Surface characterisation and modification of submicron and nanosized silicon carbide powders

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Abstract

The surface characteristics of two grades of silicon carbide powders were analyzed and modified with the aim to control and tailor their behaviour in colloidal suspensions. The as-received submicron and nanosized SiC particles were both found to be covered with a thin oxygen-containing layer, composed mostly of SiO_2 and SiC_xO_y; however, their electrokinetic behaviours in aqueous suspensions were observed to be different. We coated the powders with a thin layer of aluminium oxy-hydroxide, which was found to modify their electrokinetic behaviours in aqueous suspensions. The composition and structure of the aluminium-containing layer were characterized by X-ray photoelectron spectroscopy (XPS) and TEM analyses. This coating may subsequently serve as a homogeneously distributed source of a low amount of sintering additive in manufacturing the SiC-based material for fusion application.
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1. Introduction

The properties of silicon-carbide-based materials depend to a large extent on the composition and properties of the SiC starting powders, in particular on the chemical composition of their surfaces. In colloidal processing the preparation of a well-dispersed and highly loaded slurry of fine powder is one of the key steps towards producing high-performance ceramics. When nanosized powder is used, the role of the powder surface becomes even more important, due to the large specific surface area and increased reactivity with chemical species from the environment.

In the case of silicon carbide for fusion application, where a strict control of composition is needed in order to assure acceptable behaviour of material at extreme conditions, powder surface oxidation is one of the common sources of problems during processing. Furthermore, limited amount of homogeneously distributed sintering additive is required in production of fusion-relevant SiC-ceramics, and morever, the content of the elements

effecting the activation after irradiation with neutrons must be strictly limited.[1] One of the possible methods to meet these requirements is application of the additives as thin layers on ceramic particles.

The main motivation of the present work was to control the surface properties of fine SiC-powders in order to enable their effective processing in suspensions, and at the same time to enable better sintering with the aid of a homogeneously distributed sintering additive. To achieve this, we coated the as-received commercial submicron and nanosized SiC powders with a thin layer of aluminium hydroxide, that should act as a sintering aid. Literature survey shows, that for the coating of non-oxide powders, e.g., SiC and Si_3N_4, various processes have been used, mostly employing Al-nitrate and Al-secondary butoxide as precursors to form Al-hydroxide coatings.[2–5] The proposed procedures result either in formation of a thin layer or in adhesion of fine "coating" particles at the matrix particles. Although several papers discuss the coating procedures and behaviour of the coated powders (mostly submicron), no report on comprehensive study of the applied coating layer was found. In our work, attempts were undertaken to confirm the production of continuous coating layer at the SiC particles and to establish its composition. For this purpose we used two complementary

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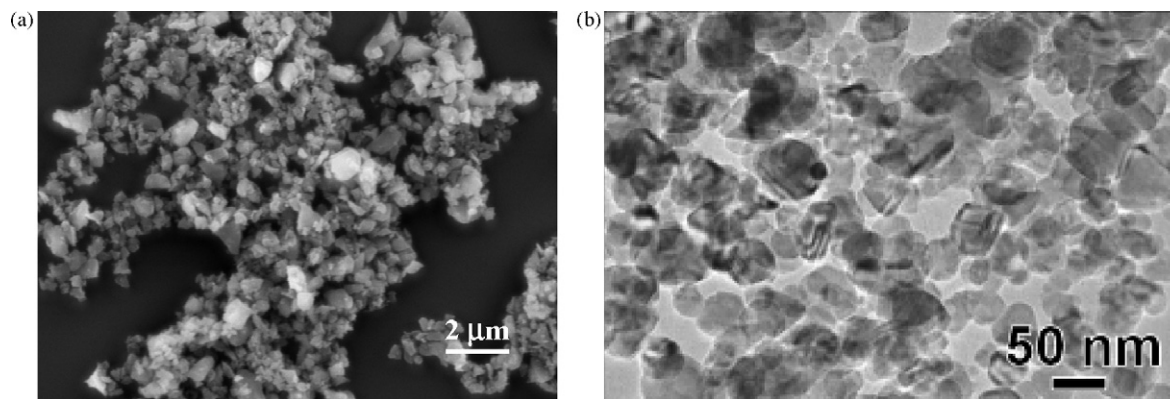*E-mail address:* sasa.novak@ijs.si (S. Novak).

