# SiC−CNT Composite Prepared by Electrophoretic Codeposition and the Polymer Infiltration and Pyrolysis Process

Saša Novak*,[†,‡] and Aljaž Iveković[†,‡]

[†]Department for Nanostructured Materials, Jožef Stefan Institute, Jamova cesta 39, 1000 Ljubljana, Slovenia
[‡]Jožef Stefan International Postgraduate School, Ljubljana, Slovenia

ABSTRACT: The paper reports on the successful anodic codeposition of submicrometer SiC powder and multiwalled carbon nanotubes from aqueous suspensions to form SiC−CNT composites. On the basis of the comprehensive analysis of the aqueous suspensions with different pHs, solids contents, and CNT contents, optimal conditions for deposition were determined. Besides having the necessary high absolute value of the ζ-potential, the suspensions that resulted in firm deposits were characterized by limited conductivity (<1 mS/cm). Lowering of suspension conductivity was achieved either by dilution of the suspension or by dialysis of the as-received CNT suspension with high intrinsic conductivity. Selected SiC−CNT deposits were further densified by use of the polymer infiltration and pyrolysis process.
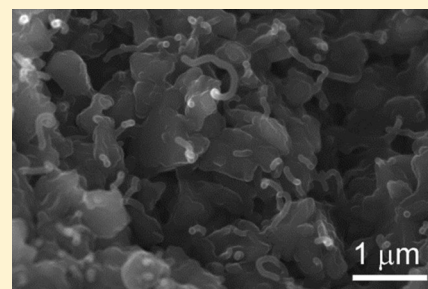
1. INTRODUCTION

Silicon carbide (SiC) is a material with high hardness and a high melting point, which is a result of its high fraction of covalent bonding. In combination with its low specific weight and oxidation resistance, it is a material of choice in many high-temperature applications. However, the brittle nature of SiC hinders its application in all areas where toughness and high thermal conductivity of metals outweigh the advantages of ceramics. Therefore, efforts have been made to overcome these shortcomings by introducing a reinforcing phase (particles, fibers, etc.) in the ceramic matrix. One of the possibilities is to introduce carbon nanotubes (CNTs), which have been known for outstanding mechanical and thermal properties.[1,2] Although there is a wide range of reported values depending on the structure, fabrication process, etc., the reported values of elastic modulus up to 1 TPa, a strength up to 60 GPa,[3] a thermal conductivity exceeding 2000 W/mK, etc. offer exciting new possibilities for improvement of the material's properties. Therefore, the CNTs have attracted the considerable attention of researchers as a stand-alone material or as a reinforcing phase in polymers,[2,4] different inorganic matrixes, ranging from glass and glass−ceramics[5,6] to various polycrystalline engineering ceramics (e.g., Al_2O_3, $BaTiO_3$, TiN, Si_3N_4, SiC),[7−9] and metals.[10,11]

The main challenge in the fabrication of CNT-reinforced materials is the homogeneous dispersion of CNTs in the matrix phase. The presence of agglomerates is undesirable since they can act as defects, increasing the probability of failure and decreasing the beneficial effect of the reinforcing phase in general.[12] One of the possible techniques to achieve good dispersion of CNT reinforcement in ceramic composites is the use of colloidal processing and shape-forming by electrophoretic deposition (EPD). It has been presented in many reports that the EPD is advantageous in many respects over dry

shaping techniques as well as over other colloidal techniques. In addition to its high versatility in coating of conductive substrates, it also enables formation of complex-shaped bulk parts with homogeneous or, oppositely, with functionally graded structures as well as infiltration of three-dimensional fibrous preforms.[13−19] Scientific reports also show that the process enables deposition of CNTs from colloidal suspensions to form ordered structures, such as coatings, thin or thick films, laminates, etc.,[20−22] or bulk composite deposits fabricated by codeposition or subsequent deposition of CNTs with various ceramic powders (e.g., SiO_2, TiO_2, Fe_3O_4, and HA).[23,24] EPD was also employed to deposit a thin layer of CNTs onto SiC fibers to form an interphase layer in ceramic matrix composites.[25] In addition to the technological benefit, colloidal processing is advantageous over fabrication from dry powders also due to the health hazard during manipulation of CNTs.[26]

In this work, we report on the fabrication of a homogeneous SiC−CNT composite material utilizing electrophoretic deposition and densification by the polymer infiltration and pyrolysis process.

