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Abstract: Ultra High Temperature SPS (UHTSPS) was used to sinter pure α-SiC at 2450 °C. Such a high temperature and partial vacuum conditions promoted SiC sublimation and condensation reactions. In the presence of an electric field, materials with graded porosity could be produced by using UHTSPS. At high temperature, the condensation of the gaseous species was controlled by the polarity of the applied electric field. Preferential condensation of SiC occurred on the negative electrode (cooler surface) due to the Peltier effect associated with the n-type thermoelectric behaviour of SiC. In absence of an electric field, condensation was driven by gravity and it resulted in dense SiC monoliths.

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Dear Editor,

We wish to submit our paper entitled “Ultra-high temperature spark plasma sintering of α-SiC” to Ceramics International. It is an original work and it describes some directional field effects occurring during the Ultra High Temperature SPS (UHTSPS) of α-SiC at 2450 °C. Considering the importance of SiC, this works might have several scientific and technological inplications.

Our findings can be summarized as follows:

In the presence of an electric field, materials with graded porosity could be produced by using UHTSPS. At high temperature, the condensation of the gaseous species was controlled by the polarity of the applied electric fieldand it was driven by the Peltier effect associated with the n-type thermoelectric behaviour of SiC. In absence of an electric field, condensation was driven by gravity and it resulted in dense SiC monoliths.

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Ultra-high temperature spark plasma sintering of α-SiC

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Abstract

Ultra High Temperature SPS (UHTSPS) was used to sinter pure α-SiC at 2450 °C. Such a high temperature and partial vacuum conditions promoted SiC sublimation and condensation reactions. In the presence of an electric field, materials with graded porosity could be produced by using UHTSPS. At high temperature, the condensation of the gaseous species was controlled by the polarity of the applied electric field. Preferential condensation of SiC occurred on the negative electrode (cooler surface) due to the Peltier effect associated with the n-type thermoelectric behaviour of SiC. In absence of an electric field, condensation was driven by gravity and it resulted in dense SiC monoliths.

Introduction

Silicon carbide is among the most widely used ceramics for both structural and functional applications. The worldwide yearly consumption of silicon carbide is expected to reach 2.4x 10^6 tons by 2019 [1]. The main applications for SiC, in terms of volume, are for the steelmaking, refractories and abrasives. A small portion (i.e. a few thousand tonnes) of its production is used for advanced ceramic applications.

Due to its strong covalent bonding, it is difficult to densify SiC without sintering additives. Depending on its application, the typical sintering additives include B, C, Al_2O_3 and others rare earth oxides. The powder mixtures are sintered using several techniques with or without applied pressure by solid state or liquid phase sintering [2]. More recently Suzuki et al. [3] successfully densified pure SiC by SPS (1950 °C for 10 minutes under 80 MPa applied pressure) starting from ultrafine grained powder (average particle size 0.2 μm). They demonstrated the effectiveness of colloidal processing combined with an optimized SPS sintering cycle for achieving fully dense monoliths.

In pressureless conditions, densification of pure SiC is not promoted by increasing the sintering temperature[4]. Recrystallized SiC (RSiC) is produced by firing green bodies in pressureless conditions at temperature up to 2500 °C in vacuum. The result is a porous self-bonded SiC with density comparable to the starting green body (2.6 g/cm^3). Presureless sintering results in nearly no shrinkage, thus, large and complex shapes can be manufactured with a certain degree of precision. RSiC has been widely used in metallurgy, aerospace and other industry due to its high temperature strength, outstanding erosion resistance and high oxidation

resistance with a continuous use temperature in air up to 1600 °C. The combination of high thermal conductivity and low coefficient make this material ideal for kiln furniture [1].

