

Aqueous Electrophoretic Deposition of ZrB_2 -SiC Nano-composites in Pulsed DC Electric Fields

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Abstract

ZrB_2 -SiC ultra-high temperature ceramic composites have been considered to be the optimal candidate for using in extreme environments. The present communication for the first time applied aqueous electrophoretic deposition for successfully preparing ZrB_2 -SiC nano-composites in pulsed DC electric fields. The deposition behavior was investigated based on the influences of applied voltage, duty cycle and frequency. A smooth, uniform and pore-free ZrB_2 -SiC nano-composite was successfully synthesized. The highest green density of 67.1% was achieved for the nano-composite with the SiC content of 26.7 wt.%. We believe that the present research will open up a new horizon in preparing bulk ceramic composites or composite working parts in industries.

Keywords: ZrB_2 -SiC; Aqueous electrophoretic deposition; Pulsed DC; Duty cycle; Frequency; Green density

Introduction

ZrB_2 -SiC ultra-high temperature ceramic composites have been considered to be the optimal candidate for using in extreme environments, due to their superior strength and good oxidation resistance at ultra-high temperatures [1-3]. Recently, colloidal processing has been attracted much attention as its easy formation of complex-shaped and uniform microstructure green body [4]. Based on the colloidal processing, several methods [5-8], including aqueous gel casting, slip casting and tape casting have been developed to synthesize ZrB_2 -SiC composites. As we know, electrophoretic deposition (EPD) is one of the most promising colloidal processing methods. Therefore, it is well expected to apply the EPD for successfully preparing ZrB_2 -SiC composites.

In an EPD process, charged particles in a suspension move towards an electrode under a DC electric field. Organic chemicals are usually used as the solvent during an EPD process as water may be electrolyzed in a high DC electric field, where the formed H_2 or O_2 bubbles may be incorporated in the deposit. Recently, aqueous EPD under modulated electric fields, including pulsed DC and asymmetric AC, has been developed in order to successfully synthesize a smooth, uniform and pore-free deposit [9-11].

In the present communication aqueous EPD in pulsed DC electric fields was for the first time applied to successfully deposit ZrB_2 -SiC nano-composites. We systematically investigated the effect of voltage, duty cycle and frequency on the deposition behavior. The composition and green density of the ZrB_2 -SiC nano-composite were also identified. It was found that the highest green density of 67.1% was achieved for the nano-composite with the SiC content of 26.7 wt.%. We believe that the present investigation may open up a new horizon in preparing bulk ceramic composites or composite working parts in industries.

Experimental

The commercialized 316 stainless steel was used as the substrate with the size of $20 \times 20 \times 2.5$ mm. Before the electrophoretic deposition, the substrate was mechanically ground up to a grit of #800, and then ultrasonically cleaned in ethanol.

The commercialized ZrB_2 and SiC powders (99.9% purity) were used to prepare the aqueous suspension with the average size of 1.5 μ m

and 40 nm, respectively. The aqueous suspension of ZrB_2 -SiC nano-composites was prepared as below. Firstly, the mixture of ZrB_2 and SiC powders with the concentration of 20 wt.% was added into distilled water. In the mixture, the content of ZrB_2 and SiC was 80 wt.% and 20 wt.%, respectively. Polyethylene imine with the average molecular weight of 10000 was used as the dispersant with the concentration of 0.6 wt.% (based on the powder mixture weight). Then, the pH value of the aqueous suspension was adjusted to be 6 by adding HNO_3 . Finally, the prepared suspension was mechanically stirred for 24 h at room temperature.

The electrophoretic deposition was conducted in a pulsed DC electric field, where the voltage was 0-60 V, the duty cycle was 10-90%, and the frequency was 25-100 Hz. The deposition time was 6 min. The distance between the anodic and cathodic electrode (316 stainless steel) was 20 mm.

The weight of the deposits was measured by an analytical balance with an accuracy of 0.1 mg. The surface macro-morphologies of the deposits were characterized by an optical microscope. In order to identify the composition of the ZrB_2 -SiC nano-composite, XRD patterns of the nano-composite were firstly conducted with Cu K α radiation ($U=40$ kV, $I=40$ mA) and the 2θ range from 10° to 90° at a scanning rate of 0.02/s, and then the Eva software was used to analyze the content of ZrB_2 and SiC. The density of the deposit was measured by a traditional Archimedes method. The theoretical density of the ZrB_2 -SiC nano-composit was calculated based on the contents and the theoretical densities of ZrB_2 and SiC ($\rho_{ZrB_2}=6.085$ g/cm 3 , $\rho_{SiC}=3.22$ g/cm 3). The final green density (% theoretical density) was calculated by the measured density divided by the theoretical density.