Fig. 1. (a) SEM micrograph of the as-received BF12 submicron powder and (b) TEM micrograph of the nanosized Nano powder.

techniques XPS and HRTEM. The findings were related to their electrokinetic behaviours in suspensions.

2. Experimental

Two grades of commercial SiC powder were used in this study: submicron BF12 powder (H. Starck, Goslar, Germany), with $d_{50} = 0.5\,\mu m$; and nanosized Hefei powder, with $d_{50} = 50\,nm$ (Hefei Kiln Nanom. Technol. Dev. Co., China). The powders were analyzed in the as-received state (BF12, Nano) and after being coated with AlOOH (BF12-Al, Nano-Al). The AlOOH coating was applied by a precipitation method using aluminium nitrate nonahydrate ($Al(NO_3)_3 \cdot 9H_2O$) (A.R. grade, Merck), for which the added amounts were calculated so as to form an approximately 1 nm thick layer, taking into account the different surface areas of the powders and assuming that all the Al ions would precipitate. The procedure was as follows. The SiC powders were first ultrasonically dispersed in distilled water with 0.4 wt.% of Doplapix CE 64 (Zschimmer & Schwarz, Germany) as a dispersant. Urea (A.R. grade, Riedel-de-Haen) was added as a precipitation agent in the molar ratio [urea]/[Al] = 20. The concentration of silicon carbide powders in the suspensions was fixed at 25 g/L. After the addition of the Al-nitrate, the suspension was heated to 90 °C for 4 h while being subjected to magnetic stirring. The resulting coated silicon carbide powders were centrifuged and washed twice with distilled water to remove the remaining NO_3^- and urea, followed by washing twice with absolute ethanol in an attempt to prevent agglomeration. The solid and liquid phases were separated by centrifugation after each washing procedure, and the redispersion was assisted by ultrasonic agitation. The resulting wet powders were dried at 60 °C for 48 h and finally calcined at 500 °C for 1 h.

The content of oxygen in the bulk powders was analyzed by IR spectroscopy of the gaseous product formed during the heating of the samples (Eltra, Germany). The electrokinetic properties of the uncoated and coated powders were analyzed in diluted aqueous suspensions, using a Brookhaven ZetaPlus (USA) zeta-meter, with Dolapix CE64 added as a dispersant. The pH was adjusted using hydrochloric acid and sodium hydroxide.

The powder particles were analysed with a JEOL 2010F transmission electron microscope, equipped with a field-emission gun. The microscope was operated at 200 kV. An energy-dispersive X-ray spectrometer (LINK ISIS-300 (Oxford Instruments), with a UTW Si–Li detector) was employed for the chemical analyses.

The X-ray photoelectron spectroscopy (XPS) analyses of the as-received and coated powders were carried out on a PHI-TFA XPS spectrometer, based on the 5700 series. The samples were in the form of 3 mm thick pressed pellets with a diameter of 8 mm. The analysed area was 0.4 mm in diameter and the analysed depth was about 3 nm. During the analyses the spectra were shifted by about 1–2 eV due to sample charging. The binding energy of 532.2 eV for the O 1s peak (characteristic for Si–O bonds) was used as the reference energy for the alignment of the spectra.[6] The sample surfaces were excited by X-ray radiation from a monochromatic Al source. The survey spectra were taken over a wide energy range of 600 eV, with a pass energy of 187 eV. The high resolution narrow scan spectra of Si 2p, C 1s, O 1s, Al 2p, N 1s were acquired with a pass energy of 23 eV, yielding an energy resolution of 0.65 eV, measured on the Ag $3d_{5/2}$ peak. The relative sensitivity factors provided by the instrument producer were applied to calculate the surface concentrations, assuming a model of in-depth homogenous distribution for the elements.