2. EXPERIMENTAL METHODS

Aqueous suspensions with a solids content from 10 to 60 wt % were prepared from β-SiC BF12 powder (H.C. Starck, Duesseldorf, Germany) with an average particle size of 0.5 μm (Figure 1a). Tetramethylammonium hydroxide (TMAH; Sigma Aldrich, Munich, Germany) was used as a dispersing agent. A commercial aqueous suspension of multiwalled carbon nanotubes (MWCNTs; Aquacyl), with an average diameter of
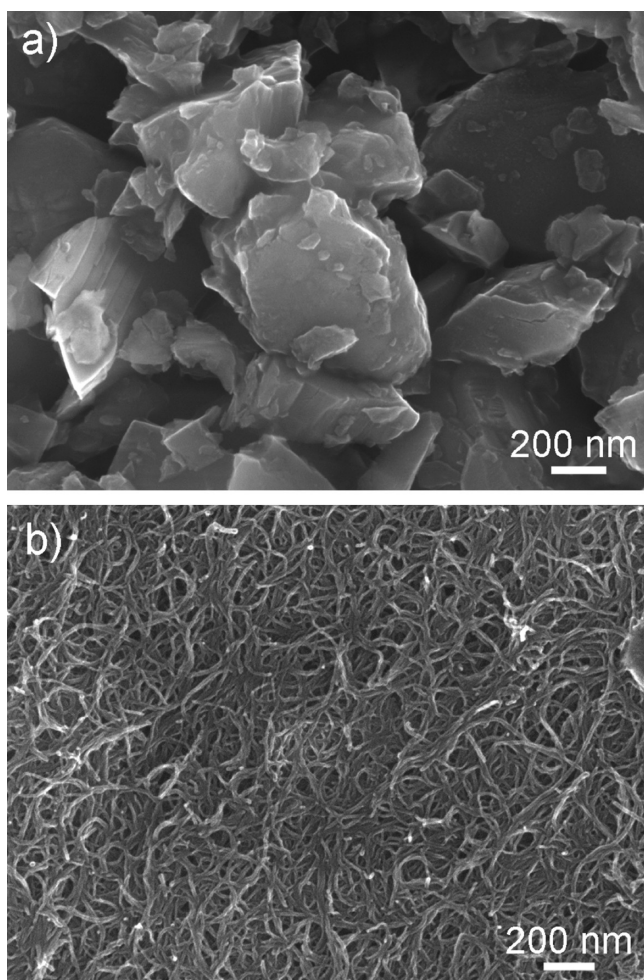
Figure 1. Micrographs of the (a) SiC powder and (b) CNTs.

9.5 nm and an average length of 1.5 μm (Figure 1b) and a solids content of 1 wt %, was provided by Nanocyl S.A. (Sambreville, Belgium). For codeposition experiments, suspensions with 10, 30, or 50 wt % solids were prepared by manually admixing the CNT suspension and the SiC powder into distilled water. The suspensions with 1, 0.5, or 0.1 wt % CNTs with respect to the amount of SiC were further homogenized for 5 min using a strong probe-type ultrasound with an acoustic power density of 109 W/m^2 (Hielscher Ultrasonics GmbH, Teltow, Germany). The electrokinetic behavior of the non-diluted suspensions was analyzed with a ZetaProbe analyzer (Colloidal Dynamics, Ponte Vedra Beach, FL). The ζ-potential of SiC suspensions with added CNTs (referred to as the "apparent ζ-potential") was estimated by using adapted parameters for the calculation from the ESA (electrokinetic sonic amplitude) signal, taking into account the relative concentration of both phases in suspensions. Conductivity was measured with a conductometer (Portamess; Knick, Berlin, Germany). Dialysis of the as-received CNT suspension was performed using a tubular cellulose membrane half-filled with the suspension and dipped into the distilled water for 4 h during constant stirring.

