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Thermal stability and hardness of ReB$_2$ type hexagonal OsB$_2$ with the addition of W

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ABSTRACT

This work attempts to understand the effect of W addition on microstructure, thermal stability, and hardness of ReB$_2$ type hexagonal osmium diboride (*h*-OsB$_2$). *h*-OsB$_2$ samples with W atomic concentration of (Os + W) from 0% to 30% were synthesized by mechanochemical method combines with pressure-less sintering. The XRD patterns of the as-synthesized powders indicate the formation of $Os_{1-x}W_xB_2$ (x = 0, 0.1, 0.2 and 0.3) solid solution, which has a ReB$_2$-type hexagonal structure. After being high temperature sintered, part of the *h*-OsB$_2$ phase of the pure OsB$_2$ transformed to orthorhombic (*o*) phase, while the *h*-OsB$_2$ phase was maintained with the addition of W, which suggests that the thermal stability of the sample was remarkably improved. A macroscopically homogeneous structure with some pores can be found from all groups of the as-sintered $Os_{1-x}W_xB_2$ (x = 0, 0.1, 0.2, 0.3) samples, with some B-rich areas distributed in the W doped samples. The lattice parameters of the $Os_{1-x}W_xB_2$ (x = 0, 0.1, 0.2 and 0.3) solid solutions linearly decreased with the increase of the W concentration. The micro-hardness of the OsB$_2$ sintered samples is 25 ± 2 GPa under an applied load of 0.49 N, which increased to 34 ± 2 GPa, 38 ± 2 and 37 ± 2 GPa, respectively when the W concentration increased from 10, 20 and 30 at%. The increased hardness of the *h*-OsB$_2$ can be mainly attributed to the improvement of thermal stability with the addition of W.

1. Introduction

Hard materials are of great scientific interest owing to their wide industrial applications [1,2]. During recent years, great lights are shed on searching, designing, and synthesizing new hard materials [3–5]. One design principle of synthesizing hard material is to introduce light elements B, C, N and O into transition metal (TM) and form corresponding compounds, such as ReB$_2$, OsB$_2$, WB$_4$, PtC, OsN$_2$, PtN$_2$, etc. [6–8]. Among them, transition metal borides have attracted a great deal of attention due to their combination of outstanding physical properties, such as metallic electrical conductivity, high impressibility, high shear strength, and exceptionally high hardness [9–11]. All of these attributes are desirable in materials for structural and engineering compounds and indicate that di-borides may be suitable replacements for current metal carbides in next-generation cutting tools.

OsB$_2$ was reported to be an ultra-incompressible material with bulk modulus of 365–395 GPa, which is close to diamond (bulk modulus = 440 GPa) [12]. However, the highest hardness value reported by experimental studies for OsB$_2$ is 37 GPa under an applied load of 0.49 N, lower than that of ReB$_2$ (45 GPa). The smaller hardness of OsB$_2$ might be attributed to the presence of a double layer of metallic atoms between each boron layer in the crystal structure that reduces the resistance to shear deformation [13–15]. This could be owing to the orthorhombic *Pmmn* (No.59, oP$_6$-type) structure of OsB$_2$ with contrast to the hexagonal crystallite structure *P*6$_3$/*mmc* (no.194) of ReB$_2$.

Hexagonal ReB$_2$-type OsB$_2$ (*h*-OsB$_2$) has been predicted to have higher hardness, bulk and shear modulus than those of orthorhombic RuB$_2$-type structure (*o*-OsB$_2$). However, the *h*-OsB$_2$ is metastable and its stable phase is *o*-OsB$_2$. Only *o*-OsB$_2$ was experimentally reported before Xie et al. synthesized ReB$_2$-type OsB$_2$ successfully by using a mechanochemical method [16,17]. In our previous work, it was found that parts of *h*-OsB$_2$ phase transfers to orthorhombic phase at a temperature as low as 600 °C, which could decrease the mechanical properties of the materials [18,19]. Therefore, efforts should be devoted to maintain the *h*-OsB$_2$ phase at sintering temperature higher than 1500 °C for the preparation of bulk OsB$_2$ with higher mechanical properties.

