DEVELOPMENT OF ELECTROPHORETIC DEPOSITION FOR SIC/SIC COMPOSITES

First A. HOU Huining[1], Second B. ZHOU Xingui[2] and Third C. LI Mingyuan[3]

[1]National University of Defense and Technology, Changsha, China, hhn_cathy@163.com
[2]National University of Defense and Technology, Changsha, China, Professor, zhouxinguilmy@163.com
[3]National University of Defense and Technology, Changsha, China, m_y_lee@126.com

Keywords: SiC$_f$/SiC composites, Electrophoretic deposition

ABSTRACT

Electrophoretic deposition (EPD) has been recognized as a novel, simple and versatile method for fabricating fiber-reinforced ceramic composites. By conducting EPD from a well-dispersed, aqueous or non-aqueous suspension, it is feasible to produce closely packed SiC green bodies. The hybrid process combined with EPD shows significant improvement in product properties to single PIP and great price competitiveness to CVI and some other conventional routes, which gains tremendous interests by researchers from all over the world. In this paper, the recent research and development of SiC$_f$/SiC composites fabricated by EPD using different parameters and device are reviewed, the properties of mechanics and thermals are introduced, together with summarization and prospect.

1 INTRODUCTION

With low neutron activation and high mechanical and thermal stability, SiC$_f$/SiC composites are considered to be the best candidate materials for structure applications of future fusion reactors. Conventional processing routes to fabricating SiC$_f$/SiC composites, for example, PIP and CVI, are usually weak in irradiation properties and long fabrication time. To overcome these disadvantages, some researchers remove their attention to a new fabrication technique combining Electrophoresis deposition (EPD) and Polymer infiltration and pyrolysis (PIP).

Why combining electrophoretic deposition and polymer infiltration and pyrolysis to produce SiC$_f$/SiC composites? According to Nannetti et al. [1], hybrid techniques offer new possibilities for the production of high-purity gas-impermeable SiC$_f$/SiC composites. On the one hand, fiber preforms were infiltrated with high packing density of SiC powders after EPD, only a few PIP cycles would be needed to achieve a relatively high density of the material. On the other hand, there were large amount of initial crystalline powder (β-SiC) before PIP, which would improve its thermal conductivity considerably. Hence this hybrid process could be an effective way to produce SiC$_f$/SiC composites with sufficient properties.

In fabrication of ceramic matrix composites by means of EPD, many parameters have to be taken into account. For example, the liquid media, the dispersants, the Zeta-potential and conductivity of suspensions, and the EPD parameters like electric field strength, current density and deposition time, etc. Besides, some other reinforcement phase with high thermal and mechanical properties (like CNTs) could be introduced to SiC_f/SiC composites through electrophoretic deposition, improving its thermal and mechanical performance, especially thermal conductivity for fusion applications.

2 SUSPENSIONS FOR EPD

With regard to the suspensions for EPD, a variety of parameters must be considered, such as the physicochemical nature of both suspended particles and the liquid medium, and the influence of different type of the dispersants, etc.

Common liquid media applied to involving powders and dissolving surfactants are usually ethanol and water. Ethanol appears to be a quite frequently used liquid in EPD, whose main drawback is the hygroscopicity that makes it difficult to limit water content. Notably, a small amount of water may significantly change the properties of SiC powder suspension that hinders control over the EPD process, which should result in bad reproducibility. As for aqueous suspension, due to high dielectric constant, water may result in relatively high zeta-potential values (usually higher than that in ethanol [2]) and more environment friendly nature, which is preferred in EPD. However, gas formation seems to be inevitable due to electrolysis. There must be solutions to prevent bubble formation from disturbing deposition densification.

S. Novak et al. did lots of researches during the decade. In their study of 2008 [3], they tried several types of surfactants, adding to the SiC aqueous suspension (25 wt.%, 0.5 μm β-SiC) and then deposited the suspension onto the electrode directly. The zeta-potential and conductivity of SiC powders was presented in Fig. 1.Then the zeta-potential, conductivity and deposition density of each suspension was measured respectively (as shown in Fig. 2 and Table 1). As a result, a high zeta-potential suspension leading to firm and dense deposits, were obtained for the addition of 0.5 wt.% of cationic deflocculant CTAB or by adding Dolapix and adjusting the pH of the suspension to 9. That is to say, a high zeta-potential is of outmost significance for EPD process, while suspension conductivity is secondly dominant.