EPD experiments were conducted in a glass beaker with the suspension in which two flat graphite electrodes (2.4 cm^2) were immersed at a mutual distance of 2 cm using a power source (0−64 V; Thrulby Thandar Instruments Ltd., Cambridgeshire, U.K.) with an applied constant current of 10 mA for 10−20

min. The deposits were carefully dried, and green densities were measured using a bulk density measurement system (Densitec; Exelia AG, Zürich, Switzerland) based on the use of the Archimedes principle.

To prevent cracking during further processing,[18] the deposits were presintered at 1600 °C in a vacuum. The presintered samples were then vacuum-infiltrated using allylhydridopoly-carbosilane (AHPCS), with the commercial name SMP-10 (Starfire Systems Inc., Schenectady, NY). More detailed information about the infiltration is described elsewhere.[27] The infiltrated samples were pyrolyzed at 850 °C in argon and crystallized at 1600 °C in a vacuum high-temperature furnace (Thermal Technologies Inc., Greensburg, IN). After densification, the fracture surfaces of the samples were examined using a field-emission-gun scanning electron microscope (FEG-SEM) (JEOL JSM-7600F) equipped with an energy-dispersive X-ray spectroscopy (EDXS) system (INCA Oxford Instruments).

3. RESULTS
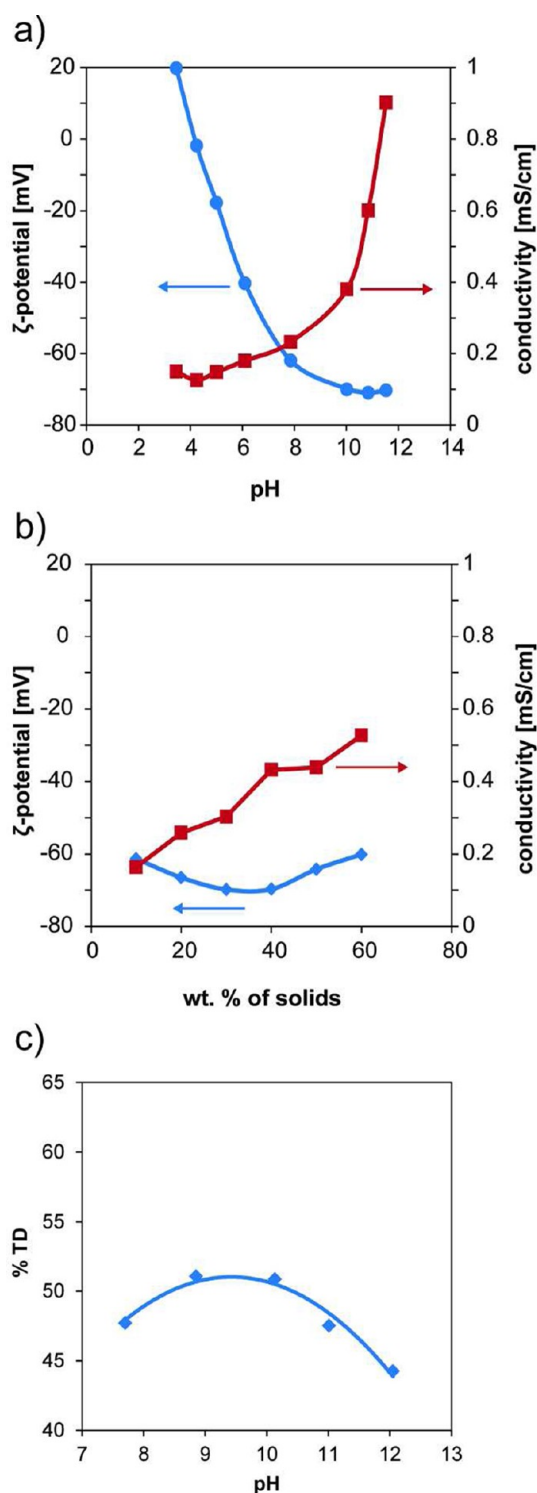
Preparation and Properties of SiC−CNT Suspensions. It is evident from Figure 1a,b that the used SiC particles and CNTs significantly differ in size and morphology: while the SiC particles are angular and range in size from 100 nm to 1 μm, the carbon nanotubes are in the form of a few micrometers long fibers with small (~10 nm) diameters. This difference makes the homogeneous codeposition challenging. Another issue is that the CNTs are provided in aqueous suspensions, which suggests water as the preferable media for the deposition of the SiC−CNT composite. Therefore, to prepare a suitable suspension of SiC powder with homogeneously distributed carbon nanotubes, electrokinetic properties and conductivity of both, SiC and CNT suspensions in water, were first thoroughly investigated. Namely, it has been shown earlier that, for successful EPD, not only the high particle's surface charge but also the level of electrical conductivity in a precise region is needed.[28−30]

