



Strain induced decomposition and precipitation of carbides in a molybdenum–hafnium–carbon alloy



C. Pöhl^{a,*}, D. Lang^{a,b}, J. Schatte^c, H. Leitner^{a,b}

^a Department of Physical Metallurgy and Materials Testing, Montanuniversität Leoben, Franz-Josef-Straße 18, 8700 Leoben, Austria

^b Christian Doppler Laboratory for Early Stages of Precipitation, Montanuniversität Leoben, Franz-Josef-Straße 18, 8700 Leoben, Austria

^c PLANSEE SE, Metallwerk-Plansee-Straße 71, 6600 Reutte, Austria

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ABSTRACT

In the present study of a sintered and thermo-mechanically processed Mo–Hf–C (MHC) alloy the strain induced decomposition of Mo–carbides and subsequent precipitation of Hf–carbides was revealed. The microstructural characterization was performed with atom probe tomography (APT), transmission electron microscopy (TEM), X-ray diffraction (XRD) and optical light microscopy (OLM). During annealing of deformed conditions it can be shown by TEM analysis that Hf–carbides were preferentially formed on dislocations and occasionally on (sub)grain boundaries. XRD and OLM investigations revealed that the required C for the Hf–carbides was delivered by the decomposition of Mo–carbides which are originally located at former grain boundaries in the as-sintered condition. It has been shown that for this decomposition mechanical strain prior to annealing was required. In the early stages of precipitation APT analyses revealed a significant segregation of C and Hf atoms to dislocations and boundaries. Finally, the authors deduced that due to the dislocation–precipitation interaction the misfit strain was effectively reduced and therefore, the Hf–carbides are located on dislocations and (sub)grain boundaries.

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1. Introduction

In order to utilize entirely the high temperature potential for structural applications, it is essential to increase the strength of pure molybdenum. An effective way to achieve higher strength at elevated temperatures is the realization of second phase particles in the matrix. In the case of molybdenum, rare metal oxides (La_2O_3 , Y_2O_3) and group IV monocarbides (TiC, ZrC, HfC) are effective second phase particles [1–4]. Due to the higher solubility of the alloying elements Ti, Zr, Hf and C compared to La, Y and O, these Mo alloys are heat treatable. Therefore, the advantage of carbide strengthened Mo alloys can be found in their processability. In the present study the material of interest is a particle strengthened molybdenum–hafnium–carbon alloy denoted as MHC, which is powder metallurgically produced. The main field of application is for metal forming tools such as extrusion dies and dies for isothermal forging of superalloys and titanium alloys. Recent applications of MHC are rotating anodes for X-ray tubes in medical devices [4].

Intensive research in the 1960s revealed that ZrC, TiC and HfC are effective strengthening particles in molybdenum. Hafnium–carbide possesses the highest energy of formation, which is an essential requirement at elevated temperatures for dispersed second

phase particles [1,5–14]. Ryan and Martin [15] investigated the hardening behavior of solution annealed and aged Mo–Hf–C, Mo–Zr–C and Mo–Ti–C alloys which contained 1 vol.% of the relevant carbides. The Mo–Hf–C alloys showed the highest peak hardness and a homogeneous distribution of HfC in the molybdenum matrix. Furthermore, they revealed that Mo–Hf–C alloys show a classical progressive hardening response with time, i.e. peak hardness and over-aging behavior. The most extensive study of Mo–Hf–C alloys was performed by Raffo [16,17]. In this work, the alloys were studied in the solution annealed condition and in several aged conditions. Additionally, Raffo investigated the as-swaged and the recrystallized conditions. It has been shown that molybdenum alloys, which were strengthened with HfC, possess a significant higher strength than those strengthened with niobium, titanium and zirconium–carbides. However, the former studies dealt with arc-melted Mo–Hf–C whereby the main interest was focused on the mechanical properties such as strength and creep resistance. Solely Ryan and co-workers [15,18] have reported that Hf–carbides precipitate homogeneously in the Mo matrix during aging of an arc-melted and supersaturated material. Furthermore, Raffo [16,17] has observed that small prestrains of the solution annealed condition increase the strength at higher temperatures. However, the literature does not report the formation mechanism of HfC particles in sintered and thermo-mechanically processed Mo–Hf–C alloys. Only in other molybdenum based alloys the precipitation mechanism of carbides was investigated. For example,

* Corresponding author. Tel.: +43 3842 402 4214; fax: +43 3842 402 4202.