Semiconductor [5] and nuclear [2, 6] industries require high purity SiC products. To produce these materials sintering routes are not viable, instead, Chemical Vapor Deposition (CVD) [7] and Physical Vapour Transport (PVT) techniques are used [8]. These techniques are also employed to grow large SiC single crystals (i.e. 15 cm diameter discs). The literature on pressure assisted sintering techniques operating in sublimation temperatures range is quite limite, this is because such temperatures are barely achievable by conventional apparatuses. In this work we have developed a novel UHTSPS process able to reach a temperature as high as 2450 °C [9]. At this temperature SPS acted as a PVT growth cell. The UHTSPS gave an insight of the thermo-electric interactions [10, 11] occurring during the SiC sublimation/condensation reactions. Even if there is a plenty of literature on both sintering and PVT process of SiC [2], to the authors best knowledge no paper has been published so far accounting the electric field effects during the simultaneous events of SiC particles sintering and sublimation/condensation reactions (PVT). This work aims to fill this gap.

Experimental procedure

The starting powder of the investigation was UF-10 α-SiC produced by H.C. Starck (Germany). This powder was produced by the Acheson process, and it mainly consisted of the α-polytype. The average particle size measured by laser diffraction analysis (ASTM B 822) was 0.7 µm ($D_{90\%}$=1.8, $D_{50\%}$=0.7, $D_{10\%}$=0.2), the specific surface area was 9.0 - 11 m^2/g. The purity of the starting powder was 98.5 %wt. The main impurities were O (<1.1% wt), Al(<0.03% wt), Ca (<0.01% wt) and Fe (<0.05% wt).

In order to understand the effect of the electric field on the physical vapour transport, two SPS *configurations* were employed. In both of the *configurations* the temperature was 2450 °C. All the experiments were carried out using an SPS furnace (HPD 25, FCT Systeme GmbH, Rauenstein, Germany) in argon partial pressure of 1200 Pa.

Configuration 1 is shown in Figure 1 (a). The as received SiC powder (1 g) was poured in a hollow graphite die with 20 mm inner diameter. The SiC powder was heated under an applied uniaxial pressure, resulting in a good electric contact between the sample and the pressing punches. This allowed the effective application of an electric field across the sintering specimen as detailed in Ref. [12]. In the UHTSPS configuration, thick graphite felt was employed to reduce the heat loss by radiation. The UHTSPS experiments were carried out in 2 steps heating mode, in the first step pressure was kept constant at 16 MPa while heating up to 2000 °C at a rate of 200 °C/min, in the second step the pressure was linearly increased up to 40 MPa while heating up to 2450 °C at a rate of 50 °C/min. The dwelling time under 40 MPa was 40 minutes, and the cooling rate was 100 °C/min. The temperature was measured using a top pyrometer focused inside a hole in the punch at distance of 4 mm from the sample.

Configuration 2, is shown in Figure 4 (a). It was designed to minimize the contribution of the electric current (electric field applied across the compact) on the PVT of SiC. The loosely packed SiC powder were not in contact with the top punch (i.e. the mould was not completely filled up) and the powder (1 g) was not pressed between the punches. *Configuration 2* consisted of a hollow mould with inner and outer diameters of 14 and 20 mm respectively, its height was 20 mm. The mould was pressed between two graphite punches, and the temperature was probed by the top pyrometer pointing at punch inner wall (point 1 in Figure 4 (a)) and by the surface

pyrometer pointing on the outer die wall (point 2 in Figure 4 (a)). The temperature probed at the die surface was raised up to 2450 °C in 3 minutes and dwelled for 3 minutes.

The samples were characterized using an SEM (FEI, Inspect F, Hillsboro, USA).

Results and discussion

In order to perform UHTSPS experiments a novel punch die setup was developed. This configuration aimed to reduce the localized overheating occurring between punch and spacer as described by Giuntini et al. [13]. The modified SPS set-up consisted of a punch with tronco-conical shape which is sketched in Figure 1 (a). The UHTSPS set-up avoided overheating and consequent creep failure of the SPS punch die assembly at temperatures exceeding 2200 °C. The SPS apparatus applied pulsed unidirectional (rectified) DC current with waveform of 15 ms on and 5 ms off. The SPS current flows in an upward direction with respect to a gravity, as shown in Figure 1 (a) the bottom ram of the SPS machine corresponds to the positive electrode.