Without additives, SiC powder in an aqueous suspension (30 wt % solids) exhibits positive values of ζ-potential near its isoelectric point (IEP) at pH ∼ 5 (Figure 2a). By adding TMAH, the charge is reversed, and with further increasing the pH, the absolute value of the ζ-potential is highly increased, reaching the value of −70 mV at pH 10. At the same time, conductivity increases, reaching 0.4 mS/cm at pH 10, while a further increase in pH results in an exponential increase in conductivity.

ζ-potential and conductivity are also affected by the solids content (Figure 2b): with increasing concentration of the SiC suspension at pH 10, conductivity slightly increases, while the change of the ζ-potential (as well as pH) is minor.
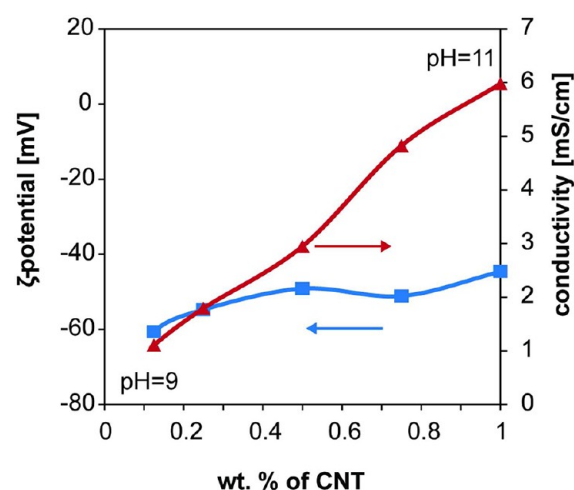
With the aim to define the most suitable conditions for the deposition, EPD experiments were performed with the suspensions having an alkaline pH, and green densities of deposits were measured. The highest density was obtained at pH 9−10 (Figure 2c), while lower and, in particular, higher pH values resulted in deposits with lower densities and apparently lower strength.

In the case of CNTs, the effect of solids content on ζ-potential and conductivity is much more pronounced. The as-received suspension containing 1 wt % of the CNTs is alkaline (pH 11), and the nanotubes are negatively charged (ζ-potential = −45 mV). As is evident from Figure 3, the conductivity of the as-received 1% CNT suspension is significantly higher than that for the SiC suspensions (note the different scale on the right-

Figure 2. ζ-Potential and conductivity of the aqueous SiC suspensions as a function of (a) pH and (b) solids content. (c) Density of green deposits as a function of pH.