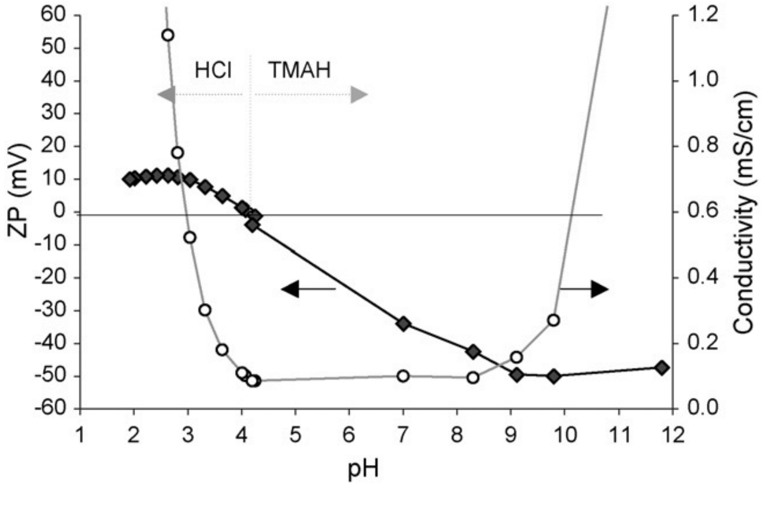

Figure 1: The influence of pH change on the zeta-potential (ZP) and the conductivity of an aqueous suspension of SiC powder (solids content: 25 wt.%; pH adjusted by HCl and TMAH).

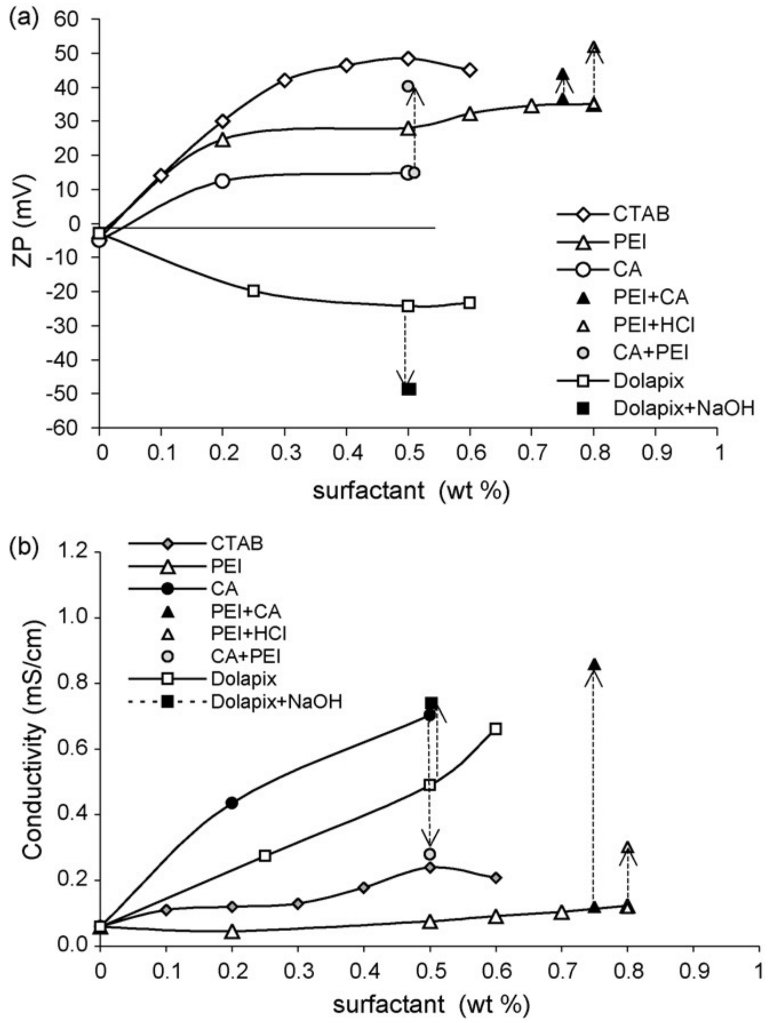

Figure 2: The zeta-potential (ZP) (a) and conductivity change (b) due to the addition of different surfactants to SiC suspensions (solids content: 25 wt.%). The arrows show the effect of a further pH change for a particular surfactant addition.

