



## Near-net shape manufacture of $B_4C$ -Co and $ZrC$ -Co composites by slip casting and pressureless sintering

Angel L. Ortiz<sup>a,\*</sup>, Victor M. Candelario<sup>b,c</sup>, Rodrigo Moreno<sup>d</sup>, Fernando Guiberteau<sup>a</sup>

<sup>a</sup> Departamento de Ingeniería Mecánica, Energética y de los Materiales, Universidad de Extremadura, 06006 Badajoz, Spain

<sup>b</sup> LiqTech International AS, Industriparken 22C, 2750 Ballerup, Denmark

<sup>c</sup> Department of Energy Conversion and Storage, Technical University of Denmark, Risø Campus, Frederiksborgvej 399, DK-4000 Roskilde, Denmark

<sup>d</sup> Instituto de Cerámica y Vidrio, Consejo Superior de Investigaciones Científicas, 28049 Madrid, Spain

### ARTICLE INFO

#### Keywords:

Cermets

$B_4C$

$ZrC$

Colloidal processing

Pressureless sintering

### ABSTRACT

Fabrication of near-net shaped  $B_4C$ -Co and  $ZrC$ -Co composites by slip casting and pressureless sintering is described. It is shown how  $B_4C$ -Co and  $ZrC$ -Co concentrated suspensions can be prepared by aqueous colloidal processing, and optimized (in terms of pH, deflocculant contents, and sonication time) to have a shear-thinning rheological behaviour suitable for the near-net shaping of the corresponding cermet compacts by slip casting. It is also demonstrated that the robust, highly-dense compacts so obtained have a uniform green microstructure without macro-defects or gradient density, and which can be fully densified by pressureless sintering. Specifically, it is shown that  $B_4C$ -Co compacts densify by reactive and transient liquid-phase sintering, thus resulting in multi-component ceramics.  $ZrC$ -Co compacts densify however by persistent liquid-phase sintering, thus resulting in cermets. An explanation is given for these observations, and general implications are discussed for the near-net shape manufacture of these and similar carbide-metal composites for use in engineering applications.

### 1. Introduction

Ceramic-metal composites (i.e., cermets) have great interest as structural materials for a broad variety of engineering applications because they appropriately exploit the benefits of the hard ceramic matrix and of the tough metal binder, reason for which they are known with the collective name of “hardmetals”, or “cemented carbides” if the ceramic matrix is specifically a refractory carbide [1]. The most widely used and investigated of the hardmetals is WC-Co/Ni, but other formulations of cemented carbides are equally possible as long as the metal binder allows the liquid-phase sintering of the carbide. In this context, pure  $B_4C$  and  $ZrC$  are two refractory carbides (a covalent carbide the former, and an interstitial carbide the latter) with great appeal in structural applications [2–4]. Thus for example, owing to their high or ultrahigh hardness, they may find use in the field of contact mechanics and tribology [5–8]. Also, by virtue of its extreme lightness,  $B_4C$  is ideal ceramic armour for both personnel and vehicle protection [9], while, due to its great refractoriness,  $ZrC$  belongs to the short list of ultra-high-temperature ceramics for extreme environment applications [10]. Unfortunately however, the great potential of  $B_4C$  and  $ZrC$  as engineering ceramics is limited by their brittleness and poor pressureless sinterability. This latter also conditions the near-net shape

manufacture of  $B_4C$  and  $ZrC$  ceramics, as they are best densified with the aid of external pressure (for example using hot pressing, hot-isostatic pressing, or especially spark-plasma sintering) [2,5–8,11–18]. They thus appear to be appropriate candidates for the fabrication of cermets [19–23].

Recently, we have demonstrated that it is possible to obtain robust  $B_4C$ -Ni compacts by slip casting from  $B_4C$ -Ni concentrated suspensions prepared by aqueous colloidal processing [23]. This combination of techniques is certainly interesting since aqueous colloidal processing allows the challenging co-dispersion of the ceramic and metal phases in the form of environmentally-friendly suspensions with optimized rheological properties, whereas slip casting allows the subsequent near-net shaping of compacts demanded by industry. A Co binder offers some benefits over Ni binder, for example, in terms of hardness and corrosion resistance [24,25]. The former is very relevant because high hardness is an important attribute of the covalent and interstitial carbides required in many engineering applications, and especially in those within the field of contact mechanics and tribology. Therefore, it seems timely to extend the previous study on  $B_4C$ -Ni to the potentially appealing  $B_4C$ -Co composite and, in addition, to expand it to the also potentially interesting  $ZrC$ -Co composite to thus cover two representative types of different refractory carbides. Moreover, the earlier study on  $B_4C$ -Ni was

\* Corresponding author.

E-mail address: [alortiz@unex.es](mailto:alortiz@unex.es) (A.L. Ortiz).