At 2450 °C in partial vacuum conditions volatilization of SiC occurs. In fact, SiC single crystals are grown using PVT process, which is carried in argon partial pressure of 6700 Pa and temperature of 2200 °C [14], resulting in deposition rate between 0.2 to 2 mm per hour [15]. In the PVT process the SiC recrystallization in driven by a thermal gradient created on the surface of a growth cell (a quasi-closed graphite crucible). Typically the hotter zone (top of the crucible) is at a temperature higher than 2200 °C while the colder zone (bottom of the crucible) is at a lower temperature of about 2150 °C with a gradient of 10 °C/cm [5]. It should be noted that the UHTSPS conditions in terms of both temperature (2450 °C) and vacuum (1200 Pa) promote greater evaporation rate than the one typically reported for the PVT process. The sublimation not

only produces SiC (gas) but also depending on the processing conditions, others molecular gaseous species (Si, C, SiC_2, and Si_2C) [16].

Figures 1 show the microstructures observed at the top (b) and the bottom (c) surfaces of the SiC powder processed by UHTSPS dwelled at 2450 °C for 40 minutes. Comparing the top surface (a) with the bottom one (b) there is a significant difference in the density. The relative density estimated by image analysis of the top surface (Figure 1(b)) was 93±5%, while the bottom surface of the sample was clearly more porous and the relative density was 75%±5% (Figure 1(c)). As evidenced in Figure 2 (a) the sample had a graded densification along an axial direction, which indicates a marked directional field effect. Figures 2 shows the cross section of the samples presented in Figures 1. This confirmed the higher relative density of the top of the sample 94±5 (Figure 2 (b)) compared to the bottom 74 ± 5% (Figure 2(c)). The arrows in Figure 2 (b,c) point at porosity, which was closed and open at the top and bottom of the sample respectively. As apparent in Figure 2 (a), the preferential condensation followed the applied electric field, with sublimation from the bottom with condensation at the top. As modelled by Maizza et al. [17], no large asymmetric (respect to the sample mid-thickness plane) thermal gradient is expected to be generated along an axial direction across the sintering sample (see Fig. 24 in their work), so, the preferential densification of the sample should be attributed to other effects than simple Joule heating.

In order to understand in more detail the mechanism related to the preferential density distribution of the sample, a further UHTSPS run was performed using *configuration 1*. In this case the sample was heated twice in two separate cycles. Each cycle was performed as detailed in the experimental condition and the dwell of each cycle was 20 minutes at 2450 °C. During the second cycle the mould was turned upside down (referred as *turned configuration 1*). This

allowed us to investigate whether the preferential density distribution was reproducible with respect to the applied field. Figures 3 show cross section the samples, obtained using the *turned configuration* 1. The relative density of the region near the top of the sample was 96±4% (Figure 3 (b)) while the bottom was (d) 91±5% (Figure 3 (c)). The relative density in the sample mid-thickness (Figure 3 (c)) was significantly lower and it was 73 ±5 % which is still comparable with the one shown in Figure 2 (c). By analogy with the results obtained in *configuration 1*, Figure 3(a) shows open porosity in the central area of the sample, while closed porosity at the bottom and top surfaces. The results obtained in *configuration 1* and *1 turned* suggest that the condensation mainly occurred on the top surface of the sample (negative electrode).

The polarity of existing SPS hardware could not be inverted (i.e. make the top electrode positive). This would have been useful to investigate the condensation reaction for different polarities. In order to overcome this limitation, *Configuration 2* was employed. This configuration is sketched in Figure 4 (a). The loosely packed SiC powder was heated in a graphite crucible. There was no pressure applied to the powder since the pressing punches applied the load through the graphite mould. The powder was heated up to 2450 °C (measured at point 2 in Figure 4 (a)) in 3 die wall minutes and dwelled for 3 minutes. Unlike the experiments in *configuration 1*, the condensation occurred on the bottom punch as shown in Figure 4 (b). Residual SiC powder was left in the mould, this suggest that only part of the powder sublimated and condensed. Figure 4 (c) shows the fracture surface of condensed SiC. The monolith exhibited a pore free structure as shown in the high magnification inset of Figure 4 (c). As reported in Ref. [18], SiC condensation is driven by two contributions, the first one is the temperature gradient between the die wall and the punches, the second one is gravity. During the SPS experiments the die wall was 200 °C hotter than the temperature probed by the top

pyrometer. As results, in *configuration 2*, the absence of electric current flowing across the sample and the symmetric temperature distribution respect to die mid-thickness plane resulted in a preferential condensation driven by a gravity.