No.	Composition		Suspension		Deposit	
	Additives	wt.%	pH	Conductivity	ZP	wt.% solids
1	0		4	0.08	-3	/
2	HCl		2.8	0.78	14	/
3	CTAB	0.4	3.9	0.24	48	67
4	PEI	0.8	8	0.12	35	/
5	(PEI)+CA	0.75+2	2.8	0.86	44	54
6	(PEI)+HCl	0.8	8	0.3	52	64
7	CA	0.5	2.6	0.7	15	/
8	(CA)+PEI	0.5+0.3	3.3	0.3	40	59
9	NaOH		9	0.15	-54	66
10	TMAH		9	0.15	-50	67
11	DCE64	0.5	6.3	0.5	-24	/
12	(DCE64)+NaOH	0.5	9	0.74	-49	62

Table 1: Compositions and properties of the characteristic suspensions used in the EPD experiments and corresponding properties of deposits

In S. Novak's following study in 2009 [4], they tried three surfactants mentioned above, cetyltrimethylammonium bromide (CTAB), tetramethyl-ammmonium hydroxide (TMAH) and polyethylene-amine (PEI) adding to SiC aqueous suspension (60 wt.%, 0.5μm β-SiC) again. The suspension was homogenized by strong probe-type ultrasound. The SiC-fibers woven was pre-treated in sodium dioctyl-sulfosuccinate (SDOSS) to increase its wettability and zeta-potential. The fabric was attached to the semi-permeable membrane and placed in front of the anode, in order that bubble formation due to electrolysis would not disturb fabric densification. As a result, high particle packing density (68 vol.%) can be achieved by adding TMAH as a dispersant. The average pore size in the bulk deposit was only 60nm and the remaining porosity was 35%.

In A. Iveković et al.'s study [5] , a more detailed and comprehensive research was done. Results showed that EPD infiltration was enhanced at higher suspension concentrations (~50 wt.%). Submicron and nanosized SiC powder were tried respectively. Compared with submicron SiC particles, nanosized powders resulted in good intrabundle infiltration, however, lower packing density (< 45% TD) and hence more cracks after drying and heat-treatment. Therefore, it was concluded that better EPD results would be obtained with bimodal particles, taking the advantage of both intrabundle infiltration with nanosized powders and high packing density with submicron powders.

3 DIFFERENT DESIGNS OF EPD CELL AND PARAMETERS

For the purpose of attaining high deposition density and preventing water decomposition, different designs of EPD cell and other assistant device have been tried and improved.

In K. König et al.'s study [6], new cell for aqueous-EPD of SiC_f/SiC composites was studied, as shown in Fig. 3. If SiC fabric was attached to the anode when processing EPD, the fiber would act as the deposition electrode directly, so that the particles would form a coating on the surface of the fiber mat, which would prevent further infiltration of the gaps deeper inside the fabric. This behavior is schematically described in Fig. 3a. To enable sufficient deposition of the SiC particles between the fibers, the fabric was separated from the anode by a Teflon film. The SiC particles were drive to move through the negatively charged fiber mat to reach the electrode under the electric force, then filled the fabric gradually.

