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Microstructure and phase stability of W-Cr alloy prepared by spark plasma sintering

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ABSTRACT

Tungsten alloys currently represent prospective candidates to replace tungsten in the first wall applications in future fusion facilities. Tungsten has many advantageous features; however, it is rather susceptible to oxidation at temperatures above around 500 °C. To mitigate/suppress this, various oxide-forming elements are being added to tungsten to induce self-passivation. The most common ones are chromium, titanium and silicon. The alloyed powder is frequently prepared by mechanical alloying and then consolidated by a sintering method. Most of the published results are related to alloys consolidated by HIP process that leads to formation of multiphase material. In the presented study, W-10Cr alloy with hafnium oxide particle dispersion was prepared by spark plasma sintering. Unique features of the microstructure are discussed and compared with other processing methods Phase and thermal stability of the alloy was evaluated at three fusion-relevant temperatures using detailed X-ray diffraction analysis, differential thermal analysis and microstructural observations in a scanning electron microscope. Impact of the heat treatment on crucial properties such as thermal conductivity and heat capacity was evaluated.

1. Introduction

Tungsten alloys currently represent prospective candidates to replace tungsten in the first wall applications in future fusion facilities. They are anticipated to suppress unfavorable mechanical properties of commercially pure tungsten and/or to gain additional properties such as ability of self-passivation under accidental conditions. The self-passivating alloys are designed to minimize possible accident consequences related mainly to a LOCA (Loss of Coolant Accident) event with simultaneous air ingress into the reactor vessel. A LOCA would lead to a temperature rise of the in-vessel components up to 1200 °C (depending on the reactor design) due to the nuclear afterheat [1]. In the case of tungsten at temperatures above 500 °C, presence of air or water in the reactor may lead to chemical reactions producing volatile tungsten trioxide which would be the cause of mobilization and potential release of radioactivity. Unlike pure tungsten, self-passivating tungsten alloys contain additions with the ability to form compact and thermally stable oxide scale. As soon as the oxide scale is formed, activated tungsten oxides cannot be released to the surroundings.

The main oxide-forming elements added to tungsten are chromium, titanium and silicon [2–5]. Promising results have been achieved by alloys with chromium addition in the amount of 10–12 wt.% and prepared by magnetron sputtering [3,6,7]. Nevertheless, layers produced by this method are very thin and therefore not suitable for application in fusion reactor. Such an amount of Cr can be dissolved in W lattice also by mechanical alloying; however, subsequent powder consolidation by conventional methods frequently leads to decomposition of the solid solution to secondary phases [4]. For example, W-Cr materials produced by HIPping at temperatures between 1200 and 1300 °C contain isolated islands of Cr-rich regions with tungsten regions depleted of Cr. Generally, formation of Cr-rich regions is unfavorable due to low melting point of the phase, susceptibility for oxidation, and related decreased content of Cr in tungsten matrix. Thus, current efforts are focused on fast sintering techniques such as spark plasma sintering. First W-Cr-Y alloys currently show the best achieved passivation properties [6].

Surface temperature of tungsten on the first wall is predicted to be in the range of 500–1300 °C, depending on the chosen cooling concept [8]. Generally, it is necessary to understand the behavior of the new materials in the whole temperature range including specific

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temperatures around 1000 °C that are predicted for accidental conditions of vessel with water-cooled concept.

In the presented study, W-10Cr alloy with hafnium oxide particle dispersion was prepared by spark plasma sintering. Hafnium was used as alternative element to yttrium to control grain size. The study aims to point on unique features of the microstructure of the W-Cr materials prepared by spark plasma sintering and discuss consequences of long high temperature exposure. Phase and thermal stability of a W-Cr alloy was evaluated last in few papers from 60 s and 70 s [9–11]. The presented study continues the analysis evaluation of W-Cr alloys using modern SEM and XRD and points out important issues in the alloy behavior that might be relevant for their application in a fusion device. Moreover, the study was complemented with evaluation of heat treatment effect on crucial properties such a thermal conductivity. Phase stability and thermal properties are important to study for any fusion relevant W-Cr system and the information can be used for further development of the alloys.

2. Materials and methods

The alloyed powder was prepared in a planetary ball mill Pulverisette 5 (Fritsch, D) from the following powders: W (1.2 µm average powder size, purity > 99.5%), Cr (0.4 µm average powder size, purity > 99%) and Hf (bimodal 15 and 45 µm, purity > 99.2%). The powders were processed in tungsten carbide vials with tungsten carbide grinding balls with ball to powder ratio 11: 1. Argon was used as a protective atmosphere preventing oxidation during the milling process. The overall milling time for a W-10Cr-1Hf (wt%) alloy was 28 h at a speed of 240 rpm. A spark plasma sintering machine SPS 10-4 (Thermal Technology, USA) was used to consolidate the mechanically processed powder at 1750 °C and 70 MPa with 3 mins hold time at the sintering temperature; tungsten foil surrounding the sintered powder was used as a carbon contamination barrier.

