Ceramic **Processing Research**

Effect of TaB₂ on densification and hardness of tantalum carbide/boride composites

Behzad Mehdikhani^{a,*}, Gholam Hossein Borhani^a, Saeed Reza Bakhshi^a and Hamid Reza Baharvandi^b

^aDepartment of Materials Engineering, Malek-e-ashtar University of Technology, Isfahan, Iran ^bDepartment of Materials Engineering, Malek-e-ashtar University of Technology, Tehran, Iran

Tantalum carbides/boride composite were synthesized by spark plasma sintering (SPS), using the powder mixtures of TaC and B_4C as the starting materials. In this work densification, phase formation, microstructures, and mechanical properties of the materials were investigated. The densification of tantalum carbide (TaC) was enhanced by adding 2.0 wt% B₄C, reaching 97% relative density by SPS at 1900 °C using a 30 MPa applied pressure. X-ray diffraction analysis identified two phases, TaC and tantalum diboride (TaB₂), with no peak shifts, indicating a solid solubility was not significant at these temperatures. Densification of TaC was enhanced while the grain growth was suppressed by adding 2 wt% B₄C, which allowed mechanical properties to be analyzed. Relative density of >97% was achieved for TaC with B₄C additions by SPS at 1900 °C. By comparison, additive-free TaC could be sintered to only 76% relative density at 1900 °C. The effect of B₄C addition and sintering temperature on hardness measured by microhardness has been studied. Hardness of samples contain 2.0 wt% B₄C was 15.10 vickers.

Key words: Tantalum carbide/boride, Microstructure, Microhardness, densification, Spark plasma sintering.

Introduction

It is well recognized that Zr-, Hf- and Ta- carbides and diborides based composites, the so-called ultra high temperature ceramics (UHTCs), are suitable in several traditional and innovative application fields due to their high melting temperatures (above 2700 °C) as well as additional attractive chemical, physical and mechanical properties (hardness, electrical and thermal conductivity, inertness, resistance in extreme environments, etc.) [1]. Production of TaC through sintering is difficult [2], due to its high melting point of 3880 °C (the highest for stoichiometric compounds). Since sintering typically occurs above 50% of the melting point, it is difficult to sinter TaC in conventional furnaces or hot pressing. The cost of furnaces designed for these very high temperatures is often prohibitively expensive. Furnaces for hot isostatic pressing that can reach the needed temperatures operate with heating rates which may be as low as 5 °C min⁻¹, thereby rendering unacceptable productivity rates [3-4]. Performance of tantalum carbide at high temperature needs good oxidation resistance [5]. Researchers have found that TaB₂ is a suitable additive [6]. Tantalum borides have not been studied as extensively as other borides, likeTiB₂ [7], ZrB₂ [8], and HfB₂ [9]. On theformation of tantalum borides, a variety of processingroutes have been utilized. For example, Hideaki et al. [10] produced TaB₂, TaB, and Ta₃B₄ by solid statereactions of mixed

Ta and amorphous boron powders under corresponding compositions at 800, 900 and 1800 °C respectively. Peshev [11] obtained TaB₂ through borothermic reduction of Ta₂O₅ at 1650 °C for 1h. The ternary phase diagram has been known since 1963 [12]. It is well known that the properties of composite $TaC-TaB_2$ are strongly dependent on the relative amounts and types of thevarious phases formed. It has to be noted that B₄C, which is also a component of the Ta-C-B ternarysystem, is not chemically compatible with Ta or TaC. Itreacts with Ta and TaC forming TaB₂ and free carbon that has been used for the synthesis and processing of diboride-containing ceramics [13]. SPS, is known as the field assisted sintering technique, is becoming a widely used process in sintering research. SPS consists of conjoint application of high temperature, axial pressure and field-assisted sintering [14]. The field component is associated with an electric current passed through a powder specimen. SPS has advantages over conventional sintering or hot pressing, such as higher heating rates, shorter holding times, smaller post-processing grain sizes and denser final materials, many of which have been researched vigorously in the past few years [15-17]. This article demonstrates the formation of TaC-TaB₂ by Spark plasma sintering (SPS) for investigation effect of increasing B₄C and formation of TaB₂ on densification and hardness of the composite.

