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Preparation of TiC ceramics through aqueous tape casting

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Abstract

TiC laminates are prepared through aqueous tape casting and hot pressing technique. Commercial TiC powders were firstly treated and the surface charge was determined through zeta potential measurement. The stability of concentrated TiC suspensions was characterized by rheological test. Results showed that the isoelectric point of as treated TiC particles moved slight toward more acid region, while the zeta potential curves decrease significantly. TiC suspensions exhibit a high degree of particle stabilization. After tape casting, TiC sheets are laminated and hot pressed. The strength and fracture toughness of TiC samples at 1850 °C are 532 MPa and 6.41 MPa $m^{1/2}$, respectively. The fracture mode is a mixture of intergranular and intragranular type.

Keywords: A. Tape casting; A. Suspensions; C. Fracture; C. Toughness and toughening; Laminates; Titanium carbide

1. Introduction

Tape casting is a convenient and well-developed technique for the preparation of ceramic substrates, capacitors and multilayered composites for various applications [1–5]. In recent years, tape casting is also used for the structural design of laminated composites [6–8]. Traditionally organic solvents were used to prepare concentrated suspensions due to their low surface tension and high compatibility with binder. Due to environmental and health considerations, aqueous tape casting processes have received more and more attention [9]. It is evidenced that laminated design is a feasible path to increase the strength and the fracture toughness [8,10]. However, multilayered composites without residual stress or component design also showed an increase in toughness [10].

In the present work, TiC laminates were prepared with aqueous tape casting and hot pressing. To lower the sintering temperature, we used Al_2O_3 and Y_2O_3 as sintering additives. The correlation between preparation technique and the mechanical properties of TiC laminates was investigated.

2. Experimental procedures

2.1. Starting materials

The material was prepared from commercially available TiC powder (Zhuzhou Hard Alloy plant, China). The mean particle diameter, the specific surface area and purity were 0.90 μm, 14.55 m^2/g and 98.7%, respectively. Five weight percent Al_2O_3 and Y_2O_3 was used as sintering additives. The dispersant was a secondary polyamine, polyethylene imine (PEI, Acros Organics, M.W. 50–60,000). The binder and the plasticizer were Polyvinyl alcohol 1788 (Qidong Chemical Plant, China) and glycerol (Analytical, Shanghai Chemical Reagent Corporation, China), respectively. Details about the selection and stability of dispersant were reported in previous papers [11–13].

The impurity of TiC powders were characterized by an X-ray fluorescence spectrometry PW2404 (Philips, Netherlands), see Table 1. To obtain well-dispersed slurries, the

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Table 1
Impurities in TiC powders

Components	Al_2O_3	SiO_2	Fe_2O_3	Cr_2O_3	NiO	ZrO_2
Content (wt.%)	0.137	0.031	0.317	0.804	0.019	0.019

surface of TiC powders was treated with acidic and alkaline solution in advance. The surface treatment procedure could be summarized as follows: the as-received TiC powders were first added to deionized water with hand stirring, followed by ultrasonication for 10 min to make suspension with the solid content as 15 vol.%. The pH was adjusted to 5 with HNO_3 (Analytical, Shanghai Chemical Reagent Corporation, China) and ultrasonication allowed for another 10 min. Then the suspensions were conditioned over a 6-h period. A filter was used to remove water in the slips. After filtration, new suspensions (15 vol.%) were prepared by ultrasonication of the obtained wet TiC cakes in deionized water. Suspension pH was adjusted to 11 with addition of $NH_3{\cdot}H_2O$ (Analytical, Shanghai Chemical Reagent Corporation, China) prior to conditioning for another 6 h. Following conditioning, the suspensions were subjected to additional filtration to remove the solvent. Finally, the obtained TiC cakes were dried and passed through a 200-mesh screen.

2.2. Zeta potential test

Zeta potential of as-received and as-treated TiC powders was determined by Zetaplus (Brookhaven Instruments Corporation). Suspensions were prepared by dispersing TiC powders (0.01 vol.%) in 0.001 M KCl (Analytical, Puqiao Scientific and Technological Corporation, China) solution. The pH was adjusted with 1 M HCl (Analytical, Shanghai Chemical Reagent Corporation, China) and 1 M NaOH (Analytical, Shanghai Chemical Reagent Corporation, China). The samples were ultrosonicated and stirred for 15 min prior to the measurements to ensure that only the mobility of the single particles was measured.