Considering the observations in Figures 1-3, it seems that the condensation of SiC gaseous species might have been driven by an electric field via ionization process where the gaseous particles acquire a positive charge. However the voltage applied in the SPS is below 10 V and the corresponding electric field across the sample is usually below 5-10 V/cm [12]. Such a low field strength was probably not sufficient to generate ionization of gaseous species. As reported by Yasufumi et al. [19], no arcing could be generated in the case of 99% SiC in any atmosphere even when the voltage was 30 V [20]. For example, the SPS electric field is several orders of magnitude lower than employed by Yacaman et al. ($0.2\ 10^4$ V/cm) [21] which affected the sublimation condensation reaction in the case of ionic crystals.

By comparing the results in *configuration 1* and *2*, it is possible to conclude that the electric current directed the condensation on the top punch (negative electrode), while in absence of an electric current it occurred on the bottom punch (positive electrode). In the presence of an electric current (*configuration 1*) through the sample, the condensation may have been driven by the induced thermal gradient generated by Peltier effect resulting from the voltage applied on the sintering sample. Only a few studies have attempted to quantify the magnitude of the temperature gradient generated by Peltier effect in the SPS technique [11]. In the case p-type thermoelectric materials, Becker et al. demonstrated by simulation and experiments, that the temperature decreased from the negative electrode to the positive one [11]. Here the gradient is expected to have the opposite sign because of the n-type nature of SiC. It is well known that pure α-SiC is a thermoelectric material with n-type behaviour [22]. Pai et al. [23] measured the

thermoelectric properties of SiC up to 1000 °C; both the Seebeck coefficient and electrical conductivity (in absolute value) increase with increasing temperature. As a result of the Peltier effect, the temperature is expected to be lower on the top electrode (negative) compared to the bottom one (positive). The latter might explain the preferential condensation on the cooler electrode as in the case of PVT process. Unfortunately the thermoelectric properties (Seebeck coefficient, electric and thermal conductivities) of SiC at temperature higher than 1000 °C are not known, so, the thermal gradient generated in *configuration 1* cannot be quantified. However, in the case of PVT a small temperature gradient of 1 ^{o}C/mm is sufficient to drive the condensation [18].

Conclusions

In the presence of an electric current through the sintering SiC particles, UHTSPS resulted in preferential condensation driven by the thermal gradient generated by the Peltier effect associated with the n-type semiconductor behaviour of pure α-SiC. Comparable results were obtained even by inverting the orientation of the sample. In the absence of current flowing through the material, the condensation of SiC was mainly driven by the gravity and resulted in a pore free material. The newly developed UHTSPS made possible to perform PVT of SiC at high temperature 2450 °C. The results shows that UHTSPS is an effective tool for manufacturing high purity SiC either in the form of dense monoliths or materials with graded porosity.

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Figure captions

Figure 1. (a) Schematic of the UHTSPS punch die assembly (*configuration1*). The polarity of the punches is also marked in. SEM of the polished sample observed at (a) the top and (b) the bottom surfaces. The samples were heated processed at 2450 ℃ for 40 minutes under an applied pressure of 40 MPa.

Figure 2. SEM of sample cross (a) section evidencing graded densification microstructure is evidenced. Higher magnification images observed at the (b) top surface and (c) the bottom surfaces confirms the graded density. The sample was processed as in Figure 1.

Figure 3. Figure (a) shows a full cross section and it confirms higher density of the top and the bottom surfaces compared to the sample mid-thickness. Higher magnification images of sample cross section observed at (b) the top, (c) the middle and (d) the bottom surfaces. The sample was processed accordingly *configuration 1 inverted.*

Figure 4. (a) Schematic of the UHTSPS *configuration 2*. The SiC powder was loosely packed in a hollow mould and heated to 2450℃ and dwelled for 3 minutes. The PVT results in a dense compact condensed on the bottom punch as highlighted by arrow in Figure (b). The result is a dense pore free compact as illustrated in Figures (c).