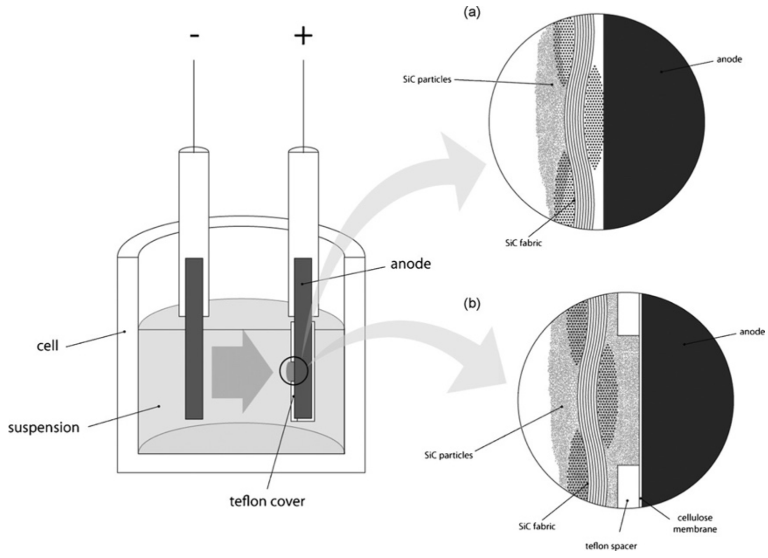

Figure 3: Schematic representation of the EPD cell used for infiltration of SiC fiber fabric with SiC particles: (a) SiC-fabric is in contact with the electrode and (b) SiC-fabric is not in contact with the electrode.

A. Iveković et al. [5] also made a detailed research on EPD parameters. With the same procedure as before, they found that infiltration of the fiber preforms immersed with SiC suspension in evacuation prior to EPD was significantly improved in comparison to non-evacuated ones, especially interbundle areas. The effective time needed for complete infiltration of 5.4mm thick fiber preform was 10 min. The highest degree of infiltration of SiC-fiber fabric (inter- and intrabundle areas) was conducted at a current density of 2.5 $mAcm^{-2}$. High current densities result in porosity behind fiber bundles in the direction of infiltration.

G-Y Gil et al. [7] combined EPD with ultrasonication to increase the degree of matrix particle infiltration into the deep voids of the SiC fabrics and minimize surface sealing effect [8]. EPD was performed under a 10V electric field for 30 minutes. The SiC_f/SiC composites fabricated by EPD combined with ultrasonication showed a better degree of infiltration than those without ultrasonication. After hot pressing at 1750 ℃ for 2 hours, the density of the composites by the combined process was 99.5%, which reaches the highest SiC_f/SiC density ever reported.

The method combined EPD with ultrasonication can be seen in several other literatures. Ji Yeon Park et al. [9] tried a new EPD cell with a dual-electrode system and an ultrasonicator. This dual-electrode was used for SiC fabrics' efficient impregnation from both sides as the SiC fabric acted as cathode, simultaneously, minimizing the influence of electric field shielding effect [10]. The pH was adjusted to 3 using NH_4OH, CH_3COOH and HCl. The EPD was performed under 10V electric field for 10 min. The maximum density of the composites fabricated by combined process of EPD with ultrasonication was 3.14 ± 0.04 g/cm^3. The flexural strength was 531 ± 26 MPa for a composite with a single interlayer of (200 nm PyC + 600 nm SiC).

After that Alberto Ortona et al. [11] improved the EPD process for fabricating tubular SiC_f/SiC skin layer. EPD was preformed for cylindrical sample with 10V DC for 1 h under the application of 10 W ultrasonic pulse at 60 Hz for the first 50 min to prevent surface sealing effect and enhance deep voids densification. Hyun-Woo Yu [12] adopted the same processing route when depositing SiC powders, the schematic diagram is shown in Fig. 4.

