1 alloy shows presence of grain boundary and blocky Cr-carbides while CoRe-1B alloy shows presence of σ phase particles. Both alloys have a fine lamellar structure of Cr$_{23}$C$_6$ carbide (b and d).](image-url)
Fig. 2: Full diffractograms of CoRe-1 at RT between the first and the second cycle (hcp phase: before phase transformation) and at 1290°C (fcc phase: after phase transformation) measured at Stress-Spec (a). Limited 2θ scattering range of CoRe-1 during phase transformation at 1230°C (hcp and fcc phase) measured at Stress Spec (b).

As an example of the measured neutron diffraction data, Figure 2a shows full diffractograms of CoRe-1 alloy taken at RT and at 1290°C. It contains the peaks from the matrix and the minority phases.
present in the alloy. The main phases are the Co solid solution with Re as the matrix, the Cr-carbide phase Cr$_{23}$C$_6$ and the $\sigma$ phase Cr$_2$Re$_3$. Due to the $\varepsilon$ to $\gamma$ phase transformation the hcp peaks from the Co-matrix are present at the RT diffractogram, while the fcc peaks from the Co-matrix are to be found at the 1290°C. The peaks of the Cr$_{23}$C$_6$ and the $\sigma$ phase differ in intensities in the two diffractograms. Figure 2b displays a typical confined angular region used at Stress-Spec during the temperature loop. From the intensities of the peaks of the individual phases, the temperature dependence of their relative volume fraction was deduced. All the diffractograms were analyzed by FullProf program [9]. Resulting phase fractions can be estimated from the peak integral intensities because the scattering contribution in the 2$\theta$ range (42°-68°) covers all strong peaks of the relevant phases. It should be mentioned that due to the small amounts of $\sigma$ phase and Cr$_{23}$C$_6$ phase in the sample the low measured values of integral intensity are difficult to determine and have a certain inaccuracy.

The volume fractions of the different phases in CoRe-1 alloy during the two cycles (called first and second cycle) are shown in Figures 3a-d. The second cycle on CoRe-1 sample does not change the temperature of the hcp$\leftrightarrow$fcc transformation of the Co matrix compared to the first cycle [4], neither during the temperature increase (centre of transformation at 1235°C), nor during the temperature decrease (centre of transformation at 1140°C) (Fig. 3a, b). The only difference is the lower volume fraction part of hcp phase at RT before and after the second cycle with respect to RT before the first cycle.

In CoRe-1 alloy the hysteresis exhibited by the Cr$_{23}$C$_6$ carbides (Fig. 3c) in the second cycle is almost identical to the one observed in the first cycle and also very much follows the hysteresis of Co-hcp phase. On heating the Cr-carbide starts to dissolve at around 1120°C and it is completely dissolved above 1250°C (Fig. 3e). During cooling the precipitation of carbides do not start before the temperature reaches 1150°C, but then the volume fraction reaches the original value within a short time around this temperature only. In the second cycle (measured at Stress-Spec) the hysteresis is better defined as the number of measured data points is much larger than in the first cycle (Fig. 3e). After cooling in both of the cycles, the Cr$_{23}$C$_6$ phase reaches the same volume fraction value which is a little bit above the starting value before the first cycle.

On the other hand, the $\sigma$ phase evolution is significantly different in the first and in the second cycle (Fig. 3d). Its volume decreases on temperature increase above 1120°C, i.e. earlier than the decrease in the hysteresis loop of hcp and Cr$_{23}$C$_6$ phases. The $\sigma$ phase amount increases after the first cycle but after the second cycle return to this same value. The $\sigma$ phase evolution during heating and cooling follows a slightly different path in the first and the second cycle. Much less change in volume fraction is observed in the second cycle for this phase. The volume fraction of $\sigma$ phase is similar after the first and the second cycle and the second cycle starts at RT with higher volume fraction than the first cycle. The change of $\sigma$ content at RT before and after cycling is connected with the change of hcp matrix content. Similarly, the change of sigma content at HT between the first and the second cycle is connected with the change of fcc matrix content.