E-mail address: Christopher.Poehl@unileoben.ac.at (C. Pöhl).

Ryan and Martin [15] reported that carbides precipitate uniformly at dislocations in Mo–Zr–C alloys, although general matrix precipitation also occurred.

Thus, the overall aim of the present study was to carry out fundamental investigations of the Hf-carbides precipitation mechanism during thermo-mechanical processing of sintered MHC. In contrast to former studies, the alloying elements, Hf and C, are not entirely dissolved in the matrix of the starting condition (as-sintered MHC) [19]. However, the distribution of Hf and C in the as-sintered condition plays a key role for the precipitation mechanism of Hf-carbides during thermo-mechanical processing. Therefore, the present work was focused on the distribution of Hf and C and in a further consequence on the evolution of the Hf-carbides during thermo-mechanical processing. Within this study atom probe tomography (APT), transmission electron microscopy (TEM), X-ray diffraction (XRD) and optical light microscopy (OLM) investigations were carried out.

2. Experimental

The starting condition of the MHC specimens was manufactured via powder metallurgy. The details of sintering are shown elsewhere [19]. The total composition of the sintered MHC is listed in Table 1. The as-sintered MHC was thermo-mechanically processed without prior solution annealing. Two different thermo-mechanical processes were carried out to investigate the precipitation mechanism. From the first process three different conditions (i, ii, ii') with the following parameters were studied:

- (i) Forging at 1300 °C to a reduction of 24% (in height) and then quenched to room temperature with approximately 100 K/s.
- (ii) Forging at 1300 °C to a reduction of 24% (in height) followed by an annealing for 50 min at 1600 °C and then quenched to room temperature with approximately 100 K/s.
- (ii') The identical temperature regime as for condition (ii) was carried out but without deformation.

From the second thermo-mechanical process the condition (j) was investigated:

- (j) Forging was carried out at 1100 °C to a reduction of 80% (in height) followed by an annealing for 12.5 h at 1200 °C and then cooled to room temperature with air in turbulent flow.

OLM and XRD investigations were performed to track qualitatively the molybdenum carbide (Mo₂C) content of the different conditions. In the case of the OLM investigations the specimens were etched with the color etchant according to Hasson [20]. OLM micrographs of the etched specimens were taken with a Zeiss Axio Imager M1m. XRD patterns were recorded using a Bruker-AXS D8 Advance diffractometer. The specimens were investigated in Bragg-Brentano geometry ($\theta/2\theta$ -mode) from 25° to 80° with a step size of 0.02° using a Cu K α radiation. In terms of the preparation, the specimens were mechanically ground and polished. The detailed description of the preparation technique is given in [19]. In addition, the specimens for XRD were electropolished using the electrolyte Struers A3 at 293 K and an operating voltage of 28 V.

In order to perform TEM investigations, specimens of 3 mm in diameter were ground and polished to a thickness of 80 μ m. The final preparation step was done by electropolishing in a twin jet apparatus using a solution of 12.5 vol.% H₂SO₄ in ethanol at 268–273 K [11]. The applied voltage for polishing was 18.5 V. Conventional TEM investigations were performed with a Philips CM12 microscope operated at 120 kV. Quantitative energy dispersive X-ray spectroscopy (EDS) was carried out with an EDS system from EDAX. The TEM studies were carried out in bright field imaging mode. To obtain crystallographic information, high resolution TEM investigations were performed with a FEI TECNAI F20 operated at 200 kV.