Besides the pure systems, transition metal borides doped with other elements may have even better properties. For example, several ternary transition metal borides such as $Re_{0.5}W_{0.5}B_2$ and $Os_{0.5}Re_{0.5}B_2$, $Os_{0.5}Ru_{0.5}B_2$ etc., were theoretically reported to adopt a stable ReB$_2$

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structure (*h*-phase) [20–24]. Another material, $Os_{0.5}W_{0.5}B_2$, in the ReB_2 structure (*h*-phase) was successfully synthesized in experiments and had a hardness value of 40.4 GPa under an applied load of 0.49 N, much higher than that of *o*-OsB_2 [25]. These indicate that the stability of metastable binary transition metal borides can be improved by doping the third element into the host materials.

In our previous study, Re element was doped into *h*-OsB_2 and it was found that the mixed metal borides $Os_xRe_{1-x}B_2$ (x = 0.05 and 0.10) has a stable ReB_2 structure, which is thermal stable at sintering temperature of 1700 °C and has higher hardness than pure OsB_2 [19]. In this paper, another element, W, which is much cheaper than Re, was added into *h*-OsB_2, and the effects of W concentration on phase composition, microstructure, thermal stability and micro-hardness of the OsB_2 were studied.

2. Experimental procedures

Powders of osmium (Os, 99.95% pure, 80 µm average particle size), tungsten (W, 99.99% pure, 75 µm average particle size) and amorphous boron (B, 99.50% pure, 40 µm average particle size) commercially supplied by China New Metal Materials Technology Co., Ltd (Beijing, China) were used as raw materials. Borides were then synthesized by using mechanochemical method in a SPEX 8000D Mixer/Mill (Metuchen, New Jersey, USA). The detailed powder synthesis process could be found in our previously published works [18,19]. The powders were mixed in the moral ratio M(Os + W):B = 1:3. W was substituted for Os at concentration in the range of 0–30 at% such that the total M:B moral ratio is maintained. Excess boron is needed to ensure the thermodynamic stability of the $Os_{1-x}W_xB_2$. The as-milled powders were dry-pressed at 256 MPa followed by iso-statically cold pressed at 200 MPa to form disks with 10 mm diameter and 3–4 mm thickness. The disks were sintered at ambient pressure in a home-made atmosphere furnace at a temperature of 1600 °C for 90 min under the protection of flowing high-purity argon atmosphere.

X-ray diffraction (XRD) analysis (D8 ADVANCE, BRUCKER AXS, Karlsruhe, Portland, Germany) with a copper source (Cu Kα1 = 1.5418 Å) was applied to analysis the crystal structure of the as-synthesized powders and the as-sintered bulk samples. Rietveld Refinement of the diffraction data of the samples was undertaken using Highscore Plus software. Thermal stability of the as-synthesized powders was investigated in air using a Simultaneous Thermal Analyzer (NETZSCH, Germany). The as-synthesized powders were heated up to 1200 °C in air at a rate of 5 °C/min and then air cooled at the same rate. The relative density of the as-sintered samples was measured by Archimedes method in the distilled water. The microstructure of the sintered samples was examined by scanning electron microscope (SEM, Nova NanoSEM430, FEI, Hillsboro, Ohio, USA) with energy-dispersive spectroscopy (EDS) for elemental analysis. Micro hardness measurements were carried out at the surface of the well-polished samples using a micro-indentation system (HXP-1000TMC/LCD, Taiming optical instrument factory, Shanghai, China) with a Vickers indenter. A load of 0.49 N was applied with a dwell time of 15 s. At least 10 indentations were made on each sample at randomly chosen locations to ensure accurate measurements.

3. Results and discussion

The sample powder X-ray diffraction pattern for Os-W-B powder mixture with W concentration from 0 to 30 at% after high energy ball milling for 40 h are shown in Fig. 1. As can be seen from Fig. 1, the main phase detected in the end-product of Os-W-B powder mixture is mixed metal borides $Os_{1-x}W_xB_2$ (x = 0, 0.1, 0.2 and 0.3) with a ReB_2 structure (matched the PDF# 17-0370 for hexagonal ReB_2). This is an indication that single-phase solid solution of W in OsB_2 can be formed over the entire composition range studied in the present work. Excess B may exist in all samples obtained as the M(Os + W):B is 1:3, which is not observable from the XRD patterns of the as-synthesized powders since B powders used in the present study is in amorphous state. It is also worth to note that WC diffraction peaks can be also detected which is contaminated from the WC vial and balls (see Fig. 1).