2.3. Rheological measurements

Shear dependent behavior of the examined system under steady shear conditions was evaluated by ascending and descending shear rate ramps from 0 to 400 s^{-1} in 10 min, and from 400 to 0 s^{-1}in 10 min, respectively. To avoid undesired influence from different mechanical histories, fresh samples were homogenized by shearing at an identical rate of 100 s^{-1} for 3 min and left standing for an additional 3 min prior to measurement (SR5, Rheometric Scientific).

2.4. Mechanical properties

The green sheets were cut into a rectangular size (40 mm × 50 mm) and stacked in a graphite die. Binder removal was carried out under an argon atmosphere. Samples were hot pressed at 1750–1850 °C and 35 MPa in Ar atmosphere for 0.5 h. The laminated green bodies were also sintered by spark plasma sintering for comparison. A cylindrical graphite pressure die was used with an inner diameter as 30 mm. The sintering temperature was set to 1600 °C and soaked for 4 min. The pressure, 30 MPa, was applied at the sintering temperature. TiC samples were also prepared by directly hot pressed dry TiC powers (with the same composition) in graphite die at 1850 °C and 35 MPa in Ar atmosphere for 0.5 h.

Tests of flexural strength were performed by three point bending from specimens of size 3 mm × 4 mm × 36 mm. Fracture toughness was determined by single-edge-notched beam (SENB) method at room temperature. The microstructure of the specimen was investigated by SEM and TEM. Energy dispersive X-ray (EDX) spectroscopy was also used to determine local components at the grain boundary.

3. Results and discussions

3.1. Aqueous tape casting process

The zeta potential of TiC powders before and after treatment is shown in Fig. 1. After surface treatment, the isoelectric point moves slight toward more acid region, while the zeta potential plot decreases significantly. These results suggest the increase in surface charge density of TiC particles. This change might be due to the removing of impurities on TiC powder surface, see Table 1.

Based on the study in a previous paper [11], TiC suspensions were prepared with 1.2 wt.% PEI as dispersant. The stability of 55 vol.% TiC slurries is characterized by rheological measurement. See Fig. 2.

At low shear rate (<120 s^{-1}), TiC slurries exhibited shear-thinning behavior with a decrease in viscosity when the shear rate increases. This could be explained by the formation of weak flocculation induced by free polymers [14,15]. At high solid loading, suspensions become too crowed and the average inter-particle distance is shorter than in the dilute situation and the frequency of particle collisions

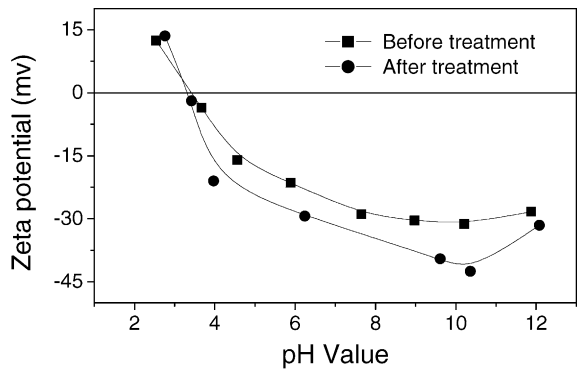


Fig. 1. Zeta potential of TiC powders before and after surface treatment.