Experimental

Raw materials

The raw material characteristics are listed in table 1. The TaC content in the TaC powder was higher than

^{*}Corresponding author: Tel:+98-26-32806031-8

Fax: +98-26-32818844

E-mail: beh mehdikhani@yahoo.com

 Table 1. Raw material characteristics.

Material	Purity	Particle size	Supplier
TaC	99%	1.25 μm	Ningxia Orient
B_4C	>95 wt%	300 nm	Jingangzuan

Sample	Milling time(hr)	Composition
A: TaC	0	TaC
B: TaC-TaB ₂	0	TaC-B ₄ C
C: $TaC-TaB_2$	6	TaC-B ₄ C
D: TaC-TaB ₂	12	TaC-B ₄ C

99%. The mail impurities were 0.3 wt% Nb, 0.1 wt% Fe, 0.20 wt% 0, 0.15 wt% free carbon, 0.05 wt% N, and Al, Ca, K, Na, Ti with a total amount < 0.05 wt%. The B_4C was > 95 wt% pure with major impurities of free carbon.

The powder compositions are given in table 2. About 25 g of powders were mixed in a WC cylinder (250 ml) using 150 g WC balls as mixing media. Ball milling of powder mixture was carried out in a planetary ball mill at room temperature in n-hexane and under argon atmosphere. The ball-to-powder weight ratio and the rotational speed of vial were 20:1 and 250 rpm, respectively for 0, 6 and 12 hr.

The milling was interrupted at selected times and a small amount of powder was removed for further characterizations. Batches of the powder mixtures were loaded into graphite dies, with an inner and out diameter of 15 mm and 45 mm respectively. SPS was performed in vacuum at 1900 °C for 10 min under 30 MPa. The SPS temperature was first increased automatically to 700 °C and the SPS pressure to 30 MPa in 4 min. Then 100 °C/min was applied from 700 °C to 1900 °C. After hold for 5 min, the pressure was released and the SPS power was shut off. Phase transformation during milling were determined by X-ray diffraction (XRD) in a Philips X'PERT MPD diffractometer using filtered Co K α radiation ($\lambda = 0.178$ nm).Crystallite size and internal strain of specimens (μ) were calculated from broadening of XRD peaks using the Williamson-Hall method [18], (eq.1).

$$\beta \text{Cos}\theta = K\lambda / d + \mu \text{Sin}\theta \tag{1}$$

Where θ is the Bragg diffraction angle, d is the average crystallite size, k is a constant (with a value of 0.9), λ is the wavelength of the radiation used, and β is the diffraction peak width at half maximum intensity. Theoretical density for the sintered composites was determined by the law of mixtures. Bulk densities were measured by the Archimedes method. Microstructure was observed by field emission scanning electron microscopy (FE-SEM). The samples were sectioned, ground, and were polished to 1 µm diamond finish. Microhardness was measured using Vickers' indentation (Model 3202, zwick) by applying a load of 2.0 kg (19.6 N).

Results and Discussion

Phase compositions

A commercial software program (HSC Chemistry) was used to identify the probable reaction using thermodynamic data. Fig. 1, shows X-ray diffraction patterns of the TaC and TaC-TaB₂ samples after sintering. Analysis of the XRD patterns (Fig. 1) showed a progressive increase in the amount of the TaB₂ phase formed during SPS. The amounts of TaB₂ formed could be as high as 14 wt% for a B₄C addition of 2 wt%, if all of the B₄C were consumed by reaction (2). Further, no XRD peaks were observed for B₄C, suggesting that a reaction had occurred in the system. The change in standard Gibbs free energy (Δ G^o) indicated that reaction (2) was favorable across the range of processing temperatures, which suggested that B₄C reacted with TaC to form TaB₂ and C:

$$2\text{TaC} + \text{B}_4\text{C} = 2\text{TaB}_2 + 3\text{C}, \ \Delta \text{G}^\circ = 66.4 + 0.0103 \text{T(kJ)}$$
(2)