3. Results and discussion

The morphologies of the as-received BF12 and Nano powders observed using the SEM and the TEM are presented in Fig. 1a and b. In contrast to the BF12 particles, which had very angular shapes, the Nano powder had particles that were more spherical.

Additionally, the analyses of the bulk powders revealed that the Nano powder contained a larger amount of oxygen (1.99 wt.%) than the BF12 (0.78 wt.%) powder, presumably as a result of its larger surface area. The oxygen content for the powders thoroughly washed with distilled water was only slightly higher, i.e., 2.07 wt.% for the nano- and 0.81 wt.% for the micron-sized powder.

3.1. HRTEM of the as-received and AlOOH-coated powders

HRTEM analysis was employed in order to reveal the morphology and the structure of the particles' surface layer for the
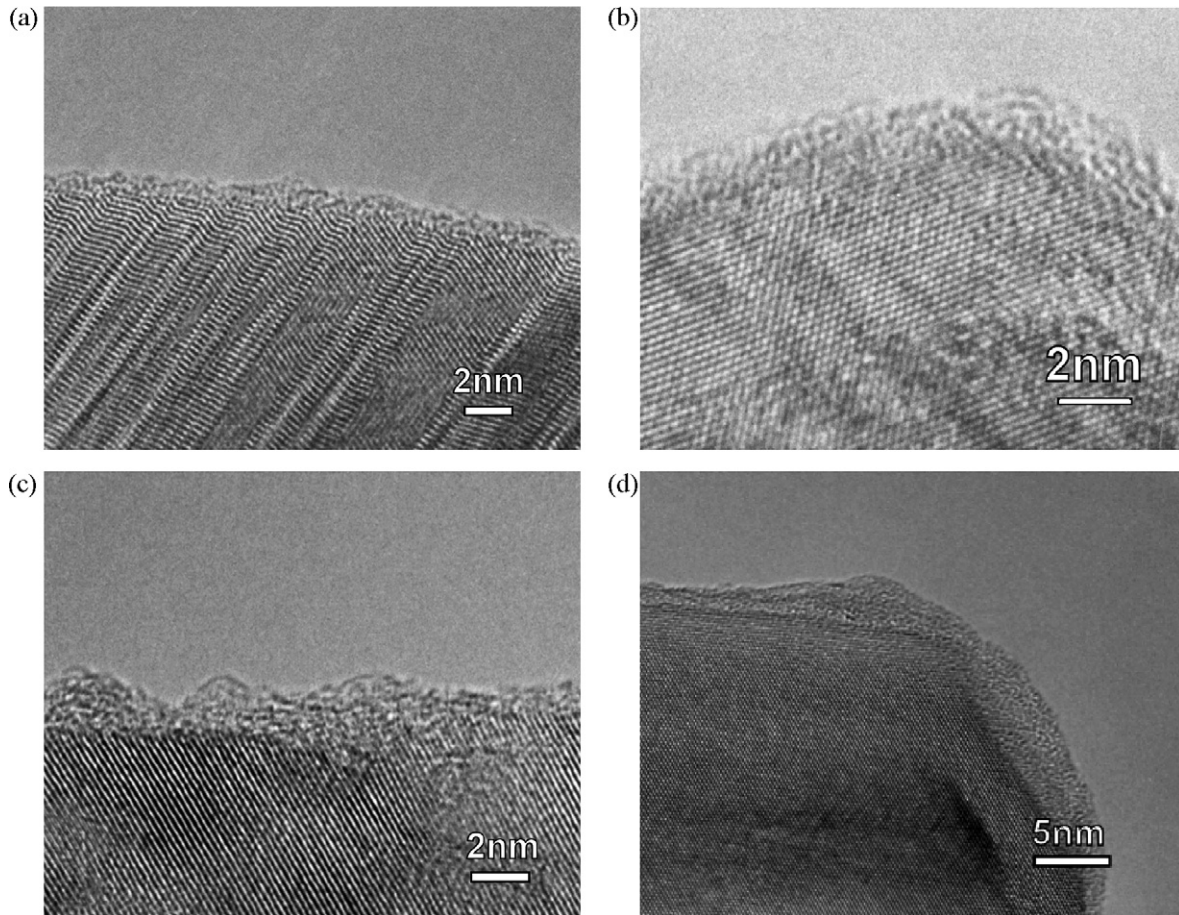
Fig. 2. HRTEM images of as-received BF12 (a) and Nano (b) powders, and the coated BF12-Al (c) and Nano-Al (d) powders.

