Materials Characterization xxx (xxxx) xxx–xxx

Contents lists available at ScienceDirect

Materials Characterization

journal homepage: www.elsevier.com/locate/matchar

The role of tungsten phases formation during tungsten metal powder consolidation by FAST: Implications for high-temperature applications

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ARTICLE INFO

Keywords:
Fusion
FAST
Tungsten
Tungsten oxide
Electron microscopy
Microstructure

ABSTRACT

Tungsten is a candidate material for the demonstration fusion power plant DEMO. To ensure high density and structural stability, Field-Assisted Sintering Technique (FAST) is proposed as a consolidation method. This study discusses the formation of phases during sintering of tungsten by the FAST. Scanning electron microscopy, X-ray diffraction and transmission electron microscopy were used to evaluate the microstructure in tungsten-based materials. The results of microscopic examinations revealed the *in-situ* formation of tungsten oxide and a formation of tungsten carbide shell around tungsten core. Tungsten carbide-rich shell is formed due to the carbon diffusion from the graphite die used in the FAST into tungsten at high temperatures. In contrast to easy removal of tungsten carbide shell by mechanical grinding, the formation of tungsten oxide in the W-matrix can influence the performance of such material when used as plasma-facing material in the fusion reactor. High-temperature experiments at 1873 K showed that tungsten-oxide phase starts to decompose, which results in material degradation and formation of voids and surface blisters.

1. Introduction

It is expected that fusion power will significantly contribute to clean and safe energy supply for future generations [1]. To achieve high efficiency and safe operation of future fusion power plants, researchers are putting much effort into the selection and optimisation of suitable functional materials capable of withstanding the extreme conditions within the fusion reactor [2]. One of the key challenges is to find a suitable plasma-facing material for the divertor [3], which will be exposed to high transient thermal events, neutron irradiation and helium and hydrogen isotopes irradiation. Tungsten (W) is a promising material for fusion applications due to its high melting point (3695 K), high thermal conductivity (174 $Wm^{-1}K^{-1}$ at 300 K), low thermal expansion coefficient ($4.32 \times 10^{-6} K^{-1}$ at 300 K), low sputtering yield and low tritium retention [4]. Its main disadvantage is relatively poor oxidation resistance; hence, hydrogen reduction atmosphere or vacuum conditions during sintering are required. Vacuum-assisted sintering is used to provide, oxygen-free atmosphere, reduced adsorption of oxygen on the surface of starting W powder, which should consequently result in a defect-free single phase tungsten microstructure. This type of sintering effects the mechanical properties of tungsten by improvement in hardness, yield strength and ultimate tensile strength [5]. Densification of W by a conventional solid-state sintering process in the reductive atmosphere requires high temperatures and lengthy sintering time due to the high melting point of W. However, this often results in W microstructure with an included porosity which will decrease the mechanical properties, such as strength at elevated temperatures [2,4]. To improve the material's density, additional processing such as forging, swaging or rolling is required [4,5].

Recently, an alternative sintering method, named *Field-Assisted Sintering Technique* (FAST), was proposed to improve the sinterability of W and to minimise grain growth during the sintering process. FAST offers vacuum environment under uniaxial compression and rapid consolidation of powders, which are heated directly by a low-voltage, high-intensity current flowing through the die and through the sample itself [5–7]. Short sintering time, the order of magnitude shorter than in conventional sintering prevents or minimises tungsten grain growth during the sintering [5–7]. Finer grain size can improve mechanical properties, such as microhardness and bending strength [2]. Furthermore, sintering under an applied pressure leads to higher materials' densities. However, FAST sintering of W has also some drawbacks, such as the formation of the external shell from the FAST graphite tooling

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https://doi.org/10.1016/j.matchar.2018.02.022
Received 5 December 2017; Received in revised form 14 February 2018; Accepted 14 February 2018

setup [7]. Moreover, secondary phases, if formed during the FAST sintering of tungsten, are usually nano-sized and scarce; therefore, their detection and identification may be rather difficult. Nevertheless, the identification of such phases and their structural stability at elevated temperatures is a prerequisite for materials used in fusion plasma-applications [2]. The normal operation temperature of tungsten is currently thought to be limited on one side by the ductile to brittle transition temperature (DBTT), which defines the minimum operation temperature, and the recrystallization of W, which on the other side defines an upper limit in the range of ~1473–1573 K [8]. The presence of impurities, such as trace amounts of oxygen (30 ppm) in tungsten can lead to the formation of a second phase at the grain boundary and consequently lead to embrittlement and increased the DBTT [9]. The "burst out" of the plasma (plasma disruption and ELMs) during fusion reactor operation is considered as a severe accident during off-normal operation condition and needs to be avoided or at least mitigated as far as possible. Thermal overloading by such undesirable, but maybe not entirely avoidable, transient events in experimental prototypes such as ITER will be discarded on the divertor [2]. The expected temperature gradient within the limited volume near the loaded material surface during off-normal events, such as ELMs will be in the range of hundreds to several thousand Kelvin, but still below the melting limit of tungsten [2,6,8]. Currently suggested reinforcing secondary phases (such as La_2O_3 [10]) in W-based materials have a far lower melting point than tungsten, so during disruptions this can lead to early melting and increased evaporation, causing the formation of pores and depleted surface layer [2]. The presence of oxide particles with a lower melting point as tungsten has a negative effect on the erosion resistance and can be potentially replaced by carbide dispersoids with higher melting point (such as HfC) [5]. In the present study, we first characterise and then discuss the formation of secondary phases formed during the FAST sintering of W powder, carried out at 2173 K and 60 MPa. To investigate the high-temperature structural stability of the phases formed during FAST, we performed the additional thermal treatment at 1873 K to investigate how the secondary phase decomposition affects the microstructure of W.

