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Research Article

Preparation of Stable ZrB_2-SiC-B_4C Aqueous Suspension for Composite Based Coating: Effect of Solid Content and Dispersant on Stability

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ZrB_2-SiC-B_4C aqueous suspension has been prepared using poly(ethyleneimine) as a dispersant. Since increasing the solid content of suspension leads to high compaction and consequently low porosities through final coat, the effect of solid content has been studied. The dispersant and solid content were changed in the range of 0.3–1.5 wt.% and 45–55 vol.%, respectively, to assess the optimal conditions effect on stability and characteristics of suspension. Results of zeta potential measurements and rheological analysis at pH 7.8 showed that the composite suspension including 45 vol.% solid content and 1.5 wt.% dispersant was in stable state.

1. Introduction

The interest in ultrahigh temperature ceramics (UHTCs) has increased significantly in recent years [1–3] because of their remarkable properties, such as high melting point, high thermal conductivities, excellent corrosion resistance, and good oxidation resistance [4, 5], which make them promising candidates for high temperature structural applications. Among the UHTCs, zirconium diboride (ZrB_2) is a material of particular interest owing to the excellent and unique combination of high melting point, high electrical and thermal conductivity, good thermal shock and wear resistance, and chemical inertness [6]. These properties make it an attractive candidate for ultrahigh temperature applications where corrosion-wear-oxidation resistance is demanded [6, 7].

In spite of the excellent high temperature and mechanical properties of ZrB_2-based ceramics, their rather low fracture toughness (3-4 MPa $m^{1/2}$) has limited the sample size because of the low reliability and, thus, has reduced the chances for application of boride ceramics [8].

Several studies have demonstrated that the addition of SiC could improve the oxidation resistance and mechanical properties of ZrB_2 ceramics, so a lot of works have been carried out on ZrB_2-SiC ceramics [9–16]. Nowadays, colloidal processing such as tape casting, slip casting [17, 18], and dip coating method, which can produce a more homogeneous green microstructure, is becoming more and more important in the fabrication of advanced ceramics because it offers the potential to produce reliable ceramic films and bulk forms through careful control of initial suspension “structure” and its evolution during fabrication [19].

For the fabrication of highly dense ceramic composites, the preparation of well-dispersed and stable ceramic suspensions is one of the most important issues in order to guarantee a homogeneous filling of the interstices among ceramic powders [8]. However, dispersion behaviors of aqueous ZrB_2-SiC-B_4C slurries have been rarely analyzed [17, 18] and reports on the successful preparation of highly concentrated aqueous suspensions have not been available. To maintain the stability through an aqueous suspension, it is needed to prevent particles to (i) stick when they collide and (ii) sediment when they are introduced in a colloidal system. This can be achieved by enhancing the charge associated with the particles, that is, zeta potential [20]. Also, the proper viscosity of suspension causes a slower settling velocity and therefore better stability of suspension.

In the present research, the dispersion behaviors of ZrB_2-SiC-B_4C (ZSB) composite in aqueous medium are investigated with the application of a dispersant (poly(ethylenimine), PEI) for the preparation of highly concentrated aqueous ZSB suspensions.

2. Experimental Procedure

2.1. Aqueous Suspension Preparation. Commercially available ZrB_2 powder (initial particle size ~6 μm), SiC powder (average particle size 1.5 μm), and B_4C powder (average particle size as 3 μm) were used as raw materials. Deionized water and PEI (molecular weight (M_w): 2,000; 50 wt.% in H_2O; Sigma-Aldrich, Belgium) were used for the preparation of ZSB aqueous suspension.

The as-received ZrB_2 powder was milled using a planetary mill with ethanol, a WC ball (diameter: 10 mm), and a stainless steel (coated by WC) jar at 150 revolutions per minute (rpm) for 2 h. The average size of ZrB_2 powders was reduced to 3–5 μm after milling (Figure 1). A mixture of 80 vol.% zirconium diboride and 20 vol.% silicon carbide powders was selected as starting materials. 3 wt.% boron carbide was also used as sintering aid which causes a better sintering of the ceramic coating through next step of preparation.

