



# Fabrication of tungsten-based composites by solid binder mixing and sintering



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## ABSTRACT

A new solid binder mixing technique is investigated for the fabrication of net-shaped tungsten-based composite in this paper. Sub-micron tungsten-based composite and paraffin wax (PW) powders are mechanically milled at room temperature. The composite powders homogeneously encompass the PW powders, reducing the PW volume fraction to 0.2 for the production of a sound tube-type compact under an ambient condition with a pressure of 200 MPa. The dimensions of the compact after the thermal debinding process are rarely changed. Further advantages of the technique are observed for the sintered sample. A volumetric decrease of the composite corresponds to the initial PW binder volume fraction, and dimensional shrinkages are equivalent in all directions. The net-shaped composite shows a reasonable mechanical property, as well as that of the simple-shaped composite without the PW. Therefore, the process of mechanical binder dispersion in the tungsten-based composite powder, suggested in this study, is very effective for net-shaped composite production.

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## 1. Introduction

Tungsten-based composites have been one of the essential materials for high-temperature applications for the aerospace, aircraft, and defense industries because tungsten has surpassing tensile strength, elastic modulus, melting point, and a low thermal expansion coefficient. In spite of these advantages, however, its high density and the drastic deterioration of the mechanical properties of the tungsten at high temperatures constrain its use in a variety of applications [1,2]. To overcome these weaknesses, second-phase components, such as titanium carbide (TiC) or zirconium carbide (ZrC), have been used in tungsten-based composites [3,4]. Tungsten based composites reinforced with ZrC can be produced using milling and hot pressing. However, this process is very slow and expensive, due to the need for high processing temperatures over 2000 °C. W/ZrC composites produced by milling, hot pressing, and sintering show another weakness in that fabricated parts are restricted to only simple geometric shapes [4].

The powder injection molding (PIM) process has been applied for refractory metals and ceramic materials with ultrahigh melting points as a net-shaping technique [5]. In general, the metal injection molding (MIM) process, which combines powder metallurgy and plastic injection molding, has four steps: mixing, injection molding, debinding, and sintering [6–11]. First, the mixing step is performed at temperatures (approximately 150 °C) higher than room temperature to give fluidity to the binder. In addition, the required amount of binder for common mixing with the metal powder is more than 40 vol.%. For such

conventional liquid binder mixing, powder dispersion is critically affected by the viscosity of the binder. A low viscosity of binder makes the binder to separate from the metal powder after liquid binder mixing [10,11]. The separation between the liquid binder phase and the metal powder causes unstable dimension variation, low densification, and degraded mechanical properties for the final product. After injection molding, the binder has to be removed because residual binder degrades the expected shape and mechanical properties of the product, introducing pores as a result of drastic vaporization during sintering. Common debinding techniques are classified into two groups: thermal debinding and solvent debinding. In the final stage, sintering produces a dense product via particle diffusion, which induce bonds between adjacent particles [12].

In order to obtain a dense tungsten body, a conventional MIM process for net-shaped tungsten-based composites demands a multi-component binder system for liquid binder mixing and sintering temperatures over 2000 °C [13–19]. A multi-component binder system is commonly used to maintain the shape of a molded part while each binder component is gradually eliminated during the debinding process by their various molecular weights. Various multi-component binder systems have been reported for the MIM process [13–18]. As previously mentioned, common liquid binder mixing has to be performed at temperatures over 100 °C. In addition, multi-component binder systems necessitate complicated multi-step processes in processes for mixing and debinding. Multi-component binder systems have been researched by Zhu et al. [17], including paraffin wax (PW), high density polyethylene (HDPE), polypropylene (PP), dioctyl phthalate (DOP) and stearic acid (SA) for tungsten cemented carbides. Multiple mixing procedures for multi-component binder and tungsten-cemented carbide powder

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were performed in a heated condition, and debinding processes were sequentially executed using solvent debinding followed by thermal debinding. Zeep et al. [18] reported that a two-component binder system of wax and thermoplastic (45 vol.%) were applied for the fabrication of a tungsten-based composite. Solvent debinding and thermal debinding were carried out in phases, then sintering and hot isostatic pressing (HIP) were performed at 2200 °C and 1500 °C, respectively.