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Received December 23, 2015; Accepted January 22, 2016; Published January 27, 2016

Citation: Zhang Y, Lin X, Chen W, Wang L (2016) Aqueous Electrophoretic Deposition of ZrB_2 -SiC Nano-composites in Pulsed DC Electric Fields. Adv Automob Eng S1: 003. doi:10.4172/2167-7670.S1-003

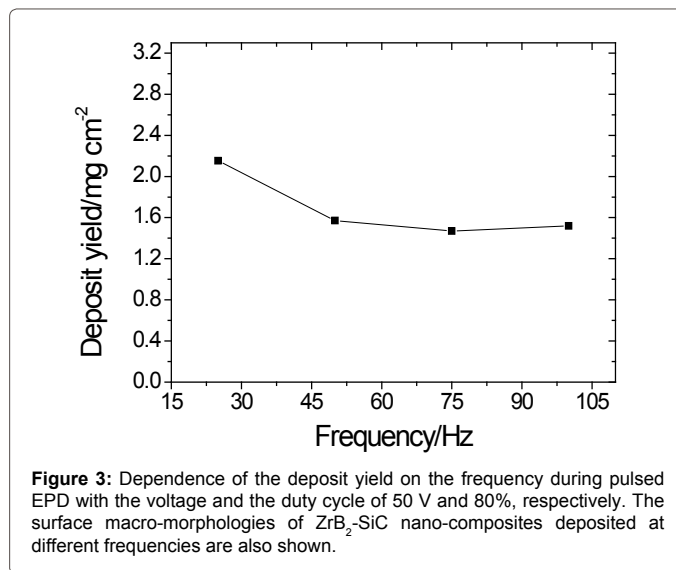
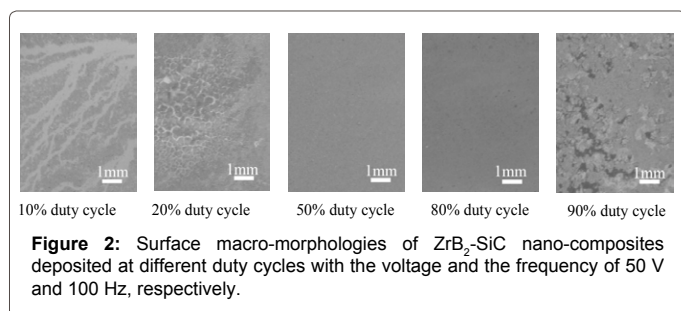
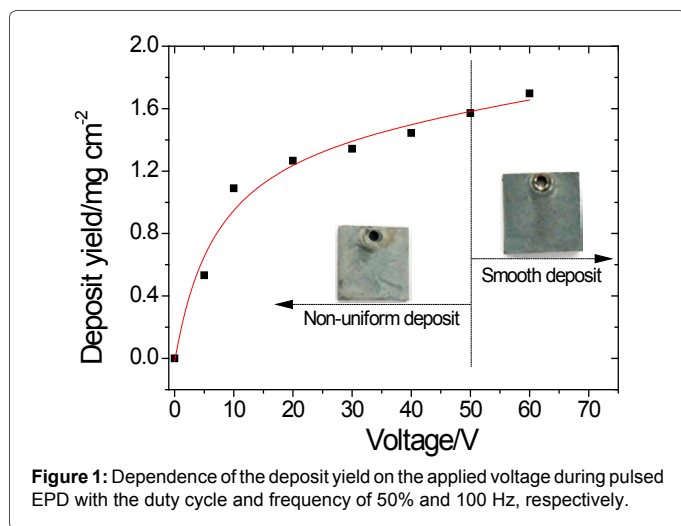
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Results and Discussion

Figure 1 shows the dependence of the deposit yield on the applied voltage during the pulsed EPD. As the voltage increased from 0 V to 60 V, the deposit yield parabolically increased up to 1.7 mg/cm². A non-uniform deposit was observed on the surface of the 316 substrate with the applied voltage below 50 V, compared to a smooth deposit above 50 V. A relatively low voltage was obviously not able to motivate the co-deposition of the ZrB₂ and SiC particles, quite different from the deposition of single ceramic particles [11,12].