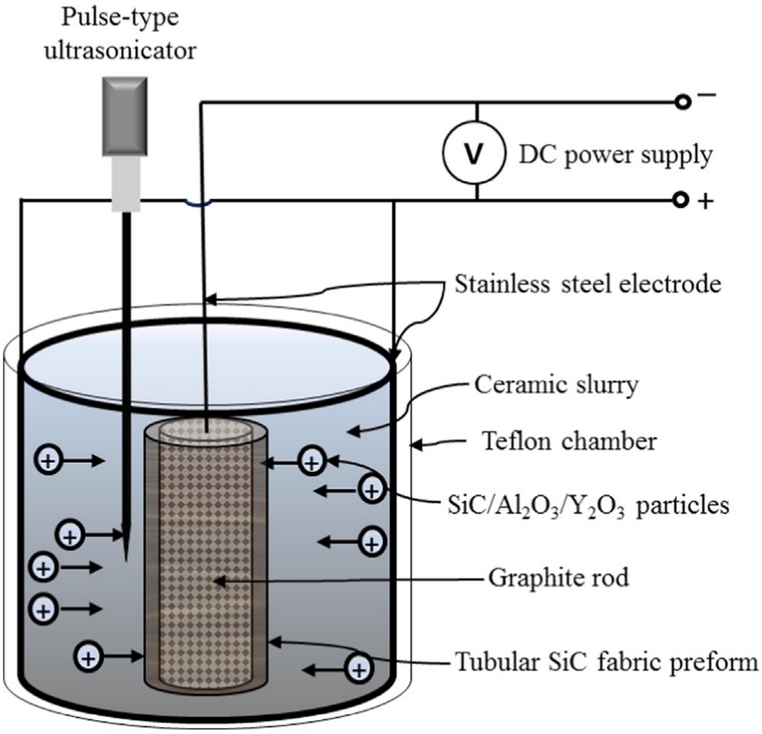

Figure 4: Schematic diagram of the experimental setup for the matrix phase infiltration for a tubular SiC preform using EPD combined with ultrasonication.

Jie Yin et al. [13] made a more comprehensive analysis of ultrasonic-EPD. Stable ethanol-based nano-SiC suspensions were prepared with KV9056 as a dispersant. The optimization of EPD parameters are displayed in Fig. 5. As a result, the optimized voltage, deposition time, alternative pulse pattern mode and ultrasonic power were 9 V, 10 min, 4:1 (direct current pulse on: pulse off) and 50% of the maximum power respectively. Seven cycles of PIP were performed for achieving a relative density as high as 91.9%. High-strength (289 MPa) SiC_f/SiC composites were fabricated, which displayed non-brittle fracture behavior.

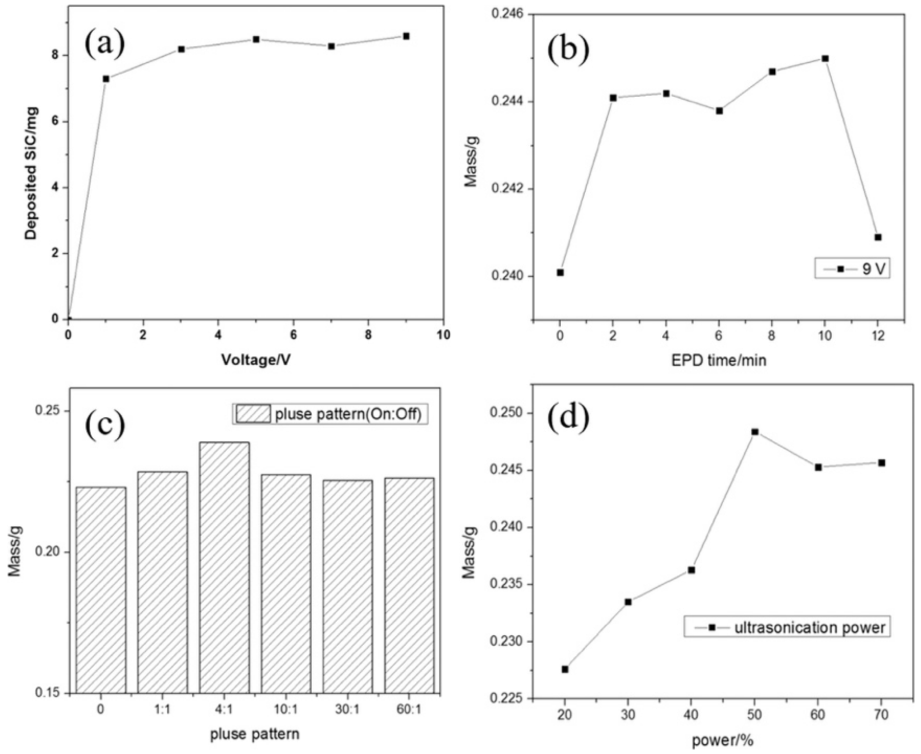

Figure 5: Optimized EPD parameters: the effect of (a) voltage, (b) deposition time, (c) alternative pulse pattern mode, and (d) ultrasonic power.

4 EPD FOR INTERPHASE LAYER OF SIC/SIC COMPOSITES

Among the strategies to improve the overall performance of SiC_f/SiC composites, in particular to increase their mechanical strength and thermal conductivity, a interphase layer with high properties is desirable.

