

In Situ Neutron Diffraction Characterization of Phases in Co–Re-Based Alloys at High Temperatures

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Co–Re-based alloys strengthened by carbides are promising candidates for new high-temperature alloys for gas turbine applications. The high temperature microstructure and its stability are of utmost importance, e.g. due to strengthening-phase selection. Neutron scattering, providing *in situ* information at high temperatures, was extensively used in the past for the Co–Re alloys research. The paper focuses on TaC strengthened alloy, particularly on the stability TaC precipitates which were previously shown not to dissolve up to at least 1300 °C. Small-angle neutron scattering shows that its finer morphological variant — most suitable for high temperature strengthening — coarsened even at relatively low temperature of 1000 °C. This coarsening is faster at higher temperatures and the mean size exceeded 1000 Å (i.e. the size — detection limit of the used facility) after 4 h hold at 1200 °C.

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1. Introduction

In the development of new high-temperature alloys for gas turbine applications, various candidates are under consideration. Co–Re-based alloys [1] strengthened by carbides, or eventually by Cr₂Re₃ type σ phase, is one promising option. They are being developed to supplement the Ni-base superalloys used in gas turbine applications at very high temperatures (≥ 1473 K [1200 °C] bare metal temperature). Unlike other commercial Co-based alloys, the Co matrix in Co–Re alloys has a stable hexagonal close-packed (hcp, also denoted ϵ) structure at room temperature. Co–Re-based alloys are strengthened at high temperatures (HT) by precipitation of fine dispersion of minority phase. Therefore, the high temperature microstructure and its stability are of great importance for applications and deserve attention.

The microstructure of Co–Re alloys is rather complex [1, 2]. For example, it contains several morphological variants of Cr₂₃C₆ carbides in different size scale. One variant is the fine lamellar morphology (Fig. 1), which strengthens the alloy to temperatures up to 1000 °C.

Neutron scattering provides an excellent tool for studying structural and microstructural changes in materials *in situ* at high temperatures. Therefore, it is extensively used in the Co–Re alloy development for structural and microstructural characterization.

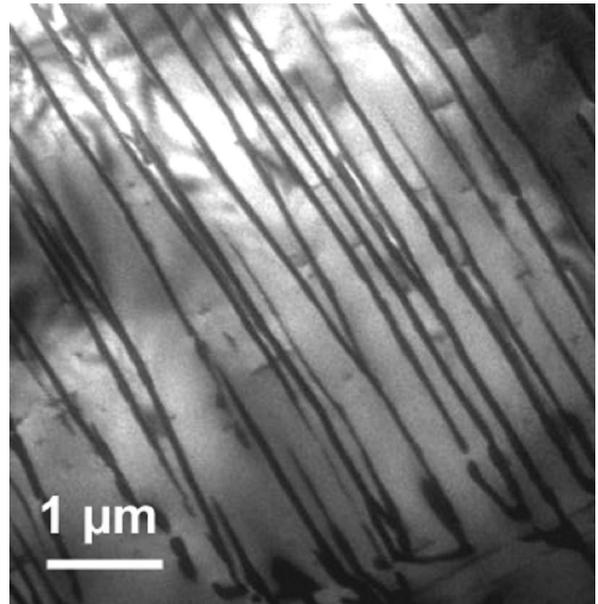


Fig. 1. Lamellar Cr₂₃C₆ type carbides in the Co–Re alloy.

Using a high-temperature vacuum furnace, *in situ* neutron diffraction study on experimental Co–Re alloy hardened by Cr₂₃C₆ carbides (the experimental alloy denominated CoRe-1, composition Co–17Re–23Cr–2.6C, in at.%) showed that the matrix undergoes a hexagonal close packed to face-centered cubic (hcp \leftrightarrow fcc) allotropic transformation when heating to high temperature (above

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1160 °C) [2]. Furthermore, it was found that this transformation has a large hysteresis (≈ 100 K) and, therefore, it takes place in a rather broad temperature range 1130 to 1260 °C.

It was also shown using neutron diffraction that the matrix transformation and hysteresis could be significantly influenced by element additions. In the ternary alloy Co-17Re-23Cr with 200 ppm (weight) boron addition, which does not contain any carbides, the matrix phase transformation from hcp to fcc structure takes place in the temperature range from 1548 to 1673 K (1275 to 140 °C) [3]. It means that the transformation is shifted to much higher temperature when compared to the CoRe-1 alloy and also the hysteresis is substantially narrower (≈ 50 K). Because any instability in the matrix during service of the Co-Re alloys is undesirable, these observations are positive with respect to the high-temperature application of the Co-Re alloys and give room for fine tuning of the alloy design. The boron addition also strongly influences the amount and stability of the σ phase (which is another potential strengthening phase) in the alloy.