To produce slurries, powders were mixed with various amounts of PEI (0.3–1.5 wt.%) as a dispersant. The pH of slurries was also set 7.8. The initial ratio of solid to liquid was set as 45 vol.% according to previous researches [17–19]. To investigate the effect of solid content on ZSB suspension properties, slurries with 45, 46, 47.5, 50, 52.5, and 55 vol.% solid contents were prepared. Table 1 shows the composition of slurries.

2.2. Characterization. Size distribution of milled ZrB_2 powders was measured by zeta size analyzer (ZEN3600, England). Rheological behavior and viscosity of slurries were characterized by rheometer apparatus (Physica CPR300, Japan). Ultrasonic vibrator (Hielscher-UP200H, Germany) was used to disperse suspensions prior to zeta potential analyzing. The zeta potential analyzer (ZEN3600, England) was also used to measure the zeta potential of slurries.

3. Results and Discussion

Prior to any investigation of a colloidal system, it is necessary to bring a proper understanding of a stable suspension to the system, for example, how could a colloidal stability be achieved? The force balance associated with the particles in the suspension is simply demonstrated in two terms [21] (1):

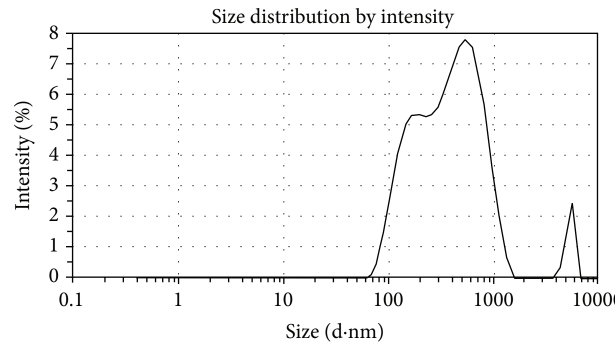


Figure 1: Size distribution of ZrB_2 milled powders.

Table 1: Characteristics of slurries.

Solid content	PEI
Investigation of effect of PEI on slurry properties	
45 vol.%	0.3 wt.%
	0.5 wt.%
	0.7 wt.%
	1 wt.%
	1.5 wt.%
Investigation of effect of solid content on slurry properties	
45 vol.%	1.5 wt.%
46 vol.%	
47.5 vol.%	
50 vol.%	
52.5 vol.%	
55 vol.%	
45 vol.%	1 wt.%
46 vol.%	

(i) gravitational forces (numerator in (1)) and (ii) Brownian forces (denominator in (1)). Consider

$$\Delta F \approx \frac{a^4 \Delta\rho g}{k_B T}, \tag{1}$$

where ΔF, a, and $\Delta\rho$ are the force balance, particles size, and density difference of particles and continuous phase, respectively. k_B and T are Boltzmann constant and temperature, respectively. In submicron colloidal systems, the Brownian motion is usually significant to overcome the effect of gravity. To maintain stability through Brownian motion, it is necessary to prevent particles sticking when they collide. This can be achieved by increasing the charge associated with the particles, that is, zeta potential of particles. Figure 2 indicates the zeta potential of a sphere particle within an aqueous medium.

By increasing the zeta potential (over ±30 mV), the significance of long range electrostatic double layer surrounding particles increases which leads to a repulsion between particles in suspension [22]. Figure 3 depicts the schematic view of the effect of zeta potential on dispersion and coagulation of particles in a suspension.

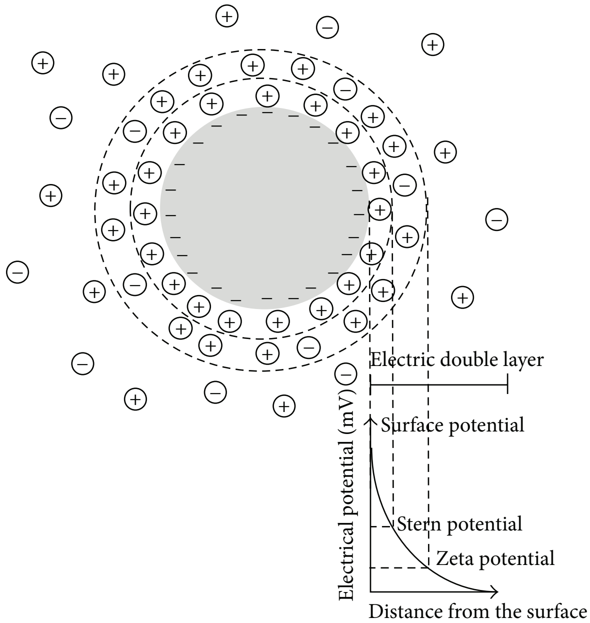


FIGURE 2: Electrostatic double layer surrounding sphere particles in an aqueous medium.