The sharp needle-shaped specimens for APT analysis were produced by electropolishing with an electrolyte of 12.5 vol.% H₂SO₄ in ethanol at room temperature. Final sharpening of the tips was performed with a FEI VERSA 3D DualBeam microscope. In the course of focused ion beam (FIB) preparation the tips were annular milled with 30 kV and then cleaned with 5 kV and 2 kV to limit the Ga⁺ ion implan-

tation. APT analyses were performed with a LEAP 3000 \times HR from Cameca, former Imago Scientific Instruments. The measurements of the as-sintered MHC, the conditions (i), (ii) and (ii') were carried out in voltage mode at a specimen temperature of 60 K with a pulse fraction of 15% of the standing voltage and a pulse frequency of 200 kHz. In the case of the higher deformed condition (j) laser mode at 60 K was used for the APT measurements. The laser energy was set to 0.6 nJ using a pulsing frequency of 200 kHz. The analysis of the datasets was done with the software package IVAS 3.4.3 from Cameca by making a background correction in the mass to charge state ratio (m/n) spectra. Frequency distribution analysis was carried out to obtain information on the elemental distribution in the analyzed volume [21]. Enriched regions in the analyzed volume, such as solute segregations at dislocations and boundaries, were defined with isoconcentration surfaces. On the basis of these isosurfaces, proximity histograms were calculated to obtain information on the average elemental composition of these regions [22–24].

3. Results

3.1. XRD and OLM characterization

In previous investigations of as-sintered MHC it was shown that the XRD and OLM technique is able to detect the Mo₂C phase [19]. In the present study XRD and OLM was used to reveal qualitatively the evolution of the Mo₂C content during the thermo-mechanical process.

In Fig. 1 the XRD patterns of the as-sintered state, the conditions (i), (ii), (ii') and (j) are shown. Based on the chemical composition (see Table 1), the peaks with lower intensity can be identified as monoclinic hafnium dioxide (HfO₂), hexagonal molybdenum carbide (Mo₂C) and face centered cubic hafnium carbide (HfC) [25–27]. The peaks with higher intensity are related to the matrix of the material (2θ : 40.5°, 58.6° and 73.7°) [28]. The slight shift of the HfC peaks to higher diffraction angles 2θ is caused by the fact that a certain amount of Hf and C was substituted [29]. The peaks for HfO₂ and Mo₂C are at the expected positions. From the XRD pattern of condition (i), directly after forging of the as-sintered MHC, it is obvious that HfC, HfO₂ and even Mo₂C still exist. Since a deformation was introduced in the as-sintered condition, the relative intensities of the matrix peaks have changed and peak broadening occurred. The XRD pattern of condition (ii) indicates that all Mo₂C peaks completely disappeared during annealing of the forged condition. In contrast to condition (ii'), which was only annealed without deformation, Mo₂C peaks are still present. In condition (j) the Mo₂C peak with the highest intensity ($2\theta = 39.39^\circ$) overlaps with the Mo-matrix peak at $2\theta = 40.5^\circ$ due to peak broadening caused by the deformation. Nevertheless, some of the remaining

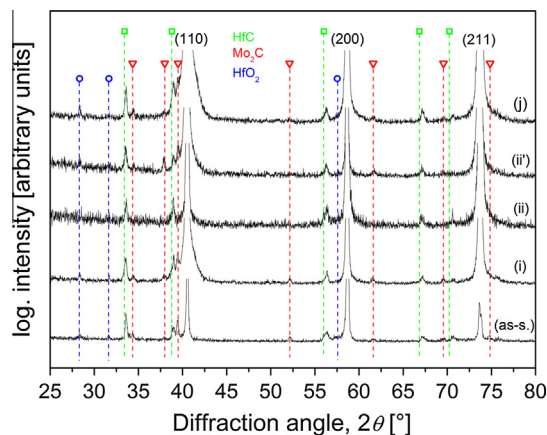


Fig. 1. XRD patterns of the following conditions: as-sintered, (i), (ii), (ii') and (j). Green line → face centered cubic HfC, red line → hexagonal Mo₂C, blue line → monoclinic HfO₂. The peaks at 2θ angles of 40.5°, 58.6° and 73.7° are related to the Mo matrix. (For interpretation of the references to color in this figure legend, the reader is referred to the web version of this article.)

Table 1

Chemical composition of the MHC alloy (at.%).

Hf	C	O	Zr	W	Mo
0.64	0.65	0.22	0.0025	0.0090	balance

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