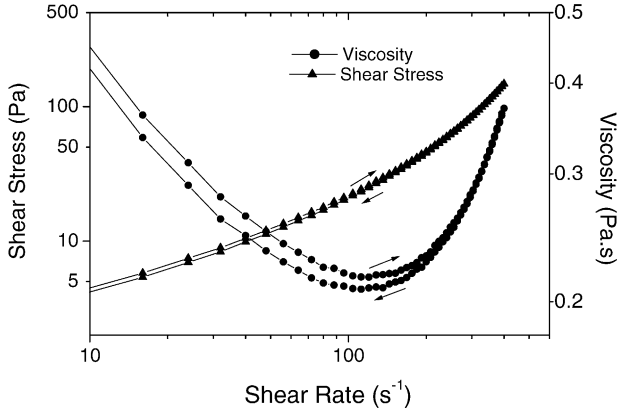


Fig. 2. Rheological properties of 55 vol.% TiC slurries with dispersant.

increase significantly. In addition, the adsorbed dispersant also took effect because of the contact with neighboring chains. The molecular motion and the resulting shear behavior become decidedly more complex. Therefore, the formation of gel-like network will be facilitated [16]. With the increase of shear rate, the suspension "structure" is broken up and exhibited shear-thinning and time-dependent behavior.

When the shear rate was in the range of 120–400 s^{-1}, the slips were characterized by a dilatant behavior, this increase in viscosity at high shear rate suggest the well stabilized slurry state.

However, compared to the result reported by Liwu Wang [17], TiC suspensions showed very limited thixotropical behavior, indicating that the time dependence effects were negligible and the TiC slips were homogeneous. At so high solid contents, this rheological behavior confirmed that the suspension exhibit a high degree of particle stabilization.

Table 2
Slurry formulation

Materials	Function	Density	vol.%	wt.%
TiC	Ceramic powder	4.938	25.18	60.92
Al_2O_3	Sintering additives	3.96	0.79	1.52
Y_2O_3	Sintering additives	5.01	0.41	1.02
PEI	Dispersant	1	1.24	0.61
Water	solvent	1	62.39	30.57
PVA	Binder	1.08	5.07	2.68
Glycerol	Plasticizer	1.113	4.92	2.68

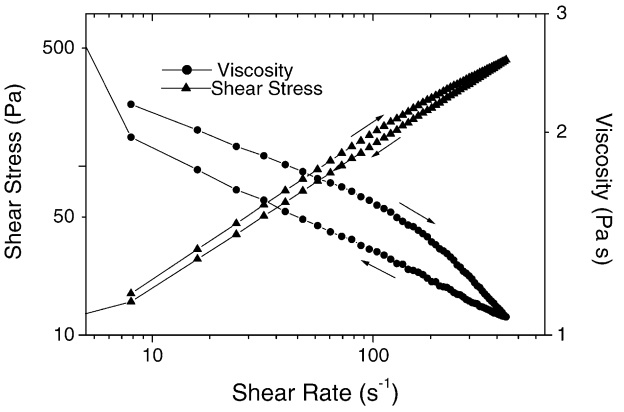


Fig. 3. Rheological properties of TiC suspensions with binder and plasticizer.

The formulation of the tape casting slurries is shown in Table 2. After the addition of binder and plasticizer, the rheological properties is also characterized, see Fig. 3.