Images of polished cross-sections were acquired using a scanning electron microscope EVO MA 15 (Carl Zeiss SMT, D) equipped with a SDD detector XFlash® 5010. Annealing was performed in a vacuum furnace (less than 1 Pa vacuum was achieved) at 700 °C, 1000 °C and 1200 °C for 10, 20 and 40 h. The heating rate to annealing temperature was 5 °C/min, the cooling to 700 °C was performed at controlled rate of 5 °C/min, and then the furnace was cooled down freely to room temperature. Annealing at 700 °C represents the temperature of tungsten at steady state reactor operation, whereas 1000 °C and 1200 °C represents rather accidental conditions. The sintering temperatures are marked with respect to the appropriate alloy composition in the miscibility gap of the W-Cr phase diagram (Fig. 1). The coexistence line, i.e. the boundary between one phase region and the miscibility gap and the chemical spinodal line, i.e. the boundary between the nucleation and growth and spinodal region was calculated using FactSage software.

The microstructural features were evaluated by means of image analysis using ImageJ software. The porosity was measured via area analysis and the grain size via Average Grain Intercept Method.

Identification of crystalline phases and quantification of their amount was done by X-ray diffraction (XRD). The measurements were carried out on vertical powder θ-θ diffractometer D8 Discover (Bruker AXS, Germany) using CuKα radiation and 1D LynxEye detector (Ni β filter in front of the detector). A parallel X-ray beam with the radius of 1 mm was formed by polycapillary unit and aimed at the cross section of vertically cut samples. Subsequent quantitative Rietveld refinement analysis [12] was performed in TOPAS V5 [13] including the corrections for high statistics powder diffraction pattern such as absorption edge of β filter and tube tails [14]. The lattice parameter of BCC phases of W-Cr solid solutions were fitted first and based on the values found in review article [15] the occupancy of BCC atomic sites was modelled by the ratio of W and Cr to ensure the correct density and therefore weight percentage of these phases.

Thermal conductivity was calculated from the measurements of the thermal diffusivity, density and heat capacity. Thermal diffusivity of the samples was measured by laser flash apparatus LFA 1000 (Linseis, Germany). The samples were sprayed with colloidal graphite to ensure complete and uniform absorption of the laser pulse and similar surface radiative characteristics for all samples. Five thermal diffusivity measurements ("laser shots") were made at RT and then at each temperature in the range from 100 to 1300 °C at the intervals of approximately 200 °C. In order to detect, if present, any influence of processes caused by the high temperature exposure, the thermal conductivity was measured up to the maximum possible temperature (1st LFA cycle), then samples were remeasured twice (2nd LFA and 3rd LFA cycle). The heat capacity values were also measured by the LFA with the pure tungsten as a reference material. The density of the samples was measured by the Archimedes method.

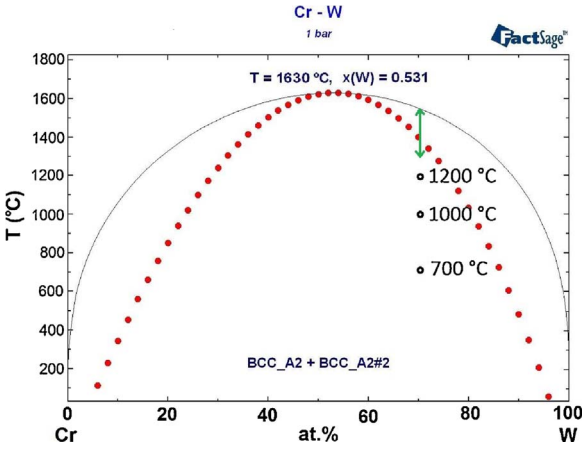

Fig. 1. Miscibility gap of W-Cr phase diagram consisting of the coexistence line (full dark line) and the chemical spinodal line (dotted red line); calculated using FactSage. (For interpretation of the references to colour in this figure legend, the reader is referred to the web version of this article.)

Thermal behavior of the sintered W-10Cr-1Hf alloy was analyzed under different thermal conditions using an STA-504 instrument manufactured by TA instruments. The differential thermal analysis (DTA) was carried out at the heating rate of 3 °C/min from 50 °C to 1600 °C in Ar atmosphere with a flow rate of 5 l/h. The analysis was performed on about 90 mg sample with an empty reference crucible. The experiments were repeated twice to ensure reproducibility.

3. Results and discussion

3.1. Microstructure and phase content of as-SPSed W-10Cr-1Hf alloy

According to the phase diagram (Fig. 1) the prepared alloy falls into the region of the miscibility gap, therefore it can be expected that the microstructure will be formed by the W-rich regions and Cr-rich regions. However the matrix of the W-10Cr-1Hf alloy consists of only one phase (Fig. 2); the second phase apparent from Fig. 2 is Hf-rich particles at matrix grain boundaries. XRD analysis identified the matrix as W-Cr solid solution and the particles as HfO_2 in monoclinic form (Fig. 3a); presence of other phases was under the detection limit (Table 1). Therefore, W-Cr solution formed by mechanical alloying was preserved during sintering by SPS and no chromium was expelled to form Cr-rich phase. Such phase composition is unique, as processing by conventional sintering methods such as HIP leads to the development of a Cr-rich phase [2,4,5]. In order to increase the amount of Cr dissolved in W matrix of as-HIPped samples, further post-processing by high temperature annealing must be applied [2] whereas SPS process involves short sintering times and high temperatures that are favorable for maintaining the full solid solution prepared by mechanical alloying.

The W-Cr matrix consists of equiaxed grains with average size of 5 µm (Table 2). The grain size was influenced by pinning effect of HfO_2