<http://dx.doi.org/10.1016/j.jeurceramsoc.2017.07.024>

Received 29 April 2017; Received in revised form 21 July 2017; Accepted 22 July 2017  
0955-2219/© 2017 Elsevier Ltd. All rights reserved.

devoted exclusively to aspects of aqueous colloidal processing and shaping by slip casting, with no information about sintering, reason by which it also seems timely to conduct additional studies on the B<sub>4</sub>C–Co and ZrC–Co composites of both pressureless sintering and microstructural characterization. These all were indeed the objectives of the present study.

## 2. Experimental procedure

The starting materials used were commercially available B<sub>4</sub>C (> 99%,  $d_{50} \sim 0.5 \mu\text{m}$ ,  $\rho = 2.51 \text{ g/cm}^3$ ; Grade HD 20, H.C. Starck, Germany), ZrC (> 99%,  $d_{50} \sim 3\text{--}5 \mu\text{m}$ ,  $\rho = 6.7 \text{ g/cm}^3$ ; Grade B, H.C. Starck, Germany), and Co (> 99.8%,  $d_{50} \sim 1.6 \mu\text{m}$ ,  $\rho = 8.92 \text{ g/cm}^3$ ; Alfa Aesar, Germany) powders. They were characterized independently by scanning electron microscopy (SEM; Quanta 3D FEG, FEI, The Netherlands) to confirm the particle sizes indicated by the manufacturers, and by X-ray diffractometry (XRD; D8 Advance, Bruker AXS, Germany) and X-ray photoemission spectroscopy (XPS; K-Alpha, Thermo Scientific, UK) to qualitatively examine the phase compositions and the bonding environments or statuses, respectively.

The procedure of aqueous colloidal processing followed the standard protocol. In particular, in a first stage the colloidal stability of the ceramic (i.e., B<sub>4</sub>C and ZrC) and metal (i.e., Co) powders was studied individually using dilute suspensions (0.1 g/l) with a short equilibrium (i.e., stabilization) time (30 min). To this end, systematic zeta potential measurements (Zetasizer Nano-ZS, Malvern, UK) were first made (in triplicate) as a function of pH (adjusted within the acidic or basic ranges using  $10^{-1} \text{ M}$  HCl or KOH solution, respectively) on single-phase suspensions prepared without deflocculant using deionized water as suspension medium and KCl  $10^{-2} \text{ M}$  as inert electrolyte. Next, additional zeta potential measurements were also made (in triplicate) at natural pH as a function of the deflocculant content (in the range 0–2.2 wt.%). In the three cases, deflocculation was done using commercially available polyelectrolytes, specifically, a synthetic polyelectrolyte of unknown composition (PKV; Produkt KV5088, Zschimmer-Schwarz, Germany – it is nonetheless thought to be of type polycarboxylic) for both B<sub>4</sub>C and ZrC, and an ammonium salt of polyacrylic acid with a molecular weight of 2400 and a content of active matter of 35% (PAA; Duramax™ D-3005, Rohm & Haas, USA) for Co.

In a second stage, multi-component concentrated suspensions were prepared in deionized water containing ceramic (either B<sub>4</sub>C or ZrC) and metal (Co) in relative concentrations of 80 and 20 vol.%, respectively. These suspensions were prepared to a total solids loading of 30 vol.% because the earlier study on B<sub>4</sub>C–Ni indicated that higher solids loadings (in the range  $\sim 30\text{--}40 \text{ vol.}\%$ ) increase the suspension viscosity thus complicating the slip casting performance without improvement of the green-body densification [23]. The suspensions were prepared with continuous vigorous mechanical stirring with helices to ensure correct mixing, using the following protocol of sequential addition. First, the pH of the deionized water was adjusted to the desired value by dropwise addition of an aqueous solution of 25 wt.% tetramethylammonium hydroxide (TMAH, Aldrich-Chemie, Germany). Next, the PAA content required to appropriately disperse the Co powder was added, followed by incorporation of the Co powder, stabilization (i.e., equilibration) for 5 min, and sonication for 1 min. Then, the PKV content required to appropriately disperse the ceramic powder was added, followed by addition of the ceramic powder, stabilization for 15 min, and lastly sonication for different times to thus investigate its effect on the rheological behaviour of the suspension. The pH was maintained at the desired value throughout the entire process.

The rheological behaviour of the B<sub>4</sub>C–Co and ZrC–Co suspensions was studied using a rheometer (Haake Mars, Thermo Fisher Scientific, Germany) operated in controlled shear rate mode. The measuring system consisted of a double-cone and plate, with cone angle of 2°, provided with a cover plate to avoid evaporation. The measurement cycle of the flow curves involved a linear stretch of shear rate increase

from 0 to  $1000 \text{ s}^{-1}$  in 300 s, then a plateau at  $1000 \text{ s}^{-1}$  for 60 s, and lastly a linear decrease to zero shear rate also in 300 s. The thixotropy/rheopexy was determined from the area of the flow curve's hysteresis loop, and the viscosity by direct reading at  $1000 \text{ s}^{-1}$  in the uploading stretch.