The XRD analysis and thermodynamic calculation were also consistent with the Ta-B-C phase diagram [13], which indicated that TaC is not chemically



Fig. 1. X-ray diffraction patterns of tantalum carbide/boride after sintering by SPS at 1900 °C.

compatible with B₄C. For the overall composition produced by adding relatively small amounts of B₄C to TaC, the phase diagram indicated that TaB₂ and C were stable with TaC. Fig. 1, shows that there is no TaB_2 peaks in samples. Fig. 1(a) shows XRD pattern of sintered sample from raw tantalum carbide powder. Fig. 1(b) shows XRD pattern of TaC-2 wt% B₄C sample. The results show that there is no new phase in powders without milling. B4C phase in the XRD spectra have not been observed in some detail because it is a small amount of 2% by weight. Fig. 1(c) shows the XRD results of sintered sample from 6 hr milled powder, there is no TaB₂ phase. The XRD analysis indicated that TaB₂ only presented in Fig. 1(d) were produced from the sintered sample (12 hr milling) of their equivalent stoichiometries. Cup and balls of ball mill was made from WC so X-ray results show that increasing milling time up to 12 hours has caused a spike tungsten carbide, Fig. 1(d) X-ray diffraction analysis identified two phases, TaC and tantalum diboride (TaB₂), with no peak shifts, indicating a solid solubility was not significant at these temperatures.

Densification

The measured densities of the samples are listed in table 3. All the materials reached larger than 76% of the theoretical densities, indicating the efficiency of SPS in synthesizing the tantalum carbide ceramics. The relative densities of TaC-TaB₂ ceramics sintered using different powders at the given temperature are shown in table 3. After sintering at 1900 °C, the relative density of sample A is still as low as 76%, indicating poor sinterability of powder A. The relative densities of TaC-TaB₂ ceramics (samples B, C) are 85% and 91% (Table 3).

Maximum relative density of samples was 97%. The powder of this sample was milled 12 hr. results shows that with increasing milling time, particle size powders have been reduced. Particle size of powder D is calculated 88 nm (eq:1). Decreasing particle size made high densification of samples after sintering (Table 3). The microstructures of the sample A was illustrated in Fig. 2. This figure shows that the fracture surface of the dense TaC ceramics prepared using powder A. During sintering sample by using powder A, fast grain growth occurred, which entrapped big pores into the TaC

Table 3. physical and mechanical properties of sintered samples.

Sample	Relative density (%)	XRD phases	Particle size (nm)	Hardness GPa
A: TaC	76	TaC, C	840	13.30
B: TaC-TaB ₂	85	TaC, C	840	13.47
C: TaC-TaB ₂	91	TaC, C	267	14.25
D: TaC-TaB ₂	97	TaC-TaB ₂ , C	88	15.10



Fig. 2. FE-SEM image of sample A.



Fig. 3. FE-SEM image of sample B.

grains, as shown in Fig. 2.

This figure shows grain structure with a large grain size of about 4-6 μ m. The ceramics prepared using powder B at given temperature show fine microstructure (Fig. 3). The particle size of powder B was 840 nm. This figure shows fine grain structure with a grain size of about 1-3 μ m. The residual pores in these samples are smaller than those of sample A.