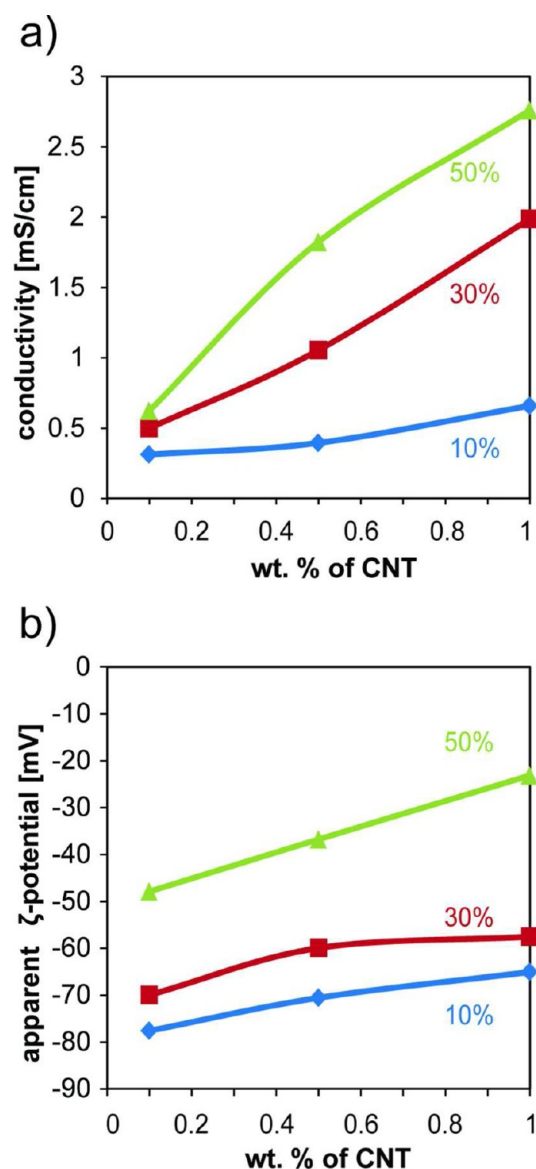**Figure 3.** ζ-Potential and conductivity of the aqueous suspensions of CNTs as a function of solids content.

dilution with water, the pH of the suspension decreases from 11 to 9.

On the basis of the above presented characteristics of the SiC suspensions and densities of the resulting deposits (see Figure 2a,c, respectively), we supposed the pH 10 value as the most appropriate also for deposition of SiC with the addition of CNTs. Mixtures with different CNT-to-SiC ratios (0.1−1 wt % CNTs with respect to SiC) and different solids loadings (10−50 wt %) were prepared and their properties evaluated.

Since the ζ-potentials of both SiC and CNT suspensions were highly negative, a similar surface charge could be predicted also for the mixed suspension. Although the true ζ-potential of suspensions with more than one solid phase cannot be properly determined by the electroacoustic measurement technique, we estimated the effect of CNT addition to SiC suspensions on the obtained value, which we refer in continuation as the "apparent ζ-potential". As expected, due to the high conductivity of CNT suspensions (see Figure 3), also the SiC−CNT suspensions containing 1 wt % CNTs were characterized by high conductivities (Figure 4a). By dilution from 50 to 30 or 10 wt % solids, the conductivity decreased, and as a consequence, the negative value of the apparent ζ-potential increased, reaching −65 mV for the suspension with 10 wt % solids (Figure 4b). Lower conductivities were also obtained by lowering the percentage of CNTs in the SiC−CNT mixture. The highest value of the apparent ζ-potential (−60 mV) and the lowest conductivity (<0.5 mS/cm) were obtained for the 10 % suspensions containing 0.5 or 0.1 wt % CNT addition in SiC.

In another attempt, we tried to reduce the conductivity of the CNT-containing SiC suspension without lowering the CNT content in the SiC−CNT composite. The as-received CNT suspension was dialyzed by immersing the tubular semi-permeable membrane with the suspension into distilled water to allow the redundant electrolyte to diffuse from the suspension. As a result, in 4 h, the conductivity decreased from initially 4.9 to 3.2 mS/cm. The conductivity of the resulting SiC-1%CNT suspension (30 wt % solids) prepared from the dialyzed CNT suspension was reduced for ∼0.5 mS/cm in comparison to the as-received suspension, while the value of the apparent ζ-potential was increased to −74 mV. Even though the conductivity of the mixed suspension was lowered by dialysis of the CNT suspension, the value of 1.5 mS/cm was still too high to form a deposit with a high packing density.