For the fabrication of the B<sub>4</sub>C–Co and ZrC–Co composites, the corresponding multi-component concentrated suspensions with appropriate rheological behaviour were next slip cast on plaster moulds to obtain compacts (at least 6 specimens per each composition) with different morphology, whose green-body microstructure was examined by SEM after drying in air at room temperature for 48 h within the moulds. The degree of green-body densification was also evaluated (in triplicate), using to that end Hg intrusion porosimetry (PoreMaster 60, Quantachrome Instruments, UK). Finally, these compacts were pressureless sintered (1000-3560-FP20, Thermal Technology Inc., USA) at  $1700 \text{ }^\circ\text{C}$  for 2 h (heating and cooling ramps of 10 and  $20 \text{ }^\circ\text{C}/\text{min}$ , respectively) in a flowing Ar-gas atmosphere of 99.999% purity. The  $1700 \text{ }^\circ\text{C}$  temperature was chosen because it ensures the existence of a low-viscosity liquid phase during pressureless sintering given that Co has a melting point of  $\sim 1500 \text{ }^\circ\text{C}$ . Once polished using conventional ceramographic methods, their microstructure was investigated by SEM together with energy-dispersive X-ray spectrometry (EDS) and XRD. The sintered B<sub>4</sub>C–Co and ZrC–Co composites were also broken, and their fracture surface was observed by SEM. The degree of densification of the sintered B<sub>4</sub>C–Co and ZrC–Co composites was evaluated by image analysis of multiple SEM images (taken randomly on both polished and fracture surfaces).

## 3. Results and discussion

Figs. 1 and 2 show representative low- and high-magnification SEM images, respectively, of the B<sub>4</sub>C, ZrC, and Co starting powders. It can be seen that the particles in the B<sub>4</sub>C powder are equiaxed and have an average size in the submicrometre range (Figs. 1A and 2A). The particles in the ZrC powder are also equiaxed (although less faceted), but have greater size dispersion. Indeed, there are particles with sizes from the ultrafine range to the micrometre scale (Figs. 1B and 2B). Finally, it can also be seen that the particles in the Co powders have a worn-like morphology, with average length and thickness in the micrometre and submicrometre ranges, respectively (Figs. 1C and 2C). This is because they are actually intergrowths of finer particles (Fig. 2C). There is also a rough mat on the surface of the Co particles (Fig. 2C), which is likely a passivating oxide layer. The XRD patterns shown in Fig. 3 indicate that the B<sub>4</sub>C powder contains B<sub>4</sub>C together with H<sub>3</sub>BO<sub>3</sub> and graphite impurities (very minor phases), that the ZrC powder contains only ZrC, and that the Co powder contains a combination of  $\alpha$ -Co (fcc) and  $\beta$ -Co (hcp). Lastly, the XPS spectra shown in Fig. 4 confirm the presence of H<sub>3</sub>BO<sub>3</sub> in the B<sub>4</sub>C powders, and also indicate that the particles of ZrC and Co in the corresponding powders are notably passivated (surface ZrO<sub>2</sub> in the former case, and both surface CoO and Co(OH)<sub>2</sub> in the latter case). Unlike what occurs for the solid-state sintering of these refractory carbides, fortunately however these oxidic impurities are not likely to play a dominant role in their densification by liquid-phase sintering.

Fig. 5 shows the variation of the zeta potential against pH for the individual dilute suspensions of B<sub>4</sub>C, ZrC, and Co. It can be seen that the B<sub>4</sub>C used here has its surface negatively charged within the entire pH range investigated, always with high absolute values of the zeta potential (approximately in the range  $-35 \text{ mV}$  to  $-60 \text{ mV}$ ) [23]. This is attributable to the formation of surface boron oxides and interfacial boron oxycarbides [26,27]. Consequently, this B<sub>4</sub>C will be very stable colloiddally in its current state under the vast majority of possible aqueous processing conditions. Note however that other B<sub>4</sub>C powders, even from the same supplier, exhibited zeta potential curves in aqueous media with an isoelectric point at pH in the range 5–6 [28], which is likely due to their different grades making them to behave differently. It can also be seen that ZrC has its isoelectric point at pH  $\sim 3.4$ , above

Download English Version:

<https://daneshyari.com/en/article/5440315>

Download Persian Version:

<https://daneshyari.com/article/5440315>

[Daneshyari.com](https://daneshyari.com)