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Figure 1

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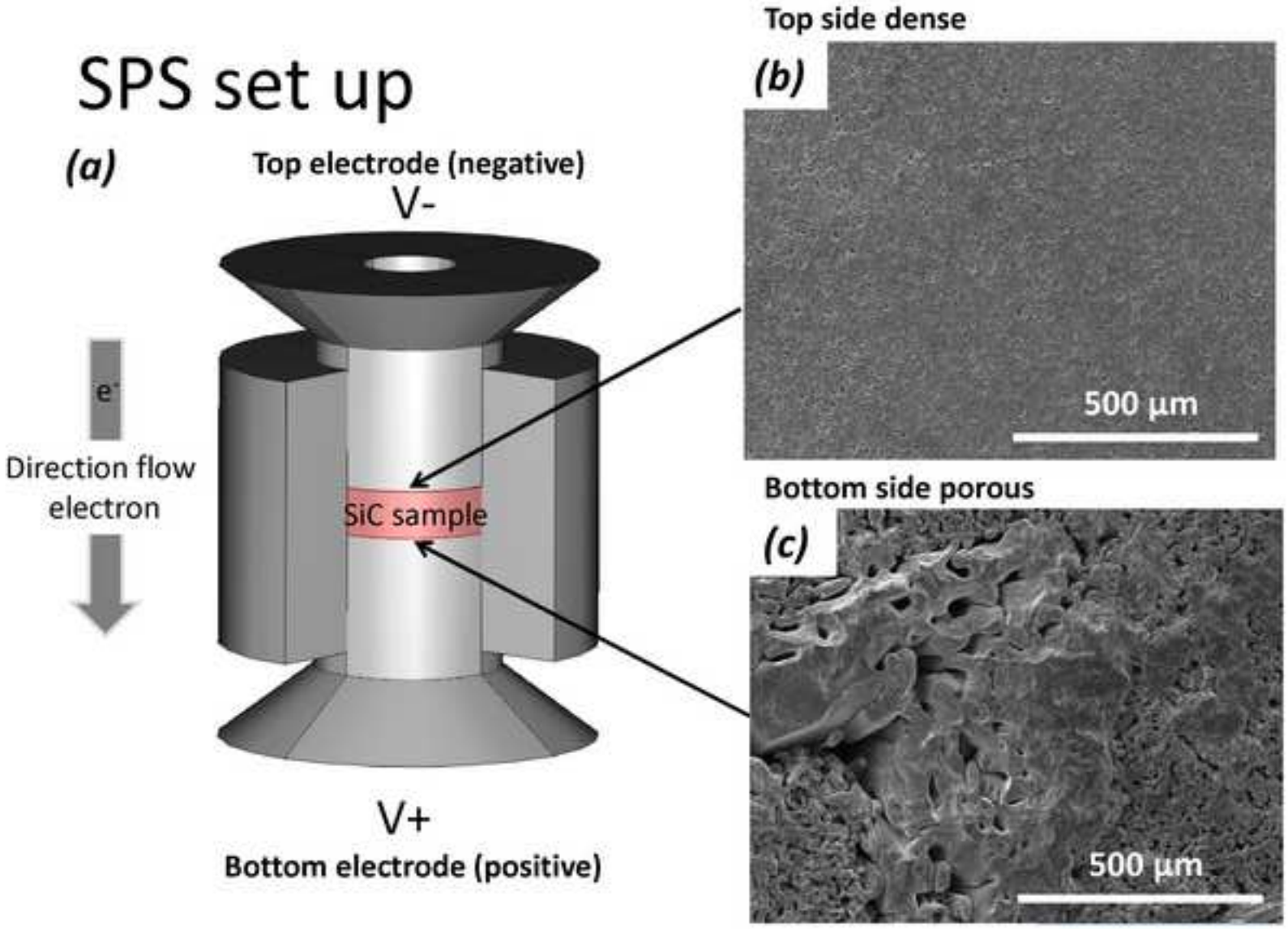