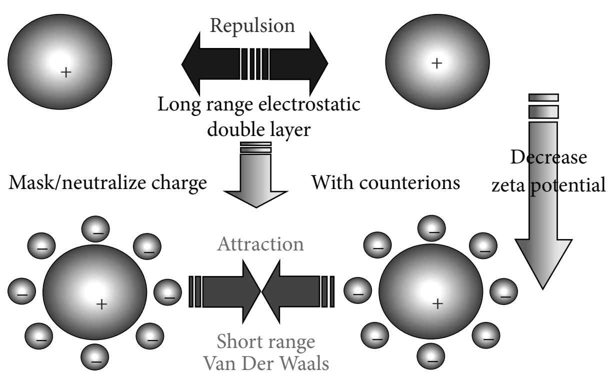


FIGURE 3: Schematic view of the particles interactions in an aqueous suspension [22].

Zeta potential (ν) of slurries including 45 vol.% solid content and different amounts of dispersant is shown in Figure 4. pH of slurries was set as 7.8. As it is indicated, the zeta potential of slurry without PEI is in unstable area ($-30 < \nu < 30$). Increasing PEI amount, 0.3 wt.%, led to the zeta potential falling in stable area ($\nu > 30$ and $\nu < -30$). A slight increase occurred in the zeta potential while PEI amount increased from 0.3 to 1.5 wt.%. This increase could be explained in terms of adsorption of PEI molecules on surface of particles [23]. Although the data concerning the reaction between ZrB_2-SiC-B_4C particles and PEI are currently unavailable, Wang and Gao [24] have reported that the adsorption of PEI on ZrB_2 is of a high affinity type, and hydrogen bonding was proposed to be the predominant mechanism between PEI and ZrB_2 under both acidic and basic conditions.

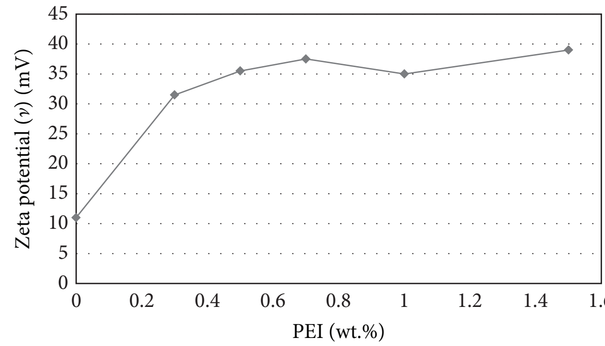


FIGURE 4: Zeta potential of ZSB slurry with various amounts of PEI dispersant.

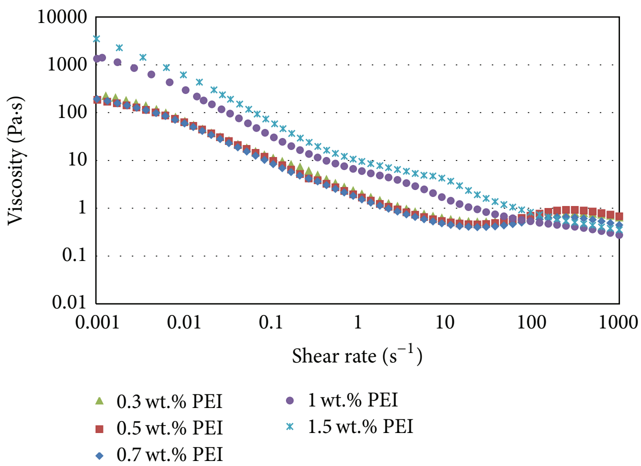
Protons are adsorbed on PEI molecules when PEI is dissolved in a neutral solution which results in the protonation of the amine group in the molecule [23]. So, the adsorption of positively charged PEI on the surface of the powder is increased. Therefore, as stated earlier, the higher the charge density on particles is, the higher the zeta potential and repulsive force on particles would be [22]. Consequently, it eventually leads to stability of suspension. On the other hand, viscosity of suspension plays a significant role in the stability of suspension. The settling velocity of suspension could be explained by Stokes equation (2) for concentrated colloidal systems. Consider