The alloy CoRe-1B was also subjected to similar heating cycles like the CoRe-1 alloy but only one thermal cycle was done in this case. A comparison of the hysteresis in CoRe-1 sample and CoRe-1B sample during the first cycle was performed. The corresponding evolution of the peak intensities of the individual phases are displayed in Figure 4. In the CoRe-1B sample, the transformation hcp$\leftrightarrow$fcc (Fig. 4a, b) on temperature increase occurs around 1225°C (centre of transformation) and on temperature decrease around 1135°C (centre of transformation). It differs slightly from the transformation temperature of CoRe-1 sample without boron addition (centre of transform was at 1235°C and 1140°C in CoRe-1 on temperature increase and on temperature decrease, respectively). The shift in alloys with and without boron is only less than 10°C and part of the error is likely due to the uncertainty of temperature synchronization in the respective in-situ experiments. The Cr$_{23}$C$_6$ phase shows no qualitative difference in CoRe-1 and CoRe-1B alloys. Again, only small shift of the hysteresis loop in the temperature scale towards lower temperatures can be observed (see Fig. 4c). As in the case of CoRe-1, the alloy CoRe-1B stabilizes a higher amount of $\sigma$ at the end of the thermal cycle compared to the initial amount before the thermal cycle (Fig. 4d). The difference in volume fraction is at the expense of hcp matrix phase as before (Fig. 4a) and [4]. It should be stressed, that the $\sigma$ phase content in CoRe-1B follows the same evolution as in the alloy CoRe-1, so apparently B addition has not a strong influence on the hysteresis.
Fig. 3: Evolution of hcp (a), fcc (b), Cr$_{23}$C$_6$ (c), and σ (d) phase in CoRe-1 sample between RT and 1300°C during the first and second thermal cycle. For a better overview error bars are not implemented. The error bars are +/- 1 for fcc and hcp phase, +/- 5 for Cr$_{23}$C$_6$, and +/- 6 for σ phase.
Fig. 4: Evolution of hcp (a), fcc (b), Cr$_{23}$C$_6$ (c), and σ (d) phase in CoRe-1B alloy at high temperatures at the first cycle together with a comparison of CoRe-1 sample measured at the first cycle. For a better overview error bars are not implemented. The error bars are +/- 1 for fcc and hcp phase, +/- 7 for Cr$_{23}$C$_6$ and +/- 3 for σ phase.

First tensile-load tests at 538°C, 800°C and 980°C were successfully conducted at Stress-Spec using a newly developed tensile rig equipped with a light furnace (Figure 5). The stability of the setup, which is to be used in future experiments with Co-Re alloys, was tested during tensile loading at the mentioned temperatures. In all tests the alloy failed already before plastic yielding.

Fig. 5: The installed tensile rig with the high-temperature equipment including four lamps at the neutron diffractometer Stress-Spec at FRM II. The heating shield is dismounted to provide an insight into the setup.
The results of the tensile test in the elastic region with heating at 980°C are shown for the applied stress versus lattice strain in Figure 6. The linear increase of lattice strain versus applied stress for (10-11) reflection of CoRe alloy results in a modulus of elasticity value of about 230 GPa for this lattice plane. Further these tests resulted in the optimization of the in situ heating system. During the initial test grips were partially heated together with the sample (mainly due to the limited length of 40 mm sample gauge length). Under such conditions 400°C was the maximum achievable temperature. After fabrication of the new set of samples with a longer gauge length and the fabrication of new grips made from Ni-base superalloy MarM247 and with additional cooling of grips, significantly higher temperatures were achieved in the follow-up experiments. Also, polishing of the mirrors, new high-power light source and adding simple heat shields using aluminum foil made the heating setup more efficient so that maximum temperature of $T = 980^\circ$C could be reached.

![Graph showing applied stress versus lattice strain](image)

Fig. 6: Result of first tensile test at high temperature ($980^\circ$C) with linear fit of applied stress versus lattice strain of (10-11) hcp reflection from Co-matrix.