two powders. As presented in Fig. 2a and b, both as-received powders are covered with a thin (1–2 nm) amorphous layer, which was, based on the results shown below, ascribed to SiC_xO_y and SiO_2. In the energy-dispersive X-ray spectroscopy (EDXS) spectra of the layer, characteristic X-ray lines for carbon, oxygen and silicon were detected, indicating that the surfaces of the SiC particles were oxidized. Due to the limitations of the EDXS method we could not differentiate between Si-oxycarbide and SiO_2.

The TEM–EDXS analysis of the powders treated according to the above described procedure confirmed the presence of aluminium hydroxide in the surface layer of both coated SiC powders. As shown in Fig. 2c and d, the layer is a few (2–5) nm thick. It is interesting to note that in some cases evidence of the presence of oxygen-containing layer was still found below the coating.

3.2. XPS analysis of the powders

The surfaces of the powders were analysed using the XPS technique in order to obtain information on the composition and the chemical bonding of the elements at the powder surface. The XPS survey spectra for the as-received and coated BF12 and Nano powders are presented in Fig. 3a–d. Si, C and O peaks are present in all the spectra. In addition, an N peak was observed
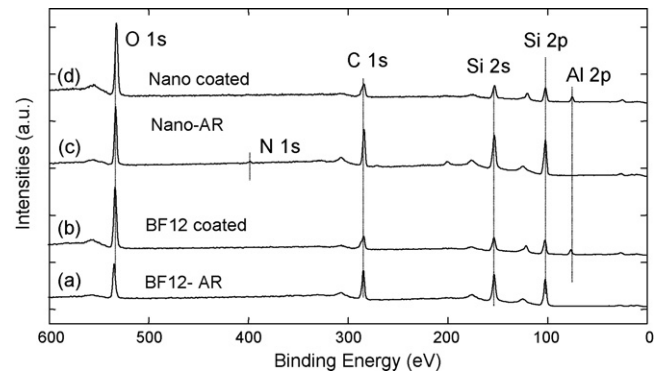

Fig. 3. XPS survey spectra taken on the as-received and coated samples of the BF12 and Nano powders.

for the Nano powder. The aluminium peaks in curves (b) and (d) confirm the presence of an Al-containing layer for the coated powders.