High-temperature cycling experiments up to 1300 °C performed *in situ* on Co-Re alloys in parallel with neutron diffraction measurements (FRM II neutron source, Garching) described in detail not only the hcp \leftrightarrow fcc phase transformation of the matrix [2], but also the evolution of minority phases during the repeated thermal cycles [2, 4, 5]. It was found that a candidate for strengthening — Cr_{23}C_6 carbides — dissolves during the hcp \leftrightarrow fcc phase transformation above 1200 °C in the CoRe-1 alloy and re-appears only on cooling below 1140 °C (following the hysteresis of the matrix). It was also observed by small-angle neutron scattering (SANS) [6] that Cr_{23}C_6 lamellae coarsen already at relatively low temperature of 1000 °C. Cr_{23}C_6 carbides alone are thus not suitable for HT strengthening, despite their fine lamellar morphology.

Therefore, a new step in the alloy development was to add tantalum in order to produce TaC carbides. It is known that MC-type carbides are generally more stable than M_{23}C_6 carbides. The new alloy (Co-17Re-23Cr-1.2Ta-2.6C) was designated CoRe-2. By means of a suitable heat treatment, very fine (< 300 Å) TaC precipitates can be dispersed uniformly [7]. Such a microstructure is promising as it is ideal for providing creep resistance due to the interaction of the TaC precipitates with dislocations.

A complex microstructure develops in this Ta-carbide strengthened CoRe-2 alloy (see e.g. [4, 8]). Various morphological variants of TaC and Cr_{23}C_6 carbides as well as Cr_2Re_3 -type σ phase are present in the microstructure. In the standard heat treated CoRe-2 alloy, Cr_{23}C_6 -type and TaC carbides are actually present in very different size scales — as large grain boundary or blocky carbides and as very fine lamellar or globular precipitates. Figure 2 shows the fine dispersion of TaC which is embedded in ϵ Co matrix. In the CoRe-2 alloy, these precipitates appear between the Cr_{23}C_6 lamellae. The fine

precipitates can provide the high temperature strengthening. Nevertheless, a long term stability of this microstructure at high temperatures is important for gas turbine applications and has to be examined.

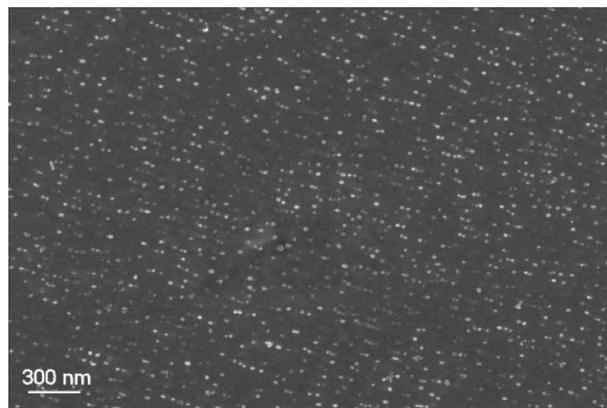


Fig. 2. SEM image of the CoRe-2 alloy sample: fine dispersion of TaC carbides.

Unlike Cr_{23}C_6 carbides and σ phase, the TaC phase in the CoRe-2 alloy seems to be stable up to at least 1300 °C as its volume fraction determined by *in situ* wide angle neutron diffraction did not change significantly during heating, and even the matrix transformation does not influence it [2, 4]. It has to be, however, noted that several morphological variants of TaC are present in the alloy: fine globular particles seen in Fig. 2 (suitable for strengthening), large Chinese-script-like precipitates at and near grain boundaries and blocky carbides within grains. Wide angle neutron diffraction cannot distinguish these morphological variants clearly.

Investigation of possible coarsening of fine TaC carbides is a task for *in situ* SANS. During the first experiments focused on the TaC morphology and stability at HT [8], it was found that the SANS curves change during the hold at 1200 °C. The model composed of lamellar Cr_{23}C_6 carbides, spherical fine TaC, and large particles giving asymptotic scattering was used for the evaluation. The results [8] indicated that the TaC carbides coarsen during the hold at 1200 °C.

In the present paper, it was tested using SANS [9] technique how the fine TaC precipitates in CoRe-2 alloy evolve during the hold at various temperatures between 1000 and 1300 °C.

2. Experimental

Ta carbide strengthened CoRe-2 alloy (Co-17Re-23Cr-1.2Ta-2.6C) was melted in a vacuum arc furnace and cast in solid Cu molds. The cast bars were homogenized under vacuum in three steps in the temperature range 1623–1723 K (1350–1540 °C) for 15 h (referred to as ST heat treatment) to remove strong segregation of heavy elements in the cast structure. The samples of around 1 mm thickness were heated up to either 1000

(sample denoted y), 1100 (v), 1200 (w), 1260 (u), or 1300 °C (z) and held for 4 h at the high temperature using special high-temperature vacuum furnace. During the hold, *in situ* SANS measurement was carried out. The pinhole SANS-II facility [10] at SINQ (PSI Villigen) was used for the measurement (some preliminary tests were also performed at NPL lab of CANAM, NPI Řež, Czech Republic [11]).