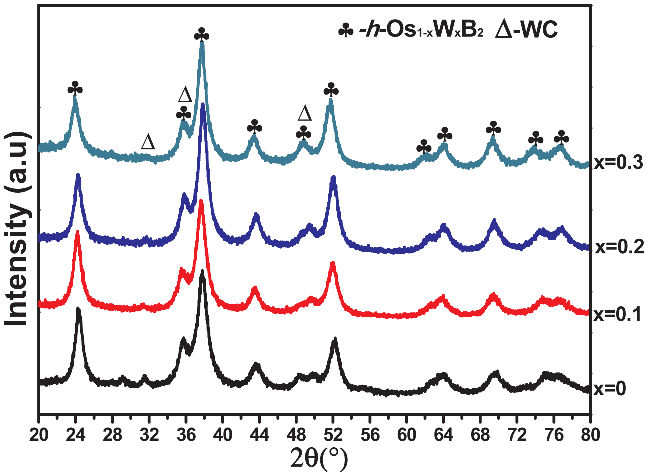

Fig. 1. XRD patterns of as-synthesized $Os_{1-x}W_xB_2$ (x = 0, 0.1, 0.2, 0.3) powders.

The as-synthesized $Os_{1-x}W_xB_2$ (x = 0, 0.1, 0.2 and 0.3) powders were then pressure-less sintered at 1600 °C for 90 min under the protection of flowing argon. The XRD patterns of the as-sintered samples are shown in Fig. 2. After being sintered, most of the hexagonal OsB_2 phase of the OsB_2 (x = 0) transformed to orthorhombic structure, indicated by the *o*-OsB_2 diffraction peaks with relatively high intensity (Fig. 2). The diffraction patterns also reveal the formation of low boron-contained Os_2B_3 phase occurs during the sintering process of the as-synthesized OsB_2 powders, which could be attributed to the B loss during the high temperature exposure. The content of *o*-OsB_2, *h*-OsB_2 and Os_2B_3 phase is 53 wt%, 38 wt% and 9 wt%, respectively, as identified by Rietveld refinement of XRD pattern. However, for the W doped OsB_2, as x = 0.1, 0.2 and 0.3, only *h*-OsB_2 phase can be detected from the XRD patterns of the as-sintered samples. This is a suggestion that, with the doping of W, the thermal stability of the *h*-OsB_2 has been improved. In addition, no low boron-contained $(Os_{1-x}W_x)_2B_3$ phase can be found in the W doped OsB_2 samples, indicates that the addition of W can also inhibit the B loss during the high temperature sintering process to some extent. It is worth to note that, diffractions peaks of WC which can be detected in the as-synthesized powder samples cannot be observed from the XRD patterns of all samples after sintering, likely

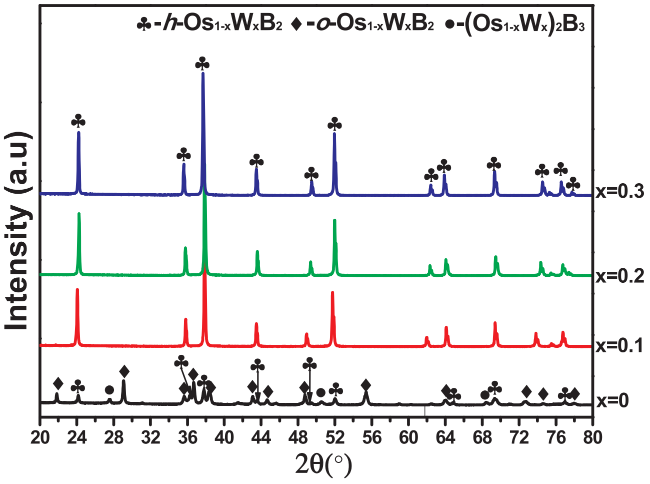

Fig. 2. XRD patterns of $Os_{1-x}W_xB_2$ (x = 0, 0.1, 0.2, 0.3) samples sintered at 1600 °C.