From the spectra we calculated the composition in surface region assuming that the elements were homogenously distributed in the surface and subsurface regions of the order of the XPS probe depth, which is in the range of about 3 nm. The model of a homogenous matrix is an approximation, as the HRTEM analysis revealed a layered structure, i.e., an oxide layer on the SiC particles (see Fig. 2a).
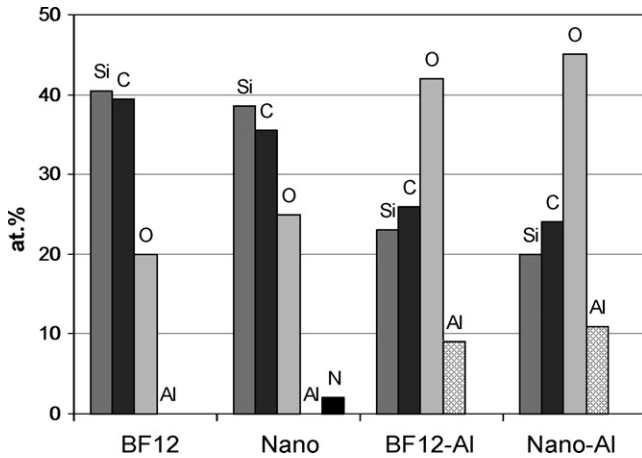
Fig. 4. XPS results on the surface concentrations of the as-received (BF12, Nano) and the coated powders (BF12-Al, Nano-Al).

The surface composition of the samples is presented in Fig. 4. We found similar Si concentrations on the surfaces of both as-received samples, whereas on the Nano sample the C concentration is slightly lower than on the BF12 sample (35.2 at.% versus 39.6 at.%). On the Nano powder the presence of 2.1 at.% of N was also detected. The surface of the as-received BF12 sample contains 19.9 at.% O, while the surface of the Nano sample contains significantly more, i.e., 25 at.%. The oxygen presence we relate to the Si-oxide and SiC_xO_y layers formed on particles during powder preparation or subsequent powder exposure to air before XPS analysis. The higher oxygen concentration on the Nano grains we attribute to higher specific surface area of the Nano powder particles, since the oxygen signal in the XPS spectra partially originates also from the side (lateral) areas of the powder particles.

The XPS technique also provides information on the chemical bonding of elements in a surface region via the so-called chemical shift of the photoelectron peaks in the XPS spectrum. Fig. 5 shows a high-energy resolution Si 2p spectrum taken on the as-received BF12 sample. Three components were resolved using a curve-fitting procedure for the Si 2p peak, indicating three different types of chemical bonding for the Si atoms. Based on the literature data we assigned these three components in the following way.[7] The peak at 100.1 eV of the binding energy
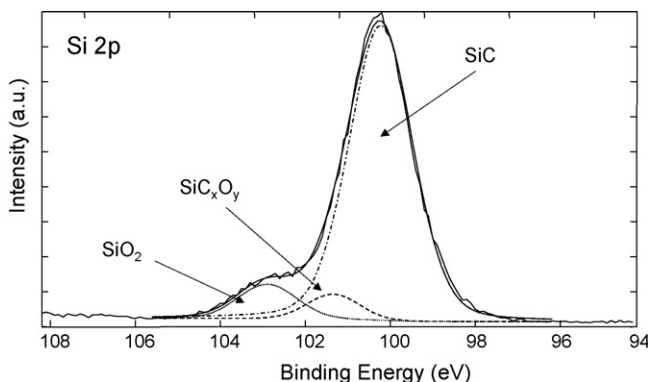

Fig. 5. Characteristic XPS high-resolution Si 2p spectrum obtained on the surface of the as-received BF12 sample.

represents the SiC bonds originating from atoms in the inner part of the SiC grains. The peak at 101.2 eV is related to the Si atoms in the SiC_xO_y layer covering the SiC matrix. On top of the SiC_xO_y layer is the SiO_2 layer, which is related to the component at 102.8 eV. The C 1s high-resolution spectrum (not shown here) shows the main peak at 282.5 eV, which is related to the Si-carbide bonds, and a smaller peak at 284.3 eV, originating from the SiC_xO_y layer and/or some in-air-adsorbed C-based molecules. The different bonding of the Si atoms (SiC, SiC_xO_y, SiO_2) detected by the XPS on the surface of the analysed samples explains the TEM images of the particles surfaces (Fig. 2). On the basis of the XPS results we assume that the outer, amorphous layer consists of SiO_2, and the intermediate region between the amorphous outer layer and the crystalline inner part consists of the SiC_xO_y layer. The inner crystalline phase is the SiC matrix. For the Nano sample the presence of a small N 1s peak at a binding energy of 398.0 eV indicates the presence of bonds between the Si and N atoms.[8]