The scattering data were collected at several (reproducible) experimental geometries of the instrument during the hold at a particular temperature, i.e. the measurements at various geometries were done with the same sample. The data acquisition time for one SANS pattern (i.e. at a given geometry) was 10 min, which enables to see possible microstructural change during the hold at a given temperature, which extended for 4 h.

The sample-to-detector distance was varied from 1.2 m to 6 m and the neutron wavelengths λ of 6.3 Å and 10.5 Å were used. The full covered range of scattering vector magnitude Q ($Q = |\mathbf{Q}| = |\mathbf{k} - \mathbf{k}_0|$, where \mathbf{k}_0 and \mathbf{k} are the wave vectors of the incident and of the scattered neutrons, respectively, and $|\mathbf{k}| = |\mathbf{k}_0| = 2\pi/\lambda$), was $5.0 \times 10^{-3} \text{ Å}^{-1}$ – 0.125 Å^{-1} (i.e. $5.0 \times 10^{-2} \text{ nm}^{-1} < Q < 1.25 \text{ nm}^{-1}$). The measured raw data were corrected for background scattering and calibrated to absolute scale using the measurement of the (attenuated) primary beam [12]. In this way, macroscopic differential cross-section $d\Sigma/d\Omega(Q)$ was obtained.

3. Results and discussion

A selected set of measured scattering curves is displayed in Fig. 3.

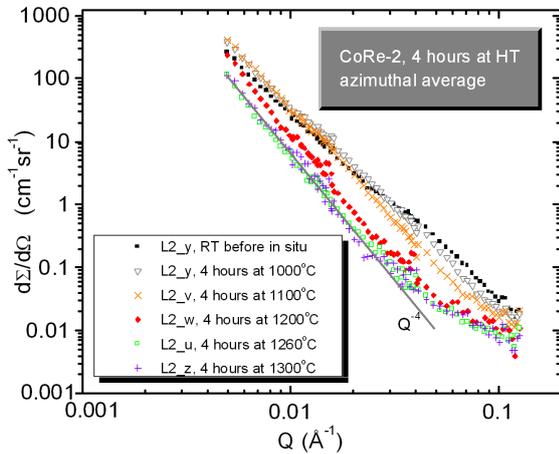


Fig. 3. Selected scattering curves: samples held for 4 h at HT.

It can be seen that relatively large scattering intensity exists at large Q -values for the ST sample measured at RT before *in situ* heating. It is the same result as the one already reported on a different CoRe-2 sample earlier [8]. The RT scattering data cannot be described

adequately by only one log-normal size distribution of inhomogeneities. Altogether three components has to be considered: (i) fine globular TaC particles, (ii) fine lamellar Cr_{23}C_6 carbides, (iii) scattering from large particles (including σ phase, large Chinese-script like TaC and large Cr_{23}C_6 carbides which are over the size-detection limit of the used SANS facility) giving Porod-law scattering (Q^{-4} dependence). Constant incoherent background has to be considered as well. For better understanding the individual contributions, the model scattering curves corresponding to the individual contributions are shown in Fig. 4.

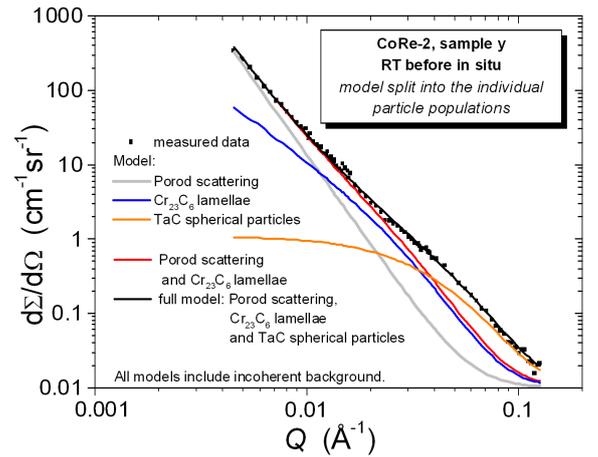


Fig. 4. Model split of the scattering contributions from the individual particle populations.

For samples held for 4 h at all tested temperatures (Fig. 3), evolution of the scattering curves is clearly visible. It should be noted that one plate-like sample (cut from the same specimen bar) was used for one high-temperature test. For the sample denoted y (which was held at 1000 °C), scattering at largest Q -values decreases with hold time and shifts towards lower Q region. Importantly, it is not possible to describe the change of the scattering curve at 1000 °C without considering coarsening of both the fine lamellar Cr_{23}C_6 carbides as well as the globular TaC precipitates. The coarsening is even more pronounced when the temperature of hold is 1100 °C (sample denoted v).