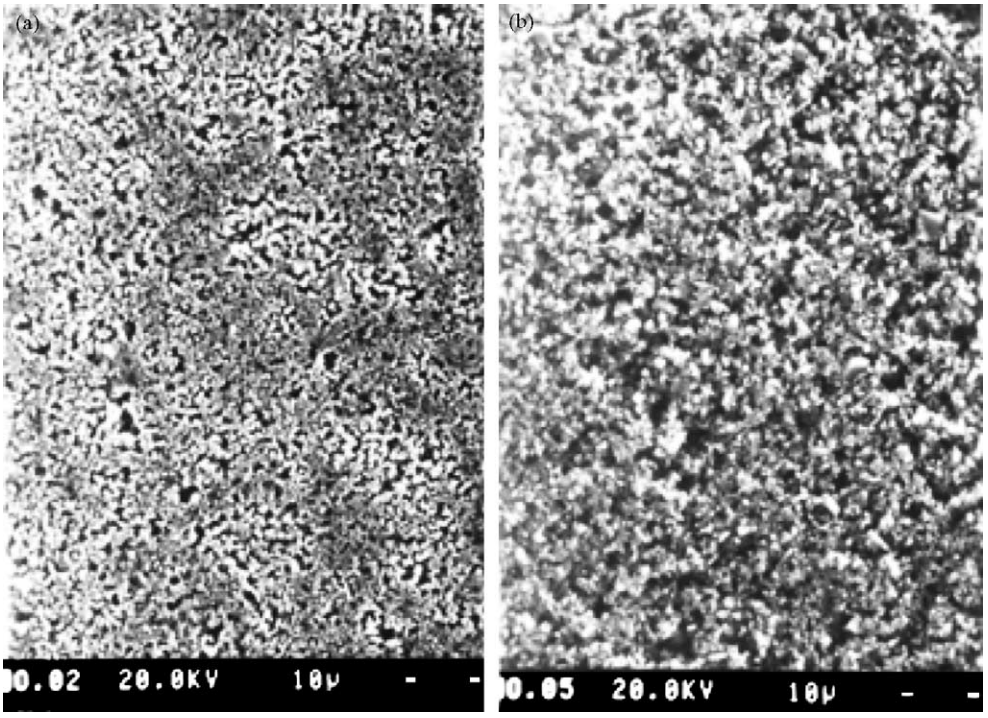


Fig. 4. SEM micrographs for dried tapes (a) bottom surface and (b) top surface.

As shown in Fig. 3, the slurries exhibit shear-thinning behavior with slight time-dependent effects. This kind of behavior is similar to that dominated by free polymers (dispersant) [14]. This time-dependent character is required for the tape casting process: During the casting process, slurry viscosity decreased under the shear stress generated by the doctor blade; immediately after the shear was released, the slurry viscosity returned to a high level (e.g. 105 Pa s at 0.01 s^{-1}). This avoided any settling of the particles and preserves a homogeneous distribution of the ceramic particles by reducing the mobility of the constituents.

TiC suspensions were cast onto fixed glass plate cleaned with ethanol to remove any debris. The casting speed was constant at 30 cm/min, and a doctor blade opening in a 100–500 μm range was generally used. The microstructure of the green sheets is shown in Fig. 4. Both sides of the tapes exhibit very smooth surfaces. The homogeneity of the particle packing might be due to the well-dispersed TiC suspensions and the high solid loading the TiC slurries.

3.2. Microstructure characterization

TiC powders is usually used as the reinforcement for other ceramic matrix composite, such as Al_2O_3 [18,19], SiC [20,21], Si_3N_4 [22,23] due to it's high elastic modulus and high hardness. In this paper, TiC ceramics were prepared by hot pressed with Al_2O_3 and Y_2O_3 as sintering additives. The mechanical properties were studied under different sintering temperatures, results are shown in Table 3. It was shown that that the strength and fracture toughness of the TiC samples increase with the increase in sintering temperature. TiC samples can be densified at 1850 °C and soaked for 30 min the strength and fracture toughness of TiC samples at 1850 °C are 532 MPa and 6.41 MPa $m^{1/2}$, respectively.