There are usages for depositing interphase layer by EPD. Due to the outstanding mechanical and thermal properties of carbon nanotubes (CNTs), they are considered suitable reinforcement for structural materials. As mentioned above, K. König et al. [6] deposited CNTs onto SiC fibers to form an effective CNT interphase layer for SiC_f/SiC composites. The EPD experiments were performed with aqueous suspension containing 0.0625-0.5 wt.% of carbon nanotubes at a constant dc voltage of 2.8 V for 10 or 20 min. This deposition was followed by electrophoretic infiltration of the CNT-coated SiC fiber mats with SiC powder. High-quality, uniform and reproducible CNT and CNT-SiC coatings on SiC fibers were produced for the first time using EPD technique. However, the space between the fibers through the thickness of the fiber mat were not completely filled and more efficient infiltration should be studied.

Wei Feng et al.[14] also introduced CNTs into the matrix of SiC_f/SiC composites through EPD. The SiC fibers were deposited with 100 nm PyC interphase. 0.05 wt.% multi-wall CNTs were dispersed in aqueous system. Tetramethyl-ammonium was used as anionic surfactant and pH modifier. EPD was performed at 10 V for 10 min. After drying SiC matrix was deposited by CVI on the CNT-SiC preform. Mechanical properties and thermal conductivity of SiC_f/SiC composites (SS) and SiC_f/SiC-CNTs (SSCS) were compared. As shown in Table 2, with the addition of CNTs, density and mechanical properties were improved. And the thermal conductivity of SSCS was 1.74 times higher than that of SS.

Samples	Density (g/cm^3)	Porosity (%)	Bending strength (MPa)	K_{IC} (MPa m$^{1/2}$)
SS	2.60 ± 0.05	11.2 ± 0.3	430 ± 12	16.8 ± 0.8
SSCS	2.78 ± 0.04	5.8 ± 0.3	484 ± 16	19.4 ± 0.7

Table 2: Density and mechanical properties of SiC_f/SiC composites (SS) and SiC_f/SiC-CNTs composites (SSCS)

Pipit Fitriani et al. [15] concentrated their attention to the electrophoretic deposition of carbon interphase layer. For the first time, the alternating current electrophoretic deposition (AC-EPD) was applied for the deposition of carbon black. The AC-EPD in aqueous systems was applied to suppress the decomposition of the water [16, 17]. Researchers conducted both DC-EPD in ethanol system and AC-EPD in aqueous system. The waveform and voltage value were shown in Fig. 6. A square-shaped asymmetric 100 Hz AC signal with an asymmetry factor of 4 and a peak-to-peak voltage of 20 V was applied for 60 minutes for AC-EPD. Both AC and DC-EPD was accompanied with 10 W ultrasonic pulses of 1 Hz. As a result, a more uniform carbon coating was achieved by AC-EPD compared with DC-EPD, indicating the potential feasibility of the eco-friendly AC-EPD using an aqueous liquid media.

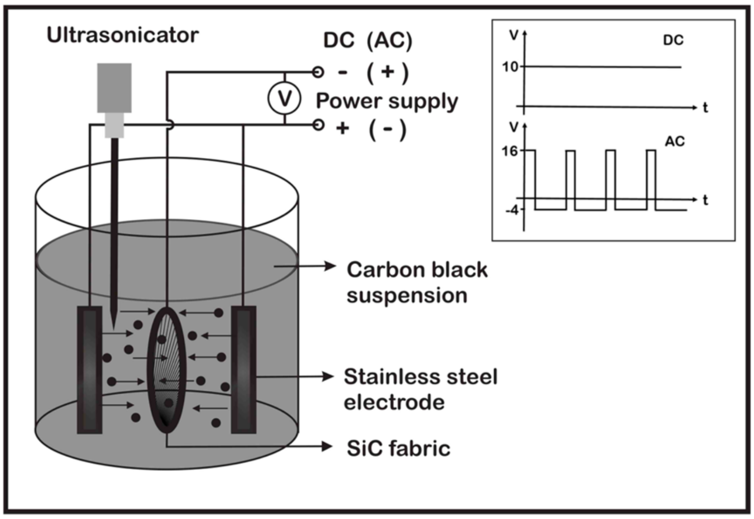

Figure 6: Schematic diagram of the experimental setup for carbon black infiltration using DC- and AC-EPD.