The survey XPS spectra of the coated BF12 and Nano powders are shown in Fig. 3, as the curves (b) and (d), while the corresponding surface concentrations are given in Fig. 4. The main difference with respect to the as-received samples is the presence of an Al 2p peak and the increase in the oxygen concentration from 20 to 25 at.% to 40 to 44 at.%. We explain this in terms of the formation of a thin AlOOH layer on the SiC grains. The concentration of Al, calculated using the model of a homogenous distribution of elements in the analysed volume of a few nanometres, was determined to be 9–11 at.%, but this value could be significantly higher in the outer few atomic layers of the grains. The binding energy of the Al 2p peak is at 74.5 eV, which means that Al is bonded to the oxygen atoms.[8] Unfortunately, the typical binding energies for Al-oxides and hydroxides overlap, so distinguishing between these two types of bonding using the XPS method is difficult. Higher concentrations of Al (10.5 at.% versus 9.3 at.%) and O on the Nano-Al sample than on the BF12-Al sample can be explained in a similar way as in the case of higher concentration of oxygen on the as-received Nano powder (see above), i.e., due to the higher specific surface area. The C 1s spectrum on the coated samples has, in addition to the SiC-related component at 283 eV, components at 285 and 287 eV. This indicates C–C, C–H and C–O bonding of the C atoms, which is different to the case of the as-received powders.[9] This is evidence that the organic and/or oxidized carbon species are left on the surface of the grains after the sample treatments in solutions.

3.3. Electrokinetic properties in aqueous suspensions

The effect of the composition of the powder surface on the behaviour of the powder in an aqueous suspension was analysed by measuring the zeta-potential (ZP) as a function of pH. It is well known that the charge is determined by the composition of the surface layer and hence the charge reflects the surface's "cleanliness". The ZP of SiC in general varies to a greater extent than it does for oxide powders. The values of the isoelectric point (IEP) for SiC are, for example, reported to be in the range from pH 2 to 6.[9,10] The lowest values, similar to
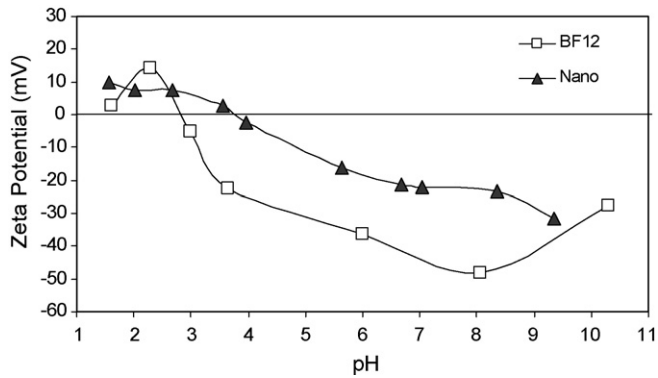
Fig. 6. Electrokinetic behaviour of the as-received powders BF12 and Nano as a function of the pH of the aqueous suspensions.

those observed for silica powders, are frequently attributed to the presence of a thin layer of SiO_2, while the highest reported values are characteristic of "pure" SiC. Our results, presented in Fig. 6, reveal that the as-received BF12 powder has a lower IEP than the Nano powder, which is not in line with the above statement, since according to the above-presented results, the surface layer of the Nano powder contains more oxygen than the BF12 powder. A possible, although speculative, explanation could be based on the observed presence of nitrogen, possibly reflecting the presence of Si-nitride or Si-oxynitride. As presented, the ZP values for the Nano powder are low across the whole pH region.