$$V = \frac{2\Delta\rho g a^2 (1-\varphi)^{5\pm0.25}}{9\eta}, \tag{2}$$

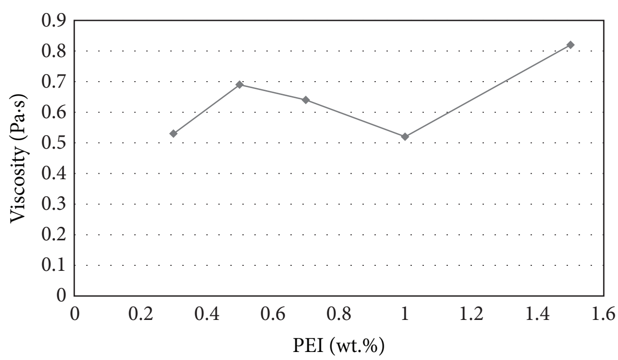
where $\Delta\rho$, a, and η are the density difference of particles and continuous phase, particles size, and continuous phase viscosity, respectively. φ is the phase volume percent which adversely affects settling velocity. Although higher solid phase volume percent decreases the velocity of sedimentation and increases viscosity, it causes a higher chance of coagulation of particles. Therefore, a proper value of solid content is necessary to be estimated in a colloidal system.

Rheological behavior of slurries including different amounts of PEI is showed in Figure 5(a). The viscosity of the concentrated slurry increased with the addition of PEI amount up to 1.5 wt.% which was due to very high charge absorbed by PEI molecules on particles surface. Thus, high charge density helps slow down sedimentation of suspension. According to the rheological behavior and viscosity of slurries (Figure 5(b)), as well as zeta potential of slurries, it seems slurries with 1 and 1.5 wt.% PEI would have appropriate stability and viscosity depending on coating process. To fabricate composite based coating by plasma spray, slip casting, and tape casting methods [17–19], the stable slurry with low viscosity is suitable. On the other hand, the stable slurry with absolute proper viscosity (almost in the range of 0.8–1.0 Pa·s) is definitely necessary to fabricate the coat by dip coating.

Previous researches [17–19, 25, 26] show that the optimum slurry which was used for coating includes 40–45 vol.% solid content and different amounts of 1–1.5 wt.% of various



(a)



(b)

FIGURE 5: Effect of dispersant content on (a) rheological behavior of 45 vol.% ZSB slurries and (b) the viscosity at 96.2 s^{-1} (pH = 7.8).

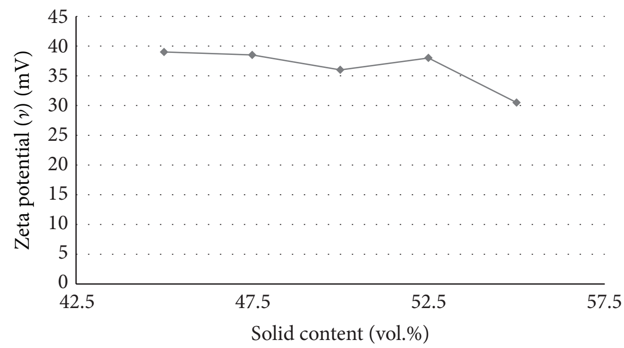


FIGURE 6: Zeta potential of ZSB slurries with 1.5 wt.% PEI and different amounts of solid content.