4. Conclusion

The neutron diffraction method provided a detailed characterization of phases at high temperatures in experimental Co-Re based alloys. In particular the evolution of the various strengthening phases could be observed in-situ and quantitatively determined. The information gained through these in-situ neutron diffraction measurements is not easy to obtain through conventional microstructural studies involving ex-situ heating/cooling cycles. The second thermal cycle performed on CoRe-1 alloys brought first information on the high-temperature structure and thus on the basic stability during thermal cycling. Neutron diffraction experiments show dissolution of $\text{Cr}_2\text{C}_6$ above 1250°C, and still presence of $\text{Cr}_2\text{Re}_3$ (σ phase) at 1300°C. Performed cycling experiments yield in an increase of σ phase volume by heating in the second cycle and again increase by cooling in the second cycle. The diffraction data taken from CoRe-1B sample containing boron addition showed that the basic phase volume fraction evolution is the same as for the alloy CoRe-1 without boron. However, it is worth to note that it cannot be concluded on the morphology of the individual phases. Such a study can be done using small-angle neutron scattering and will be reported elsewhere.

The present experiment successfully tested the capabilities of the new sample environment. For the first time tensile tests close to 1000°C (i.e. at $980^\circ$C) could be performed at Stress-Spec instrument.
and we are confident that - with further minor improvements (e.g. an improved heat shielding) - a
temperature capability of 1050°C or 1100°C will be achievable.

5. Acknowledgement

The authors would like to thank Alexander Schmidt and Manfred Teufelhart for support on the high-
temperature furnace, Jens Krueger for support on the temperature control and Christian Randau on the
evaluation process [10]. The travel support to P. Strunz for the experiment in the frame of the
programme ‘Research Infrastructures’ - contracts No. CP-CSA_INFRA-2008-1.1.1-226507 (NMI3) -
is acknowledged as well. P. Strunz also acknowledges the support by MPO project FR-TI1/378. We
gratefully acknowledge financial support of the research unit 727 ‘Beyond Ni-base Superalloys’ by the
Deutsche Forschungsgemeinschaft.

6. References

[1] J Rösler, D Mukherji and T Baranski, Adv. Eng. Mater. 9, 2007 876-881.
[2] D Mukherji, M Klauke, P Strunz, I Zizak, G Schumacher, A Wiedenmann and
J Rösler, Int. J. Mat. Res., 2010, vol. 101, 340-48.
[3] D Mukherji, P Strunz, R Gilles, M Hofmann, F Schmitz, J Rösler: Materials
Letters 64 (2010), 2608-2611.
[4] D Mukherji, P Strunz, S Pieger, R Gilles, M Hofmann, M Hoelzel and
J Roesler, Met. Trans. A, submitted.
[5] D Mukherji and J Rösler: Journal of Physics: Conference Series 240 (2010)
012066 (4 pp).
[6] M Hofmann, R Schneider, GA Seidl, J Kornmeier, R Wimpory, U Garbe and
HG Brokmeier, Physica B, 2006, vol. 385 – 368, 1035-37.
[7] R Gilles, M Hoelzel, M Schlapp, F Elf, B Krimmer, H Boysen and H Fuess,
Z. Kristallogr. Suppl., 2006, vol. 23, 183-188.
[8] M Hoelzel, A Synyshyn, R Gilles, H Boysen, H Fuess
Neutron News (2007), 18, Number 4, 23-26.
[9] T Roisnel, J Rodriguez-Carvajal WinPLOTR: a Windows tool for powder
diffraction patterns analysis Materials Science Forum,
Proceedings of the Seventh European Powder Diffraction Conference (EPDIC 7),
2000, 118-123, Ed. R. Delhez and E.J. Mittenmeijer
[10] C Randau, U Garbe & HG Brokmeier, Journal of Applied Crystallography,
44(3), 2011, 641-646. doi: 10.1107/S0021889811012064.