Ceramics International 43 (2017) 3654–3659

Contents lists available at ScienceDirect

Ceramics International

journal homepage: www.elsevier.com/locate/ceramint

Polyacrylic acid, a highly efficient dispersant for aqueous processing of tantalum carbide

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ARTICLE INFO

Keywords:
TaC
PAA
Dispersion
Surface properties
Microstructural homogeneity

ABSTRACT

Polyacrylic acid (PAA) with three different molecular weights (PAA-3000, PAA-15000, PAA-100000) was used as a dispersant to investigate the aqueous dispersion behavior of commercially available TaC powder. TaC stabilized with PAA-3000 polymer showed the best dispersion behavior according to zeta potential and rheological measurements. In addition, the TaC slurry in the presence of PAA-3000 had a minimized average particle size of merely 1.08 μm when dispersed in alkaline aqueous solutions. This was effective to break down any original agglomerates. A characteristic carboxylic peak was detected after adding PAA-3000 to the aqueous TaC system, using XPS analysis. Our TEM results confirmed that the surface properties of TaC were modified by the PAA-3000 dispersant. The slip-cast green body exhibits enhanced homogeneity compared to its dry-pressed counterpart. A dense TaC monolithic ceramic (> 99%) was obtained after sintering. This study contributes to the understanding of advanced wet-forming techniques for TaC ceramics.

1. Introduction

Owing to the high melting points (> 3000 °C), ultra-high temperature ceramics (UHTCs) can be used for several important applications including sharp leading edges, nose cones, thermal protection systems for reusable hypersonic re-entry space vehicles [1–5]. Tantalum carbide (TaC) ceramic is considered to be the ideal candidate for UHT applications because of their excellent properties, such as a high melting point (approximately 3900 °C), good thermal shock resistance, low vapor pressure at elevated temperature, and excellent mechanical properties [6].

Traditional forming techniques for UHTCs (including TaC-based ceramics) are pressure-assisted ones: for instance, dry pressing, cold isotactic pressing, and hot pressing [7]. Unfortunately, these techniques are limited to fabricate samples with relatively simple geometries and moderate dimensions. In addition, post-fabrication of components into desired shapes often requires costly and time-consuming machining. Green compacts formed from suspensions (a process also known as advanced wet-forming or colloidal processing) show technological superiority for the fabrication of large-scale components with more complex shapes. However, studies on wet-forming of TaC ceramics are rare: the dispersion of TaC poses a serious problem due to its extremely high material density (13.9 g cm^{-3}). Dispersants are technologically critical for the stabilization of high-density UHTC powders. For instance, a salt of a polyacrylate polymer was introduced for aqueous dispersion and gel-casting of ZrB_2-based ceramics in our previous work [8,9]. HE et al. adopted polyacrylic acid (PAA) as a dispersant to stabilize ZrB_2- and HfB_2-based suspensions [10,11].

Surface properties play a dominant role in influencing the dispersion behavior and advanced colloidal processing. They, thus, determine the final properties of ceramic components [12]. The aim of this research was to develop a highly efficient PAA-stabilized TaC aqueous processing system, paying close attention to the surface properties and stabilization mechanism.

2. Experimental procedure

2.1. Preparation of the aqueous suspension

Commercially available TaC powder (Aladdin, > 97% in purity; Table 1 lists impurities, mainly shown in the form of oxides), together with three types of PAA dispersants with different molecular weights (3000, 15000, and 100000; referred to as PAA-3000, PAA-15000, and PAA-100000, respectively), were used in this study.

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http://dx.doi.org/10.1016/j.ceramint.2016.11.205
Received 8 November 2016; Received in revised form 25 November 2016; Accepted 30 November 2016
Available online 01 December 2016

Table 1
XRF results of commercial TaC powder.

	TaC	Al_2O_3	SO_3	TiO_2	Cr_2O_3	Fe_2O_3	NiO	Nb_2O_5	F	Cl
wt%	97.66	0.02	0.02	1.25	0.23	0.33	0.03	0.18	0.26	0.02

The elemental content of commercial TaC powder was determined using x-ray fluorescence analysis (XRF, PW 2404 XRF, Philip, Eindhoven, the Netherlands). Zeta potential (Zetaplus, Brookhaven Instruments, Holtsville, NY) and particle size (Laser Diffraction Particle Size Analyzer, MasterSizer 3000, Malvern, UK) in the absence and presence of dispersants were tested in aqueous media. The TaC suspension with 0.01 vol% solid loading was ultrasonically prepared for 30 min before each measurement. The rheological behavior of TaC suspensions was measured using a parallel-plate system on Physica MCR 301 (Anton Paar Inc., Austria) at a constant temperature of 25 °C. The suspensions were prepared by mechanically stirring for an hour before every test. The crystallite size and morphology were recorded using a field emission transmission electron microscope (JEM 2100F, JEOL, Tokyo, Japan). The surface properties were analyzed by means of x-ray photoelectron spectroscopy (XPS, Escalab 250, Thermo Scientific, Britain). The powders were crushed after complete drying before the TEM and XPS measurements.