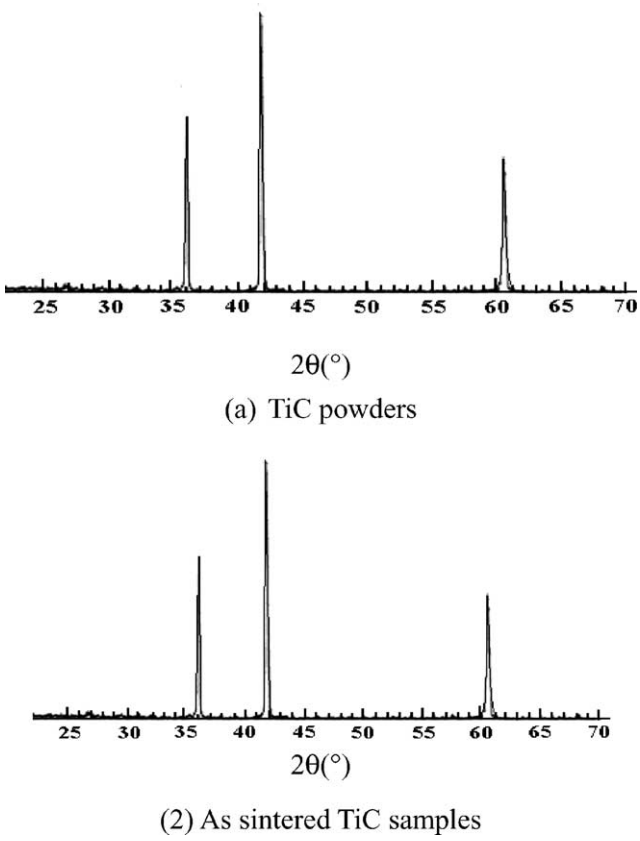
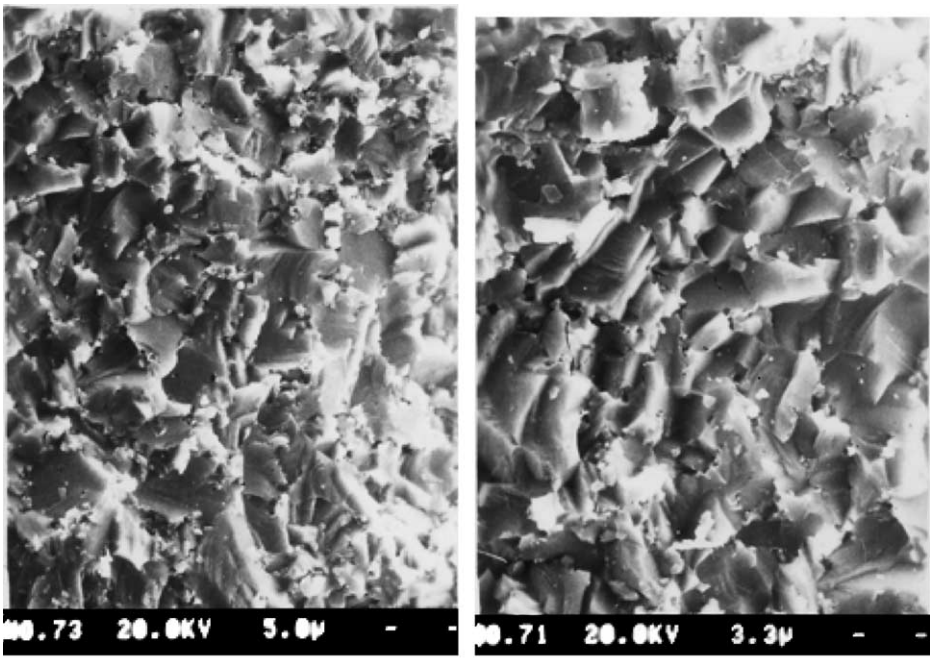


Fig. 5. XRD pattern of TiC powders and as-sintered TiC samples.



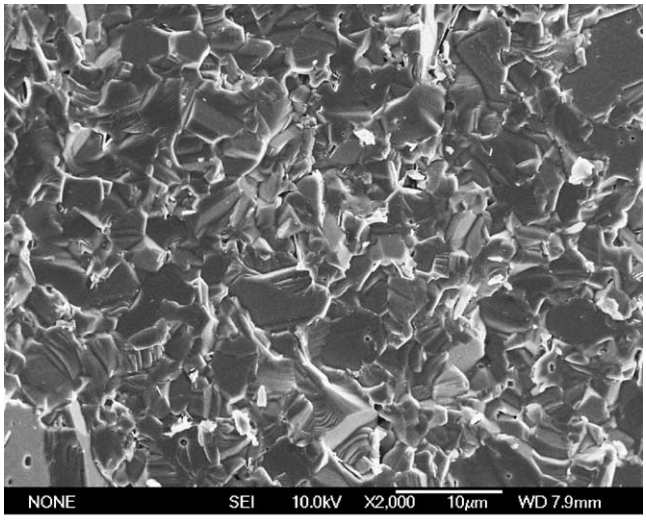
(a) ×2000 (b) ×3000

Fig. 6. SEM micrographs of the fracture surface of TiC samples (hot pressed).