hand axis compared to Figure 2a,b) despite the much lower solids content. By dilution with water, the conductivity almost linearly decreases, reaching, at 0.1 wt %, a similar value (∼0.5 mS/cm) as that for the SiC suspension with a solids content of 30 wt %. As is also evident from Figure 3, by dilution, the absolute value of the ζ-potential increases, and the highest value (−60 mV) appears at 0.1 wt % CNTs in water. In addition, by
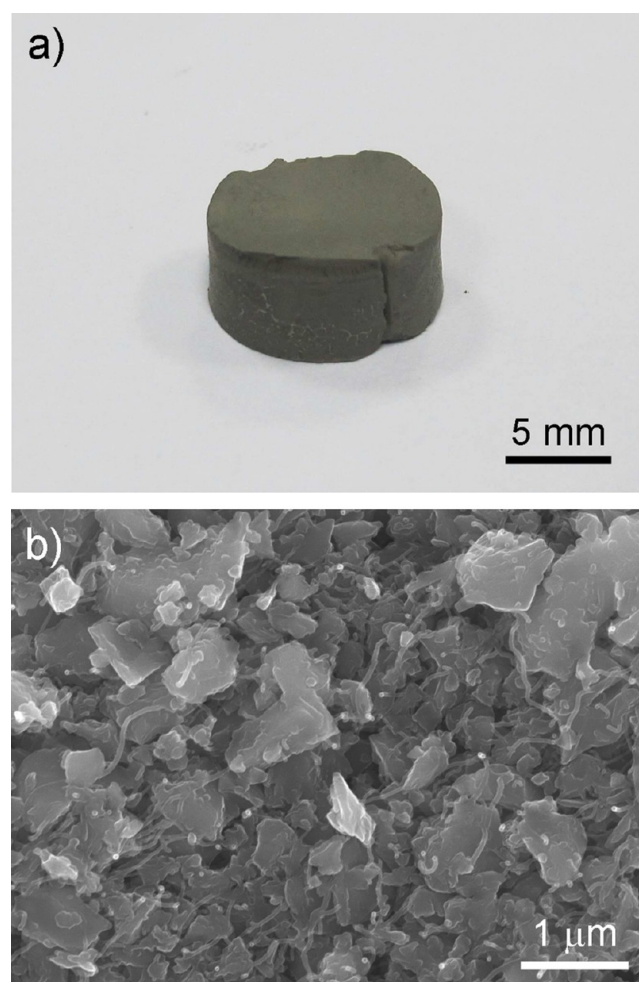
Figure 4. Conductivity (a) and apparent ζ-potential (b) of SiC−CNT suspensions as a function of solids loading and CNT content in SiC.

Figure 5. (a) Macroscopic image of a dried green SiC-0.5% CNT deposit and (b) scanning electron micrograph of its fracture surface.

Table 1. Green Density of the Deposits Prepared by EPD from Suspensions with 30 wt % Solids

sample	density of deposit (g/cm^3)	density of deposit (% TD)
SiC	1.78	56
SiC-0.1%CNT	1.75	55
SiC-0.5%CNT	1.50	47
SiC-1%CNT	1.44	45
SiC-1%CNT (dialyzed)	1.46	46

Electrophoretic Codeposition. The EPD experiments were performed using the suspension with 10, 30, and 50 wt % solids and containing different amounts of CNTs (0, 0.1, 0.5, or 1.0 wt % with respect to SiC powder). One of the suspensions was also prepared from dialyzed CNT suspensions (with reduced conductivity). As expected, the deposits formed from the suspensions with high conductivity (>1 mS/cm) were much more loose and lower in green density than deposits prepared from low-conductivity suspensions. By EPD, from suspensions with lower conductivities, in 10 min, approximately 5 mm thick deposits were formed on the anode (Figure 5a). In comparison with the SiC deposit, the SiC−CNT deposits were apparently less stiff and had lower green densities, which decreased with the amount of CNTs (Table 1). The formation of bubbles in the deposits that usually appear due to water electrolysis was successfully prevented by use of a graphite anode covered with a cellulose membrane.