When considering a pulsed DC signal, two factors, i.e. duty cycle and frequency, have been believed to significantly influence the movement and deposition of the ceramic particles. In the present communication, we significantly investigated the effect of the duty cycle and frequency on the co-deposition of ZrB₂ and SiC, as shown in Figures 2 and 3. After deposition for 6 min, a non-uniform or cracked deposit was formed with the relatively low duty cycles of 10-20% and the high duty cycle of 90% (Figure 2). A smooth and pore-free deposit was observed when the co-deposition was conducted at the duty cycles of 50-80% (Figure 2). At a low duty cycle, the T_{ON} time is short, for example, 0.6 min at 10% duty cycle. However, we again tried a relatively long-term duration up to 30-40 min for 10% duty cycle, and unfortunately a smooth or pore-free deposit was not obtained yet. The above analysis clearly reveals that the alternate between T_{ON} and T_{OFF} significantly determined the formation of the ZrB₂-SiC nano-composites.

The effect of the frequency on the deposition behavior is shown in Figure 3. Gas bubbles were only formed at the low frequency of 25 Hz, revealing the importance of high frequencies in avoiding the formation of gas bubbles during aqueous EPD. The deposits at 50, 75 and 100 Hz similarly showed a smooth surface. Additionally the small deposit yield



Samples	Frequency/Hz	Composition (weight percentage of SiC, wt.%)	Measured density/g cm ⁻³	Theoretical density/g cm ⁻³	Green density/%
1	50	28.0	2.32	4.87	47.6
2	75	26.7	3.30	4.91	67.1
3	100	30.5	1.74	4.78	36.4

Table 1: Composition and density of the ZrB₂-SiC nano-composites prepared by pulsed EPD with the voltage and the duty cycle of 50 V and 80%, respectively.

was similarly obtained at 50-100 Hz, revealing the formation of a thin deposit during the pulsed EPD for 6 min.

It is believed that the absence of drying cracks and high green densities determine the quality of a deposit, correspondingly effectively influencing the following sintering behaviors and properties. The composition and density of the ZrB₂-SiC nano-composites were presently measured, as shown in Table 1. The content of SiC was measured to be 28.0 wt.%, 26.7 wt.% and 30.5 wt.% as the ZrB₂-SiC nano-composite was deposited at 50 Hz, 75 Hz and 100 Hz, respectively. The highest density of 3.30 g/cm³ was obtained for the nano-composite deposited at 75 Hz, with the green density measured to be as high as 67.1%. A smooth deposit was similarly formed at high frequencies (Figure 3), while the deposits exhibited completely different densities (Table 1). Especially, the density of the nano-composite deposited at 75 Hz shows ~43% higher than the deposit at 50 Hz, although both nano-composites have a similar composition. The mechanism is not fully understood yet. Van Tassel and Randall [13] summarized the deposition mechanisms, including direct electrostatic force, electro sedimentary, ion depletion enhanced electrostatic, salting out, charge reduction/neutralization, squeezing out, bridging flocculation and desorption of neutral/charge polymer, polyelectrolyte neutralization. We propose that the frequency is strongly linked with the deposition kinetics.

Conclusions

The present communication for the first time reported the aqueous EPD of ZrB₂-SiC nano-composites in pulsed DC electric fields. We systematically investigated the effect of applied voltage, duty cycle and frequency on the deposit behaviors. A non-uniform deposit was observed on the surface of the 316 substrate with the applied voltage

below 50 V, compared to a smooth deposit above 50 V. A smooth and pore-free deposit was observed when the co-deposition was conducted at the duty cycles of 50-80%. The highest density of 3.30 g/cm³ was obtained for the nano-composite deposited at 75 Hz, with the green density measured to be as high as 67.1%. We believe that the aqueous EPD in pulsed DC electric fields may open up a new horizon in preparing bulk ceramic composites or composite working parts in industries.

Acknowledgements

We thank Mr. D.H. Chen for helping the preparation of the aqueous suspension. We also thank Prof. S.Z. Zhu and A/P. Y.W. Wang for useful discussions on the density of deposits.

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