Fig. 3, shows that there are phases present at the grain boundaries of TaC which could be TaB₂ and free carbon phase mixtures. Fig. 4, shows the surface of sample C. The average grain sizes of sample C after SPS were maintained at small values of about 1 μ m. relative density of this sample was 91% and in this figure there are some pines after sintering. Comparing the relative densities and microstructures of samples A, B and C, all the samples show fine microstructures, but sample C has the highest relative density among them (91%). Sample D has the highest relative density among samples A, B and C. This indicates that the favorable particle size for TaC ceramic with high relative density and small grains is smaller than 100 nm.



Fig. 4. FE-SEM image of sample C.



Fig. 5. FE-SEM image of sample D.

Fig. 5 shows that all the ceramics prepared using powder D show fine microstructures. The residual pores in these samples are much smaller than those of sample A. The average grain sizes of sample D sintered was smaller than 1 μ m. Theoretically, the driving force of sintering is the reduction of the total interfacial energy [18]. The reduction of the total energy during solid-state sintering of the TaC ceramic can be expressed as:

$$\Delta(\Sigma\gamma_{i}A_{i}) = \gamma_{sv}\Delta A_{sv} + \gamma_{ss}\Delta A_{ss}$$
(3)

Here, $\Delta(\Sigma\gamma_iA_i)$ is the reduction of the total interfacial energy during sintering TaC, γ_{sv} and γ_{ss} are the specific surface energiesof solid-solid or solid-vapor interface, respectively. ΔA_{sv} and ΔA_{ss} are areas of the solid/vapor and solid/solid interfaceschange, respectively. From Eq. (3), large ΔA_{sv} can lead to a large $\Delta\Sigma\gamma_iA_i$, which provides a high driving force of sintering. Because powder D with smaller particle size has larger surface area, the change in the interfacial area during sintering the compact of powder D is higher than those of A, B and C.

Therefore, powder D has the highest driving force of sintering and exhibits the best sinterability among these powders. The enhanced densification of TaC with the TaB_2 addition is likely due to physical pinning of grain growth by the second phase. In addition to grain

pinning, the presence of B_2O_3 on the TaB₂ particles' surface may facilitate grain rearrangement due to the formation of a liquid phase, which would enhance densification. A similar grain growth-pinning effect has been observed in the ZrB₂-SiC and HfB₂-SiC systems. In this systems, dispersed SiC particles have been shown to inhibit the grain growth and enhance densification of the matrix phase [19].

Mechanical properties

The mechanical properties (microhardness) for TaC-TaB₂, sintered by SPS 1900 °C, are included in Table 3. Vickers hardness testing was performed using 20 N loads, with a standard diamond indenter tip. The specimen was indented at the center, at the edge and halfway between. The values reported in table 3 are the average of these three data points. Result shows that vikers hardness of sample D is highest. It seems that high density of sintered sample and formation of TaB₂ made good hardness of sample. Vickers' hardness increased from 13.30 GPa for monolithic TaC to 15.10 GPa for TaC-TaB₂, which was attributed to the higher density achieved for the composite and the higher hardness of the dispersed TaB₂ phase (24.5 GPa) compared with monolithic TaC [20].

Conclusions

Using fine TaC powder with narrow particle-size distribution, monolithic TaC ceramics with a relative density of 85% was obtained by spark plasma sintering at 1900 °C with adding 2 wt% B₄C as a additives. With decreasing particle size of powders, samples after sintering had fine grain structure and density of this sample was more than the other samples. Addition of B_4C has dual advantages viz. (i) as a sintering aid and (ii) grain growth inhibitor. XRD patterns and FE-SEM images suggested that TaC reacted with B4C leading to formation of TaB₂. The TaB₂ present at grain boundaries leads to pinning of the grain boundaries and arrests grain growth. X-ray diffraction analysis identified two phases, TaC and tantalum diboride (TaB₂), with no peak shifts, indicating a solid solubility was not significant at these temperatures. The microhardness of TaC-TaB₂ was better than or comparable to those of monolithic TaC due to the higher relative density and formation of TaB_2 in the TaC-TaB₂. Vickers' hardness also increased from 13.30 GPa to 15.10 GPa.

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