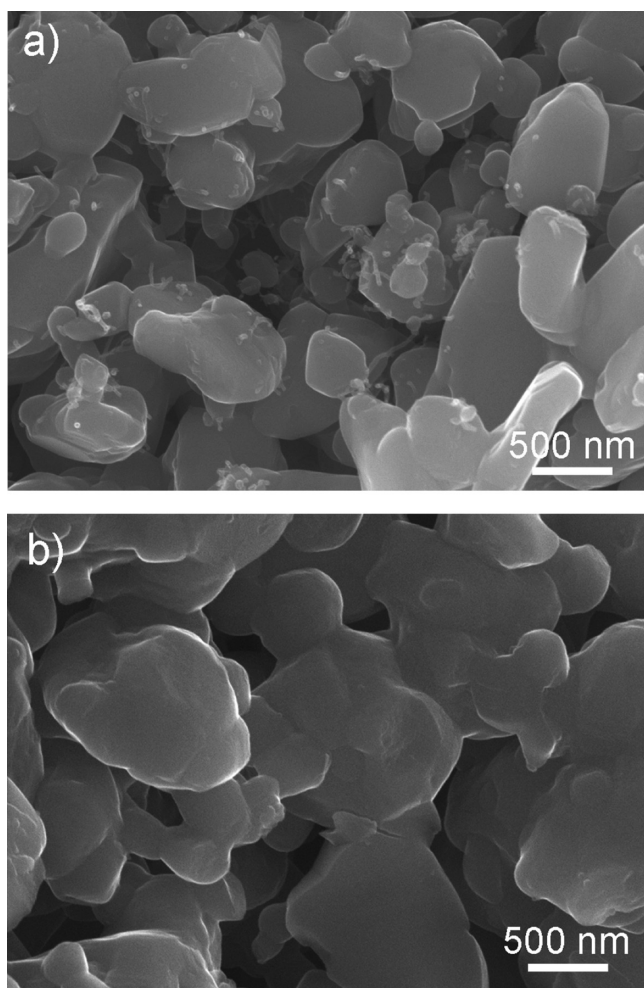The fracture surface of the SiC-0.5%CNT deposits illustrated in Figure 5b reveals a relatively uniform distribution of the CNTs in the SiC matrix. Similar microstructures were observed across the whole thickness of the deposit.

SiC−CNT Composites. The codeposited SiC−CNT samples were further densified by the polymer infiltration and pyrolysis process (PIP). To prevent cracking during the PIP process, they were, first, presintered at 1600 °C[27] and, in the next step, vacuum-infiltrated with preceramic polymer and finally thermally treated up to 1600 °C in vacuum. Fracture surfaces of the sample SiC-1%CNT after presintering and after PIP are illustrated in Figure 6a,b, respectively. The CNTs are still clearly visible after the first heat treatment at 1600 °C, but they seem to be shorter than the as-received ones. On the contrary, no CNTs can be observed in fracture surfaces of the sample after the PIP process. In addition, comparison with green microstructures (Figure 5b) reveals that the SiC grains

Figure 6. Fracture surfaces of the SiC-0.5% CNT composite (a) after presintering at 1600 °C and (b) after further polymer infiltration, pyrolysis, and crystallization at 1600 °C.

connected to form a skeleton and grew from the initial ∼0.5 to ∼1 μm.

4. DISCUSSION

Carbon nanotubes were first reported to be used as reinforcement of SiC ceramics in 1998: the composites prepared from nanosized SiC powder and CNT were consolidated by hot-pressing[8] and showed a 10% increase in bending strength and fracture toughness over monolithic SiC. Recently, Jiang and coauthors[31] reported on a SiC−CNT (0.25 wt % CNTs) composite prepared by tape-casting of a nonaqueous suspension and hot-pressing with a larger effect of a small CNT addition. A noticeable improvement was achieved by Wang and coauthors,[32] who used tape-casting, followed by the polymer infiltration and pyrolysis technique, and reported nearly a 30% increase in flexural strength and toughness for the composite with 1.5 wt % CNTs. To our best knowledge, consolidation of the SiC−CNT composites by electrophoretic codeposition has not been reported yet.