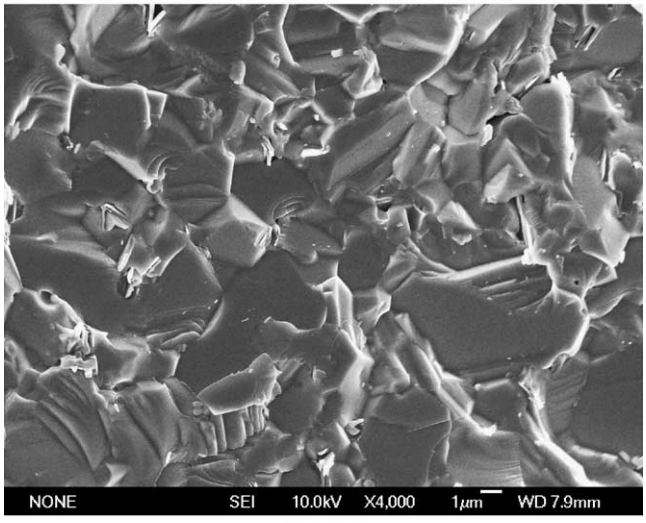
Table 3
Mechanical properties of TiC samples

Forming method	Sintered method	Sintering temperature (°C)	Strength (MPa)	Fracture toughness (MPa $m^{1/2}$)	Density (%)
Aqueous Tape casting	Hot pressing	1750	390	5.40	87.1
Aqueous Tape casting	Hot pressing	1800	464	5.40	93.2
Aqueous Tape casting	Hot pressing	1850	532	6.41	97.1
Aqueous Tape casting	Spark plasma sintering	1600	497	–	98.3
Dry-pressing	Hot pressing	1850	553	4.20	97.8

The XRD of starting TiC powders and the final TiC ceramics is shown in Fig. 5. After sintering, no second phase is observed. The microstructure of hot pressed TiC samples are shown in Fig. 6. The interface between individual TiC layers disappears and the TiC samples exhibit a catastrophic failure behavior. Based on SEM observation, the fracture mode is a mixture of intergranular and intragranular type. The microstructure of SPS (Spark plasma sintering) samples also showed the same fracture mode, see Fig. 7.



(a)×2000



(b) ×4000

Fig. 7. SEM micrographs of the fracture surface of TiC samples (SPS).

As shown in Table 3, The TiC laminates exhibited similar flexural strength and higher fracture toughness as compared to the monolithic samples. This cannot be mainly due to the thermal residual stresses in TiC samples because the mismatch of thermal expansion coefficient between TiC powders and the sintering additives (Y_2O_3, Al_2O_3) is not too larger. In addition, no second phase is observed after sintering, see Fig. 5. Therefore, differed from that for SiC samples [24], the contribution of thermal residual stress on the mechanical properties is unimportant.

There are two possible reasons for the improvement in mechanical properties: One is colloidal processing technique. As we know, colloidal processes could help to produce very homogeneous green sheets with limited flaws through colloidal control of powders [25]. Ham-Su and Wilkinson [26] had ever showed that lamination process could modify flaws to a more forgiving morphology, thus the severity of void-tape flaws could be reduced and the mechanical properties be improved. This kind of increase had been observed for laminate Al_2O_3 samples fabricated by non-aqueous tape casting techniques. In this paper, due to the well-dispersed slurries and the homogeneity of green sheets, the final TiC samples exhibit an improvement in mechanical properties either.

Another possible reason is the presence of free carbon in samples, though the state and effect of it is still unclear. Usually the binder in green sheets are not homogeneously distributed after tape casting and drying procedure [27]. The surface region is actually an organic-rich place due to the solvent evaporation effect. As we know, the organic components cannot be thoroughly removed from samples in Ar atmosphere. So after lamination and binder remove process, some free carbon will still stay in the samples. This carbon will influence the sintering process and the subsequent mechanical of final TiC samples. Further study in this area is in process.

4. Conclusions

The isoelectric point of as-treated TiC particles moved slight toward more acid region, while the zeta potential curves decrease significantly. Rheological measurement showed that TiC suspensions exhibit a high degree of

particle stabilization. Laminated TiC composites prepared by aqueous tape casting showed an improvement in fracture toughness. The strength and fracture toughness of TiC samples at 1850 °C are 532 MPa and 6.41 MPa $m^{1/2}$, respectively. The fracture mode is a mixture of intergranular and intragranular type.

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