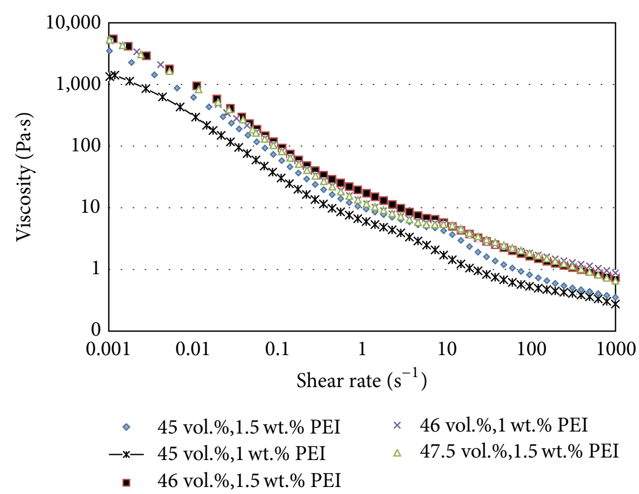


FIGURE 7: Rheological behavior of ZSB slurries including different amounts of PEI and solid content (pH = 7.8).

dispersants (e.g., poly(acrylamine), Dolapix, and Duramax). It is obviously supposed that increasing the solid content of suspension leads to high homogeneity and compaction and subsequently low porosities of coat. Accordingly, the effect of solid content has been studied to determine proper suspension to fabricate ZSB composite based coating. The changes of zeta potential of slurries with various amounts of solid content are depicted in Figure 6.

According to the zeta potential and viscosity of slurries with different amounts of PEI, 1.5 wt.% PEI was a proper amount to prepare the stable slurry for dip coating. Hence, solid content of slurries with 1.5 wt.% PEI was changed to determine the proper slurry for subsequent step, fabrication of ZSB based coating by dipping method. By increasing the solid content from 45 to 52.5 vol.%, the zeta potential of slurries was in stable area; however, increasing to 55 vol.% caused slight diminution of zeta potential falling into the unstable state.

Figure 7 depicts the rheological behavior of ZSB slurries. It indicates that increasing the solid content of slurry, up to 47.5 vol.%, leads to the high viscosity; therefore, slurry with solid content higher than 47.5 vol.% is not suitable for coating step by dip coating method. On the other hand, the high viscose suspension is not suitable for coating by slip casting or tape casting. Table 2 shows the viscosity of slurries. As it seems, the viscosity of slurries with 46 and 47.5 vol.% solid content and 1.5 wt.% PEI is very high. The rheological test was used to estimate the viscosity of slurry including 46 vol.% solid content and 1 wt.% PEI to improve solid content from 45 to 46 vol.%, but unfortunately the viscosity was high again. Indeed, increasing the solid content is very critical since it enhances the chance of the particles agglomeration and consequently increases the particle size. According to (1) and (2), increasing the particle size leads to increasing the gravitation forces and also higher settling velocity. Although increasing φ in (2) causes lower settling velocity (V) and higher viscosity (η), its effect on agglomeration and increasing particle size is more dominant than that on V and η. Therefore, the slurry with optimal condition was obtained including 45 vol.% solid content along with 1 and 1.5 wt.% PEI to be used as composite based coating by slip or tape casting and dip coating method.

Table 2: Specification of slurries.

Solid content/vol.%	PEI/wt.%	Viscosity/Pa·s (at 96.2 s^{-1})
45	1.5	0.82
45	1	0.53
46	1.5	1.64
46	1	1.84
47.5	1.5	1.82

4. Conclusion

ZSB composite aqueous suspension was prepared at pH 7.8, adjacent to the neutral state, using PEI as a dispersant. Different values of PEI (0.3–1.5 wt.%) and different amounts of solid content (45–55 vol.%) were used to investigate their effect on stability of aqueous suspensions. A slight increase occurred in the zeta potential while PEI amount increased from 0.3 to 1.5 wt.%. Increasing the solid content from 45 to 52.5 vol.% led to being the zeta potential of slurries in stable state ($\nu > 30$); however, increasing till 55 vol.% caused the sudden decrease to the unstable state. Viscosity of slurry would be low or in a proper amount depending on coating method. Incorporating zeta potential and viscosity showed that the stable composite suspension including 45 vol.% solid content as well as 1 and 1.5 wt.% PEI is an appropriate slurry to produce ZSB composite coat by slip and tape casting and dip coating methods, respectively.

Conflict of Interests

The authors declare that there is no conflict of interests regarding the publication of this paper.

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