At and above 1200 °C, the scattering after 4 h hold fulfills the Porod law in the measured Q -range (additionally, flat incoherent scattering background has to be also taken into account for Q values $> 0.03 \text{ Å}^{-1}$). Therefore, it can be deduced that all the precipitate sizes exceed 1000 Å and thus contribute only to the asymptotic part of the scattering.

At 1200 °C, the Porod scattering is more intense than at 1260 °C and at 1300 °C (Fig. 3). It is in agreement with the fact that Cr_{23}C_6 phase dissolves above 1200 °C [2, 4]. At 1260 °C and 1300 °C, the only remaining large particles causing the Porod scattering are σ phase and large TaC, whereas large Cr_{23}C_6 carbides (which were still

additionally contributing to the scattering at 1200 °C) are dissolved at these temperatures. The dissolution of Cr_{23}C_6 carbides above 1200 °C can be also indirectly deduced from the data measured at RT after HT exposure (data not shown here due to the limited space). The strong scattering increase is observed after cooling from 1260 as well as 1300 °C (due to re-precipitation of Cr_{23}C_6 lamellae), whereas no change is observed after cooling from 1000 and 1100 °C. Small increase is observed after cooling from 1200 °C, which probably indicates that Cr_{23}C_6 carbides were partially dissolved during the 4 h hold at 1200 °C.

There is no significant difference between the scattering intensity for 4 h hold at 1260 °C and at 1300 °C. It means that no dissolution of any minority phase occurred between 1260 °C and 1300 °C and, also, that the coarsening of the remaining large precipitates is not significantly different for these two temperatures.

TABLE

TaC fine precipitates – parameters determined by SANS.

CoRe-2 sample	T [°C]	hold time [h]	mean diam. [Å]	volume frac. [%]
y	RT		76	0.33
y	1000	1	102	0.32
y	1000	4	147	0.33
v	1100	1	182	0.33
v	1100	4	560	0.35
w	1200	1	970	0.33
w	1200	4	> 1000	

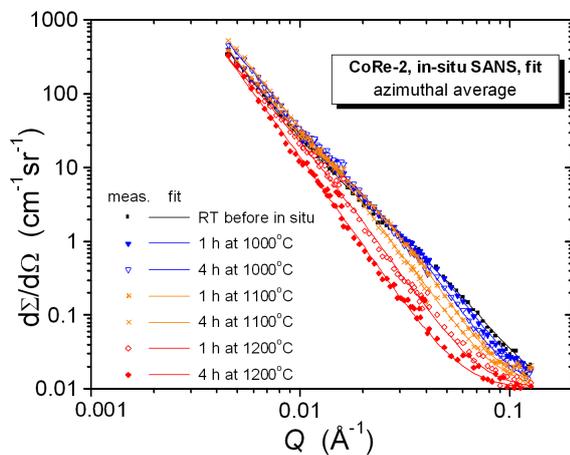


Fig. 5. The measured and fitted scattering curves at RT, 1000, 1100, and 1200 °C.

The fitted scattering curves for the measurements which exhibit an additional scattering above the Porod scattering (i.e. measurements at RT, 1000 and 1100 °C and 1 h hold at 1200 °C) are displayed in Fig. 5. The resulting volume fractions and mean sizes (volume weighted) of fine TaC precipitates from these fits are

summarized in the Table. The volume fraction of TaC particles was determined assuming a scattering contrast of $2.68 \times 10^{10} \text{ cm}^{-2}$ for TaC (stoichiometric composition) in the Co–Re–Cr matrix solid solution [8].

4. Conclusions

Co–Re-based alloys have been extensively investigated by neutron diffraction and small-angle neutron scattering for the last few years. Stability of matrix and of the minority phases was studied.

As Cr_{23}C_6 carbides were found unstable at temperatures above 1000 °C, experimental Co–Re alloy containing TaC precipitates for strengthening at higher temperatures was introduced. Wide angle measurements showed that very large precipitates of the TaC phase do not dissolve up to at least 1300 °C. However, small-angle neutron scattering showed that its finer morphological variant most suitable for high temperature strengthening — i.e. the fine globular TaC precipitates of less than 300 Å size — coarsened even at relatively low temperature of 1000 °C. This coarsening is faster at higher temperatures and the mean size exceeded 1000 Å at 1200 °C (4 h hold). They are therefore not detected in the present *in situ* SANS measurements at temperatures of 1260 °C and 1300 °C due to the limited Q range.

Acknowledgments

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