5 SUMMARIZATION AND PROSPECT

The electrophoretic deposition process is known as a versatile technique in fabrication of ceramic matrix composites. Using optimal suspensions and EPD conditions, higher green densities can be achieved. High mechanical and thermal properties SiC_f/SiC composites with interphase are able to be achieved by introducing CNTs, carbon black or other reinforcement phase through EPD. However, there is no indication yet of extensive industrial production of the SiC_f/SiC composites by EPD. As a potential tool, further optimization of process and technology are necessary to make EPD more attractive for industry. There is still room for new findings that may result in new breakthrough of higher performance and lower costs.

REFERENCES

[1] Nannetti C A, Ortona A, Pinto D A D, et al. Manufacturing SiC-Fiber-Reinforced SiC Matrix Composites by Improved CVI/Slurry Infiltration/Polymer Impregnation and Pyrolysis[J]. Journal of the American Ceramic Society, 2004, 87(7):1205–1209.

[2] Dickerson J H, Boccaccini A R. Electrophoretic Deposition of Nanomaterials[M]// Electrophoretic deposition of nanomaterials /. Springer, 2012.

[3] Novak S, Rade K, König K, et al. Electrophoretic deposition in the production of SiC/SiC composites for fusion reactor applications[J]. Journal of the European Ceramic Society, 2008, 28(14):2801-2807.

[4] Novak S, König K, Ivekovič A, et al. Infiltration of a 3-D Fabric for the Production of SiC/SiC Composites by Means of Electrophoretic Deposition[J]. Key Engineering Materials, 2009, 412:237-242.

[5] A. Iveković, S. Novak. Electrophoretic (Infiltration) Deposition of Thick Conductive Fiber Preforms[J]. Journal of the Electrochemical Society, 2015, 162(11):D3049-D3056.

[6] König K, Novak S, Ivekovič A, et al. Fabrication of CNT-SiC/SiC composites by electrophoretic deposition[J]. Journal of the European Ceramic Society, 2010, 30(5):1131-1137.

[7] Gil G Y, Yoon D H. Densification of SiC f/SiC composites by electrophoretic infiltration combined with ultrasonication[J]. Journal of Ceramic Processing Research, 2011, 12(4):371-375.

[8] Moore I D. Effect of surface sealing on infiltration.[J]. Transactions of the Asae, 1981, 24(6):1546-1552.

[9] Ji Y P, Jeong M H, Kim W J. Characterization of slurry infiltrated SiC f /SiC prepared by electrophoretic deposition[J]. Journal of Nuclear Materials, 2013, 442(1–3):S390-S393.

[10] Bao Y, P S N. Constant Current Electrophoretic Infiltration Deposition of Fiber-Reinforced Ceramic Composites[J]. Journal of the American Ceramic Society, 2007, 90(4):1063-1070.

[11] Ortona A, Fend T, Yu H W, et al. Fabrication of cylindrical SiC f /Si/SiC-based composite by electrophoretic deposition and liquid silicon infiltration[J]. Journal of the European Ceramic Society, 2014, 34(5):1131-1138.

[12] Yu H W, Fitriani P, Lee S, et al. Fabrication of the tube-shaped SiC f /SiC by hot pressing[J]. Ceramics International, 2015, 41(6):7890-7896.

[13] Yin J, Lee S H, Feng L, et al. Fabrication of SiC f /SiC composites by hybrid techniques of electrophoretic deposition and polymer impregnation and pyrolysis[J]. Ceramics International, 2016, 42(14):16431-16435.

[14] Feng W, Zhang L, Liu Y, et al. Thermal and mechanical properties of SiC/SiC-CNTs composites fabricated by CVI combined with electrophoretic deposition[J]. Materials Science & Engineering A, 2015, 626:500-504.

[15] Fitriani P, Sharma A S, Lee S, et al. Formation of a Carbon Interphase Layer on SiC Fibers Using Electrophoretic Deposition and Infiltration Methods[J]. Journal of the Korean Ceramic Society, 2015, 52(4):284-289.

[16] Kollath V O, Chen Q, Closset R, et al. AC vs. DC Electrophoretic Deposition of Hydroxyapatite on Titanium[J]. Journal of the European Ceramic Society, 2013, 33(13-14):2715-2721.

[17] Nold A, Clasen R. Bubble-free electrophoretic shaping from aqueous suspension with micro point-electrode[J]. Journal of the European Ceramic Society, 2010, 30(14):2971-2975.