In the present study, a new binder mixing technique for net-shaped tungsten-based composites is suggested. First, similar to our previous work, prior to binder mixing, mechanical milling to obtain tungsten-based composite powder is performed [20]. PW binder powders (20 vol.%) are then uniformly mixed with the pre-milled composite powders at room temperature. The mixtures are compacted to form a tube-type specimen at room temperature. The tube-type green compacts are thermally debinded in a vacuum, and then sintered. The preforms after debinding and the sintered composites are analyzed in terms of dimensional variation, microstructure, and Vickers hardness.

## 2. Experimental procedure

Tungsten-based composites were fabricated by mechanical milling, solid binder mixing and sintering. Prior to mechanical milling for the fabrication of tungsten-based composite powder, tungsten powders (20 μm diameter, 99.9 wt.% purity), multi-walled carbon nanotubes (MWCNTs; ~20 nm in diameter, and ~5 μm in length, supplied from Applied Carbon Nano Co. Ltd.) and Zr<sub>2</sub>Cu ingots were prepared. Tungsten powder and MWCNTs were mechanically milled with an atomic ratio of 1:1 for 12 h at 500 rpm under Ar atmosphere. Zr<sub>2</sub>Cu ingots were wet-milled in isopropyl alcohol at 500 rpm for 6 h. Zr<sub>2</sub>Cu of 30 vol.% is wet-milled with W/MWCNTs composite powder of 70 vol.% in isopropyl alcohol. The three-step milling process producing the composite powders was equally executed with a process using sub-micron Zr<sub>2</sub>Cu powders, and the details were described in our previous work [20]. After the pre-milling and the drying, 80 vol.% of the tungsten-based composite powders, and 20 vol.% of PW binder powders were mixed using a planetary mill at 200 rpm for 1 h without any process agent (PCA). The solid binder mixing was accomplished using a system which paused for 75 min after every 15 min milling, maintaining the room temperature.

The resulting mixture was compacted in a double-layered cylindrical mold under a pressure of 200 MPa at room temperature to produce a tube-type specimen. The compacted samples had 20 mm outer and 13.5 mm inner diameters. The moisture and PW binder in the samples were removed at 150 °C and at 500 °C, respectively. The samples were held at these temperatures for 30 min under vacuum in a tube furnace. The temperature was gradually increased at a heating rate of 2 °C/min, as shown in Fig. 2. Then, the preforms obtained by debinding, were sintered at 1400 °C for up to 48 h under an atmosphere of 3 vol.% H<sub>2</sub> in Ar at a heating rate 5.5 °C/min, similar to our previous work [20].

The microstructures of the sintered composites were analyzed using scanning electron microscopy (SEM; JSM-7001F, JEOL). Prior to the observation, the specimens were finely polished with sand papers and buffers. The compositions of the specimens were analyzed by X-ray diffraction (XRD; CN2301, Rigaku) and energy dispersive spectrometry (EDS) with SEM. The sintering shrinkages of the composites were evaluated by measuring dimensional variations in all directions. To reveal structural homogeneity of the tube-type sintered composite, shrinkage anisotropy ratio, which is the proportion of axial shrinkage to radial shrinkage, was calculated. Vickers hardness values of the composites were calculated by taking the average among the hardness values tested ten times under a load of 1 kgf.

