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The thermal properties of high purity and fully dense tungsten produced by chemical vapor deposition

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HIGHLIGHTS

- High purity and fully dense CVD-W samples were prepared.
- The deposition rate of CVD-W is higher than 0.6 mm/h.
- Thermal conductivity of CVD-W is higher than that of forged-W.
- CVD-W had a higher threshold energy of crack initiation than that of forged W.
- CVD-W has higher energy absorption than that of forged-W.

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ABSTRACT

The ultra-high purity (>99.9999 wt.%) and fully dense (19.23 g/cm^3) tungsten (W) by chemical vapor deposition (CVD) was prepared with the deposition rate higher than 0.6 mm/h. The thermal diffusivity, specific heat, heat conductivity and coefficient of thermal expansion of CVD-W at the temperature range of 473–1273 K were measured. Thermal shock tests were carried out on a 60 kW electron-beam material testing scenario to investigate the crack-resistant performance of CVD-W, and the crack initiation threshold energies of CVD-W were achieved in 5 ms heating duration. Compared to forged-W, the higher heat conductivity (160.5–111 W/(m K)) and threshold energy of crack initiation (1.1–1.65 MJ/m^2) of CVD-W can be attributed to the material characteristics including high purity, fully dense, rough surface composed of pyramid-like grains, and the columnar grain structures.

1. Introduction

Tungsten (W) has the properties such as the highest melting point among metals (3693 K), high density (19.3 g/cm^3), low vapor pressure, chemical inertness, and low erosion rate under plasma condition, which make it one of the most promising candidate materials for the lighting, semiconductor, medical, nuclear power, aerospace, defense industries [1,2]. In general, W components are manufactured via powder metallurgy (PM) and hot forming processes, and machining is necessary for the parts in complex shapes. W, however, is hard and brittle, which makes machining very difficult. As an alternative, chemical vapor deposition (CVD) is another route to produce W components, which begins by introducing tungsten hexafluoride (WF_6) and hydrogen (H_2) gases into a reaction chamber, and fully dense, high-purity W is deposited onto a suitable substrate. Typically, CVD-W is employed to produce the symmetric W components such as a cylindrical shell, conical shell, or tubes. Following deposition, the substrates are chemically or mechanically removed. Recently, CVD-W has been considered to be an interesting coating technology to manufacture W-armored plasma-facing components (PFCs) for the next generation of fusion reactors. Compared with other coating methods (e.g., vacuum plasma spraying (VPS), physical vapor deposition (PVD)), CVD-W is the only one which can produce fully dense, high purity, and mm-level thick coating with high efficiency [3–6].

The microstructure of CVD-W, however, is fundamentally different from that of the wrought W. The mechanical properties of CVD-W were investigated by Murphy et al. [7]. Previous studies have shown that CVD-W coating has comparable thermal shock and fatigue properties to wrought W [8–10]. The thermal properties of CVD-W material itself, however, have not yet been investigated intensively. In this study, the specific heat, thermal diffusivity, thermal conductivity, coefficient of thermal expansion (CTE), and thermal shock performance for CVD-W material has been analyzed and compared to that of forged-W. The mechanism

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which makes the difference of thermal properties between both types of W materials has been discussed from the view of purity, density, grain structures and surface morphology.

2. Experimental

The atmospheric pressure chemical vapor deposition (APCVD) method was employed to produce W materials with the reaction system of tungsten hexafluoride (WF_6) and hydrogen (H_2). The source material WF_6, with a purity of 99.99 wt.% was provided by Xiamen W Co. Ltd, China, and the purity of the carrier gas, H_2, was 99.999 wt.% (Linde Gas Xiamen Co. Ltd, China). An in-house made reaction chamber (600 mm diameter, 1000 mm height) was used in the experiments. The deposition temperature was 823 K and the molar ratio of WF_6 to H_2 is 1:3. The exhaust gas resulted from CVD reaction was absorbed by soda lye to avoid environmental pollution. The developed APCVD technology had a fast deposition rate, generally in the range of 0.6–0.8 mm/h, which was cost-effective way to manufacture high purity, fully dense W bulk components and thick W coatings, as shown in Fig. 1. In addition, the forged-W was used as a reference material. Using the air hammer, the W material was achieved after 5–10 passes hot working in 1300–1700 °C, and no annealing was performed.

The non-gaseous elements concentrations in CVD-W were analyzed by glow discharge mass spectrometry (GDMS) in Evans Analytical Group (EAG), USA. The inert gas fusion method was employed to analyze oxygen (O) contents in high purity W products in LECO RO-300 oxygen determinator (LECO Corp., USA). The carbon (C) was measured with LECO CS-200 analyzer (LECO Corp., USA) by burning the samples in oxygen. The nitrogen (N) and hydrogen (H) content was analyzed by burning the sample in helium carrier gas in ONH 2000 N/H analyzer (ELTRA, Germany). The densities of the CVD-W were measured by the Archimedes method in water via an electronic balance (AL204 model, Mettler Toledo, Switzerland). The microstructures were analyzed by scanning electron microscope (SEM) or light optic microscope (LOM). The samples were ground, polished, and chemically etched. Etching was performed with a 5% NaOH, 5% $K_3[Fe(CN)_6]$, 90% H_2O solution at room temperature. The grain orientation was determined by X-ray diffraction (XRD) method.