Fig. 7a and b shows that the AlOOH coating significantly changes the behaviour of the powders in aqueous suspensions.
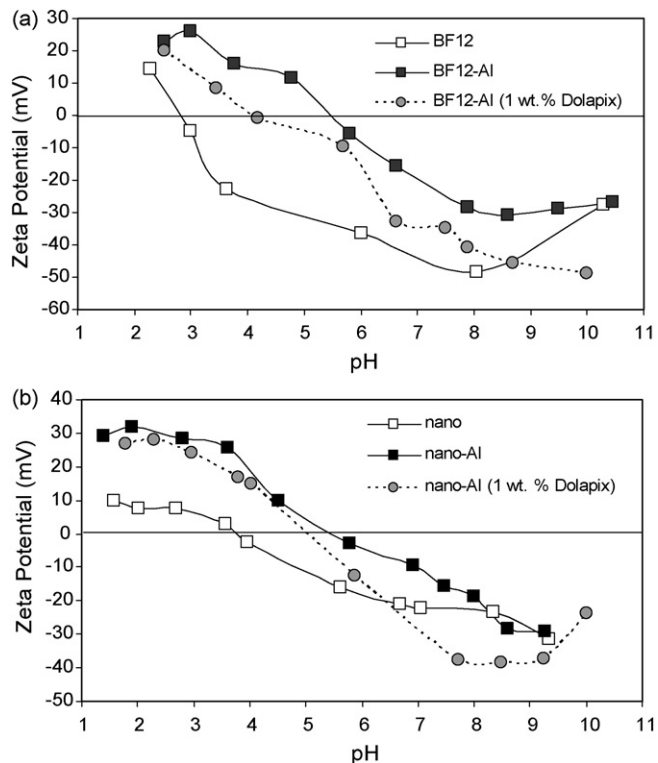

Fig. 7. The change in zeta-potential vs. pH relationship after coating and the addition of Dolapix for the BF12 (a) and Nano (b) powders.

For both coated powders, BF12-Al and Nano-Al, the curve illustrating the ZP versus pH relationship shifted towards higher pH values, and consequently the IEPs appear at higher pH values. The observed shifts can be explained by the presence of a thin AlOOH-containing layer, observed by the HRTEM and XPS, that modified the behaviour of the SiC powder to become more alike alumina.[11–13] This is also reflected in the ability of the powder to be dispersed with the addition of Dolapix CE64, a widely used defloculant for alumina, but with no significant effect on pure SiC. Namely, as presented in the diagram, 1 wt.% of Dolapix increases the negative value of the ZP in alkaline region.

Thus, the presented modification of the behaviour of the as-received SiC powders by coating with a thin aluminium-rich layer represents a versatile possibility for improved processing of the SiC-based materials that will be the objective of our further investigations.

4. Summary and conclusions

The paper presents the results of a thorough investigation of the surfaces of submicron and nanosized SiC powders and the effect of the surface composition on their electrokinetic properties. We have shown that complementary techniques with high microscopic and spectroscopic sensitivities, i.e., high-resolution transmission electron microscopy (HRTEM) and X-ray photoelectron spectroscopy (XPS) provide us with a complete characterisation on a very small scale, i.e., the nanometre thick layers on the submicron or nanosized particles. The effect of the composition of this surface layer on the behaviour of the powder in aqueous suspensions is also presented.

The XPS and TEM reveal the presence of a 1–5 nm thick amorphous layer of SiO_2 on the as-received submicron and nanosized powders, and from the XPS results the presence of an oxycarbide interlayer was also confirmed. After treatment with an Al-nitrate solution, the adsorption of a few nanometres thick amorphous layer of aluminium oxyhydroxide, AlOOH, was confirmed with both analytical techniques. In addition, the surface modification was found to significantly change the behaviour of the powders in aqueous suspensions, resulting in a more alumina-like behaviour. As a result, a SiC powder coated with a very thin aluminium-rich layer can be dispersed with a defloculant normally used for oxide powders. This reflects in a beneficial effect on the colloidal processing of SiC-based materials.

Acknowledgements

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