It is well known that EPD offers an excellent potential to produce homogeneous bulk parts with high green density.[33] However, to fully utilize this versatile technique, appropriate processing parameters have to be applied, and in particular, the suspension with optimal properties is essential. It has been already shown in our previous work[30] that, for successful

deposition in addition to high ζ-potential, a moderate, but not too high, conductivity of the suspension is needed. This was also confirmed in the present study, where the upper conductivity limit for achieving the highest green densities of deposits was defined to 1 mS/cm (Figure 2a,c). In this context, although the nearly matching pH values and ζ-potential of the as-received CNT suspension and the optimal SiC suspension were favorable for codeposition, the high conductivity of the used CNT suspension signified an issue. Namely, this high conductivity resulted in high conductivity of the mixed SiC−CNT suspensions and, consequently, in ineffective deposition or formation of loose deposits. We tried to solve this issue in three ways: (1) by lowering the CNT content in the mixture, (2) by lowering the solids content in the suspension, while keeping the CNT content the same, or (3) by lowering the conductivity of the starting CNT suspension by dialysis. The main drawback of the first method is that only composites with very low CNT contents can be prepared. The second method resulted in relatively good deposits; however, the deposition was slower. By using dialyzed CNT suspensions, the conductivity was lowered due to the reduced electrolyte content in the CNT suspension. However, in comparison with the SiC deposits, the density of the SiC−CNT deposits was still lower. This can be partly ascribed to the effect of the higher conductivity of the SiC−CNT suspension, and partly to the rigid nature of the CNTs that contain SiC particles in a deposit at a larger distance than in SiC.

As mentioned above, final densification of the SiC−CNT composites prepared so far was achieved by hot-pressing[8,31] or by the polymer and pyrolysis technique,[32] which was also employed in this study. In most of the reports, the authors provide evidence of the retained CNTs, even after treatment at a temperature as high as 2000 °C. In this study, the deposits were first presintered in vacuum at 1600 °C (to prevent cracking in a later stage) and then infiltrated with preceramic polymer, pyrolyzed, and finally crystallized up to 1600 °C in vacuum. After the first thermal treatment at 1600 °C (presintering), the CNTs were still observed in the fracture surface of the composite, but they seem to be shorter, while after another (crystallization), no CNTs was observed. This could be explained by reaction with the surrounding material during PIP processing; however, another explanation can be also given. Namely, as it was reported in ref 27, during the final stage of the PIP process, the SiC particles epitaxially grow on account of polymer derived SiC to form larger SiC grains. Thereby, during the several repeated PIP cycles, the density of the material increases without a noticeable shrinkage. In this work, only one cycle was performed, resulting in incomplete densification and a grain size increase from initially 0.5 to ∼1 μm. Thus, it is highly likely that the CNTs were captured within the grown SiC grains and are, therefore, not visible by SEM. Therefore, in further work, a more detailed examination of the SiC−CNT microstructure is proposed as well as characterization of their mechanical properties.

5. CONCLUSIONS

Electrophoretic codeposition of SiC−CNT composites was performed from aqueous suspensions with a high solids loading in the range of 10−50 wt %, a highly negative apparent ζ-potential (ca. −65 mV), and an electrical conductivity in the range of 0.3−1.5 mS/cm. The inherently high conductivity of the as-received CNT suspension that detrimentally affected the deposition was reduced by dilution of the mixed SiC−CNT

suspensions or dialysis of the starting CNT suspension. The CNTs were homogeneously distributed in the SiC−CNT deposits (0.1−1 wt % CNTs) that were further densified by use of the polymer and pyrolysis process. After presintering at 1600 °C, the CNTs appeared shorter, while they were not visible anymore after the crystallization stage of the PIP process.

■ AUTHOR INFORMATION

Corresponding Author
*Tel: (+386) 01 477 3271. Fax: (+386) 01 477 3221. E-mail: sasa.novak@ijs.si.

Notes
The authors declare no competing financial interest.

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