2.2. Slip casting and pressureless sintering

For aqueous slip casting process, a 25 vol% TaC suspension with 0.2 wt% PAA-3000 dispersant was prepared. Then, the slurry was degassed before pouring into a gypsum mold. The green body underwent careful and complete drying in order to prevent cracking: first by heating to 60 °C for 5 h, followed by 80 °C for another 5 h, before heating at 100 °C till complete drying. Dry-pressed TaC green bodies with 1.5 wt% phenolic resin (Shanghai QiNan Adhesive Material Factory, Shanghai, China) as binder was also prepared for comparison. The carbon yield of phenolic resin was 60 wt%. Cold isostatic pressing was applied to both the slip-casted and dry-pressed TaC green bodies for further improving of their homogeneity. Then, all samples were transferred into a high-temperature graphite resistant furnace (Zhuzhou Norbert High Temperature Instrument Co., Ltd., Zhuzhou, China). The pressureless sintering profile included vacuum-heating up to 1650 °C at a firing speed of 10 °C min^{-1} before switching to flowing Ar atmosphere, and a peak temperature of 2150 °C was finally reached, with a dwelling time of 90 min.

The pore size distribution of the TaC green body was characterized using an automatic mercury porosimeter (AutoPore IV 9510, Micromeritics, Norcross, GA, USA). The morphologies of both the green bodies and sintered bulks were observed by a field emission scanning electron microscope (FE-SEM, S-4800, Hitachi, Tokyo, Japan).

3. Results and discussion

3.1. Zeta potential and particle size

The morphology of commercial TaC powder is shown in Fig. 1. Hard agglomerates can be seen clearly. Such a highly agglomerated microstructure would result in strong tendency to form sediments rapidly, rather than disperse well. Thus, the addition of a dispersant to the aqueous solution was necessary.

The zeta-potential correlates with the electrophoresis mobility of particles in solution. The stability of a suspension is closely correlated with the zeta potential. The zeta-potential curves of TaC powders in absence and presence of PAA dispersants are shown in Fig. 2. For the pristine TaC powder, the zeta-potential values were negative at pH values higher than ~3. With the addition of PAA polymers, the zeta

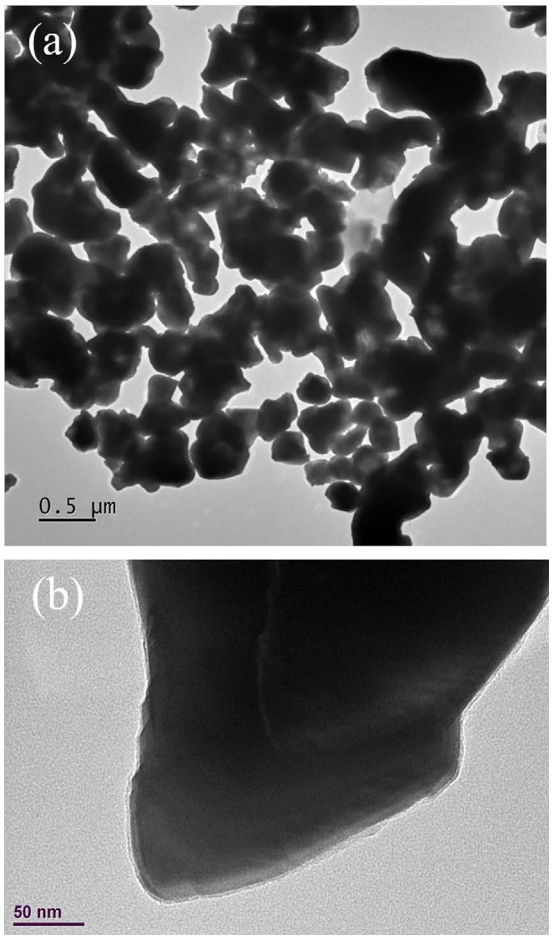

Fig. 1. TEM micrograph of the commercial TaC powder, (a) low magnification, and (b) high magnification.

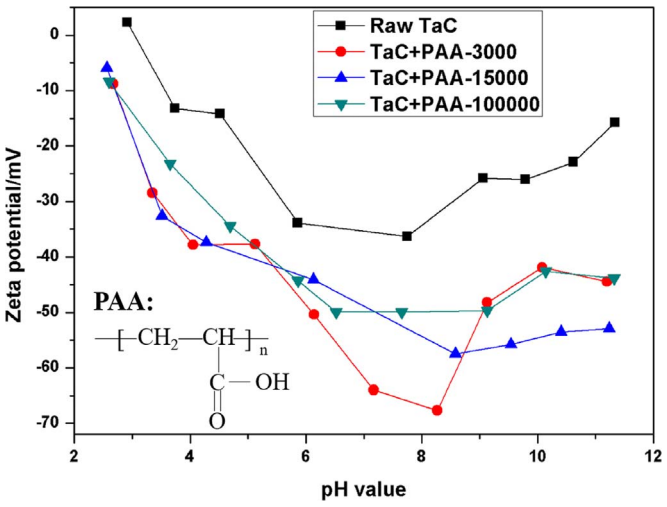

Fig. 2. Zeta potential curves of TaC powder in the absence and presence of PAA dispersants with various molecular weights.

potential values decreased further into negative numbers, i.e., the absolute values increased. Best for all suspensions, containing dispersants or not, was the alkaline region (pH 7.5–8.5). This can be attributed to the similar dispersion mechanism among all PAA species. Typically, a lowest zeta-potential value of −67.7 mV was measured for TaC powder stabilized with PAA-3000, thus, showing optimized surface charging behavior. Due to the electrostatic repulsion between highly ionized carboxylic (COO^-) groups in PAA molecules (see Fig. 2 for the