Thermal diffusivity in the temperature ranging from 200 to 1000 °C was measured by laser flash method (Flashline TM-5000 Thermal Properties Analyzer, Anter, USA). The CVD-W samples were machined to 12.7 mm in diameter and 3.5 mm in thickness. Additionally, specific heat was determined simultaneously by employing a comparative method. Thermal conductivity was calculated based on the determined bulk density, thermal diffusivity and specific heat. The CTE measurement was implemented at a vertical dilatometer (Unitherm 1161V, Anter, USA). The specimens for CTE measurement were rods in the diameter of 4.0 mm and the thickness of 2.5 mm, which were cut from CVD-W samples. For comparison, the thermal conductivity and CTE for forged-W have also been measured with the same methods.

Thermal shock tests, which were performed on a 60 kW electron-beam material testing scenario (EMS-60) in Southwestern Institute of Physics (SWIP), China, were used to investigate the crack-resistant performance of CVD-W and forged-W. The size of samples is $10 \times 10 \times 2.0\ mm^3$. The loaded area was about $4 \times 4\ mm^2$. The acceleration voltage of electron beam was 120 kV. The beam scanned across the surface with a fast frequency of 37 kHz in *x*-direction and 27 kHz in *y*-direction. The beam diameter was 1–2 mm and the loading time of electron-beam was 5 ms. The power densities employed for thermal shock tests were 220 MW/m^2, 280 MW/m^2, 330 MW/m^2, respectively.

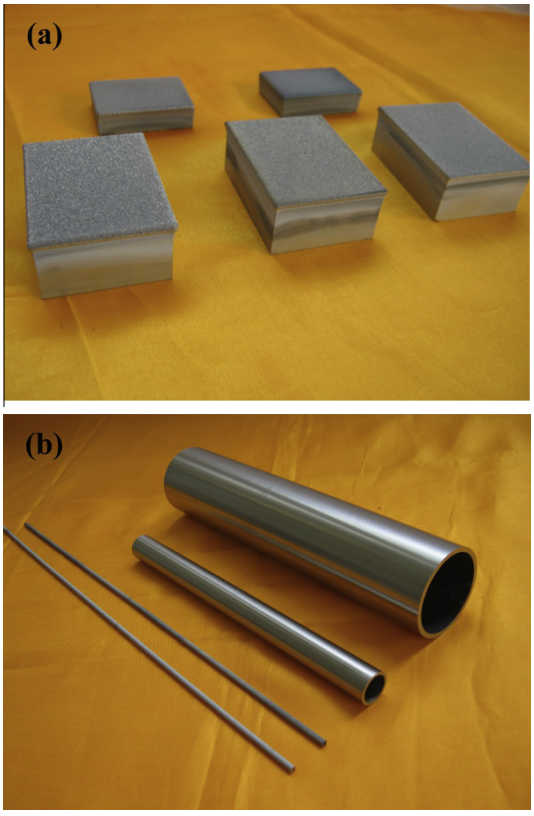

Fig. 1. CVD-W products. (a) CVD-W coating products and (b) CVD-W shell products.

3. Results and discussion

3.1. Purity analysis

GDMS analysis results (Table 1) shows that CVD-W has an ultra-high purity as 99.999978 wt.%, excluding the gaseous ingredient elements. The impurities of gaseous elements are shown in Table 2. The contents of C, N and H are less than the resolution of the measuring equipment, which is 5 wt. ppm. The O concentration as 7 wt. ppm is much lower than the specification of bulk W for ITER divertor applications (e.g., 100 wt. ppm) [11].

Murphy et al. [7] found that CVD-W was much more brittle that conventional sintered and deformed W, and suggested that fluorine segregation to grain boundaries was responsible for the increased brittleness of CVD-W. The fluorine was expected to be incorporated into the material from WF_6 precursor during the grain growth. Previous studies indicated that the fluorine concentration in CVD-W was in different levels. Festa and Danko [12] reported that the fluorine concentration in CVD-W was in the range of 10–110 wt. ppm. Hayashi et al. [13], however, found that the fluorine impurity in CVD-W was 0.31 wt. ppm. In this study, the content of fluorine is less than the resolution of GDMS equipment (i.e., 0.01 wt. ppm), which is the same as fluorine concentration in forged-W. On the other hand, the grain growth speed of CVD-W in this study is in the range of 0.6–0.8 mm/h, which is much faster than that used in [7] (i.e., 0.25 mm/h). This means that the fluorine concentration in the material is not influenced by the deposition rate. From the purity analysis, it is suggested that the increased brittleness of CVD-W, compared to conventional sintered and deformed W, can be attributed to the different grain structures.