2. Materials and Methods

2.1. Sample Preparation

A commercially available 99.9% pure tungsten powder with an average grain size of 0.7 μm (MPO7R; Global Tungsten & Powder, USA) was used as a starting material. For sintering experiments, we employed field-assisted sintering device (FAST; Dr. SINTER SPS SYNTEX 3000, Fuji Electronic Industrial, Japan). The W powder was loaded into a graphite die (inner diameter 16 mm), while additional 0.3 mm graphite foil was used to prevent adhesion of the W on the die wall (Fig. 1). Prior to sintering the FAST chamber was thoroughly purged with N_2 (99.996% pure) and evacuated (0.3 mbar–0.5 mbar). The samples were sintered at an applied pressure of 60 MPa with a heating rate of 100 K/min. To investigate the effect on microstructure, sintering time was 5 min (sample W1) and 10 min (W10).

To verify the structural stability of FAST sintered W at high temperatures, additional thermal treatments were performed in a high-temperature vacuum furnace (Astro, Thermal Technology LLC., USA) at 1873 K for 30 min or 24 h with 5 K/min heating rate. Before each experiment, the furnace was thoroughly purged with Ar (99.998% pure) and evacuated (0.2 mbar–0.35 mbar). The samples' surface was mechanically ground and polished before additional thermal treatments. To prevent carbon contamination, tungsten die was used.

2.2. Material Characterisation

For the characterisation of as-received tungsten powder, we used X-ray powder diffraction analysis, using CuKα radiation at room temperature (XRD; AXS D4 Endeavor, Bruker AXS GmbH, Germany). The other details for all the characterised samples are as follows: 20° to 80° 2θ range, step size 0.02, and 1 s per channel acquisition time. The diffracted (*hkl*) planes of reference W (ICSD collection code #167904) [11] are shown in Fig. 2 on the top of each peak. The W powder morphology was assessed with a field-emission scanning electron microscope (FE-SEM, JSM-7600F, Jeol Inc., Japan). Carbon tap was used for powder mounting on the holder. After FAST treatment, the graphite foil from the wrapping was removed by surface grinding. The crystal structure from the surface layer - carbon-contaminated layer induced by graphite die used during FAST, was evaluated by X-ray diffraction (Fig. 3a). Before the bulk sintered samples were analysed by XRD to evaluate the phase-composition (Fig. 3b), the contaminated surface layer was removed by grinding and polishing. Microstructural observation and chemistry of the synthesised product were assessed by FE-SEM. The chemical composition of the secondary phases was studied by energy-dispersive X-ray spectroscopy (EDS; X-Max, Oxford Instruments plc., UK), while their microstructure and crystallinity were studied by electron-backscatter diffraction (EBSD; Nordlys II, Oxford Instruments plc., UK) (Figs. 4 and 7). Samples for FE-SEM, EDS and EBSD analyses were prepared by mechanical grinding and polishing. To achieve an adequate surface quality and to remove a mechanically-induced damaged layer, a final polishing with 5 vol% H_2O_2 solution in colloidal silica was applied. Before high-temperature structure-stability tests, the surface of the samples was prepared by mechanical grinding and polishing. Due to the detection limit of the laboratory XRD machines [12], co-formed secondary phases were additionally investigated by transmission electron microscopy (TEM, JEM-2100, Jeol Inc., Japan) and scanning transmission electron microscopy (S/TEM, JEM-2010F, Jeol Inc., Japan). STEM images were obtained in Schottky-type field emission electron gun TEM, equipped with UHR pole piece (Cs = 0.48 mm, focal spread Δf = 8 nm), while the inner and outer annular angles for the HAADF detector were set by the optical settings of the microscope to 100 mrad and 200 mrad, respectively, while the probe semi-angle was 20 mrad. Prior to TEM observation (Figs. 5 and 6), the samples were prepared by conventional mechanical thinning and subsequently etched in ion-mill using high-energy Ar^+ until electron transparency (PIPS 691, Gatan Inc., USA).

3. Results and Discussion

3.1. Phase Identification

Grain size and morphology of the starting W powder were investigated by FE-SEM. From secondary electron images in SEM (SEI-SEM) we assessed that the size of the starting tungsten particles was < 1 μm. Tungsten particles tend to form larger agglomerates (Fig. 2a). W particles exhibit an irregular shape. XRD diffractogram of initial powder corresponds to pure tungsten with body-centered cubic structure (a = 3.165 Å, Im-3 m SG: 229) [11] (Fig. 2b). Very narrow diffraction peaks indicate crystalline material and particle size in the micron range.

During the FAST consolidation of the W powder, carbon diffuses from the graphite foil and die into the sample, forming two additional layers on the surface of the sintered specimen as shown in Fig. 1. While the first layer is a thin graphite foil from the wrapping that can be removed easily, the second layer, which has a different texture, is a hard, thick crust, enclosing the W sintered sample (Fig. 3a1). XRD analysis (Fig. 3a) revealed that this second layer is a mixture of W [11] and $W_2C_{0.85}$ [13]. The investigation of the fractured sample showed that this carburised layer is approximately 200 μm thick (Fig. 3a1), and that it is formed during sintering due to direct contact of the specimen with the graphite-foil and graphite die; this carburised layer is assumed to grow in a parabolic manner with time [7]. The thickness of this tungsten carbide-rich layer is important regarding the further sample preparation, before any microstructure characterisation, this remaining