## 3. Results and discussion

Fig. 1(a) shows the morphology of the milled powders of W/MWCNTs/Zr<sub>2</sub>Cu. Sub micron tungsten-based composite powders are fabricated by high energy milling in isopropyl alcohol. The pre-milling

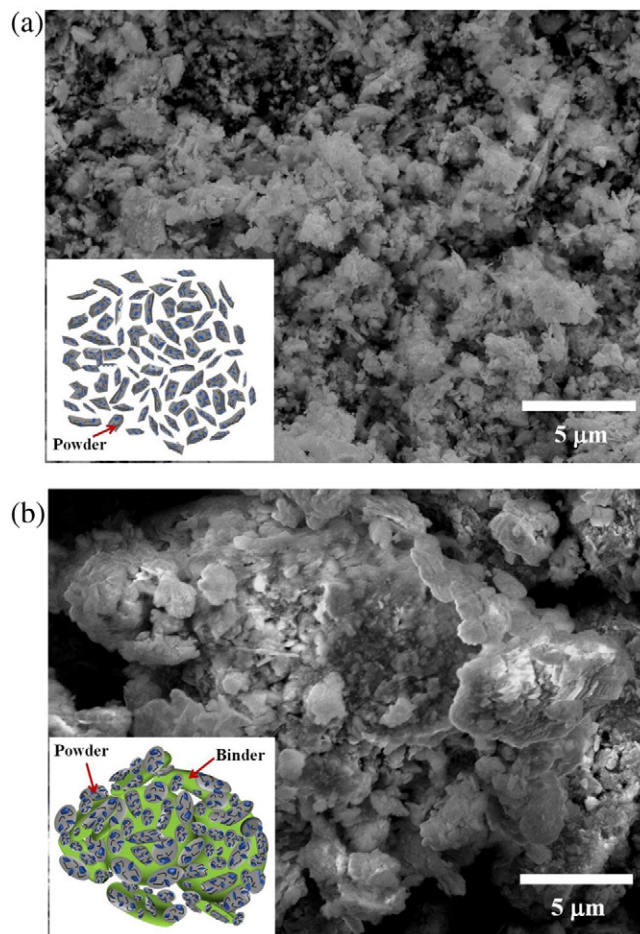


Fig. 1. Powder morphology of (a) W/MWCNTs/Zr<sub>2</sub>Cu and (b) W/MWCNTs/Zr<sub>2</sub>Cu-PW (Insets: the schematic illustrations of the powder morphology).

stage is divided into two procedures, one in which the MWCNTs are dispersed in the tungsten powder and the other in which Zr<sub>2</sub>Cu is dispersed in the W/MWCNTs powder. The initial tungsten powders are pulverized to thin flakes-type powders of several microns in size during the milling with MWCNTs and Zr<sub>2</sub>Cu. MWCNTs, which is used as the nano-carbon source for the formation of sub-micron sized zirconium carbide, are embedded into the tungsten powder and well-dispersed during the pre-milling process [20]. The size distribution of the tungsten-based composite powders in the pre-milling stage is from several hundreds of nanometers to several micrometers, as shown in Fig. 1(a). However, according to the SEM image in Fig. 1(b), the mixture of the tungsten-based composite powders (80 vol.%) and the PW (20 vol.%) binder exhibits a much larger and more agglomerated powder size by tens of microns as compared to the pre-milled composite powder without the PW. Unlike regular fabrication methods for metal composites using several binders, a single wax binder, especially PW, with its short molecular chains, is better at holding the sub-micron tungsten-based composite powders together, retaining the shape of the compact even after debinding. In solid binder mixing, the pre-milled composite powders are coagulated onto the PW powders and are homogeneously mixed with the PW powders. Also, as the size of composite powders surrounding the PW powders decrease, the pore size after the final consolidation by sintering decreases [21].

W/MWCNTs/Zr<sub>2</sub>Cu-PW mixture is compacted in a double-layered cylindrical mold, then thermally debinded (dotted line in Fig. 2) via a single process without solvent debinding. The green compact is held in the furnace for 300 min, while raising furnace temperatures up to 500 °C, to remove the PW binder, which has a boiling temperature of 370 °C. Weight loss starting temperature is close to 200 °C, and the

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