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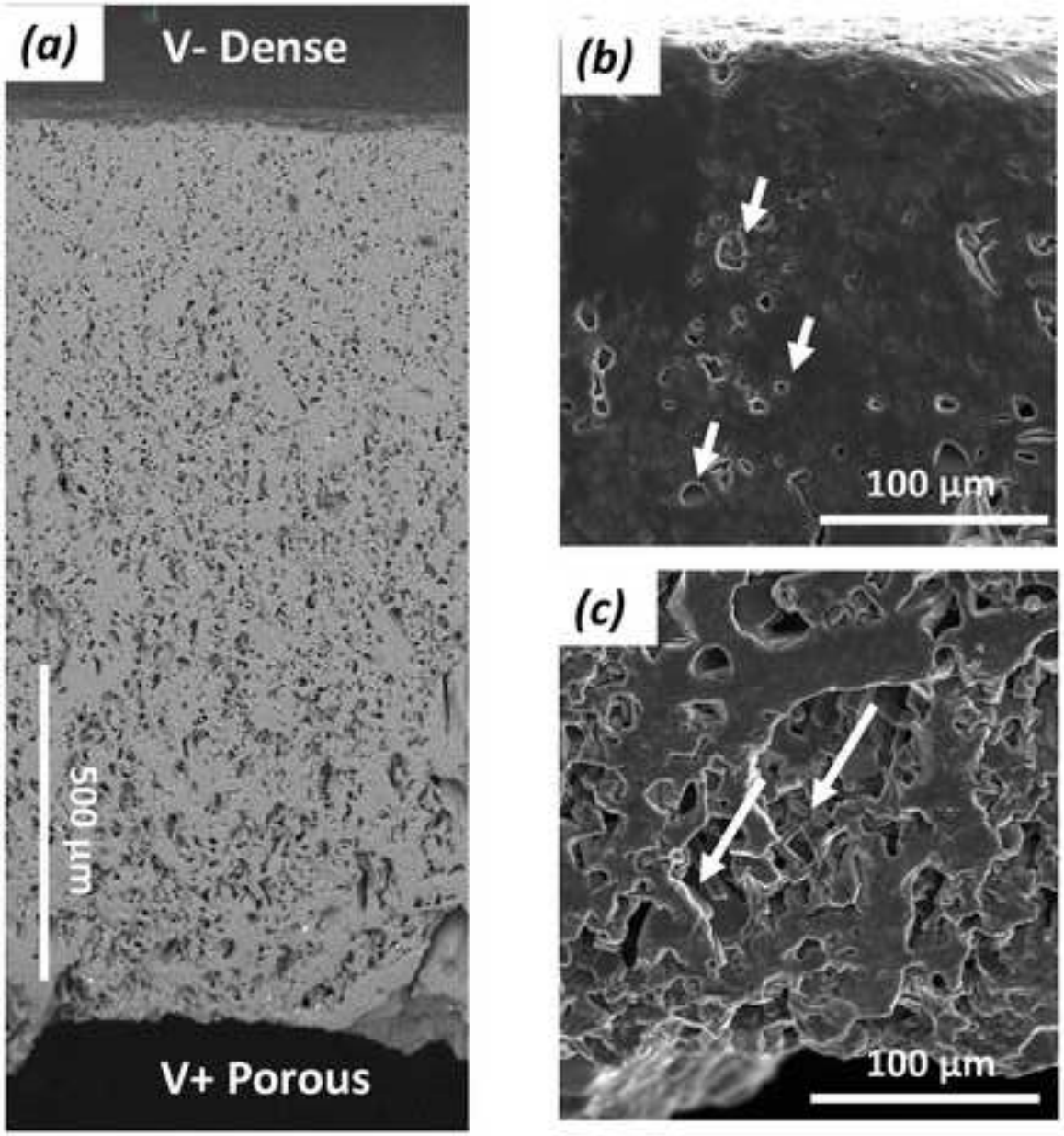

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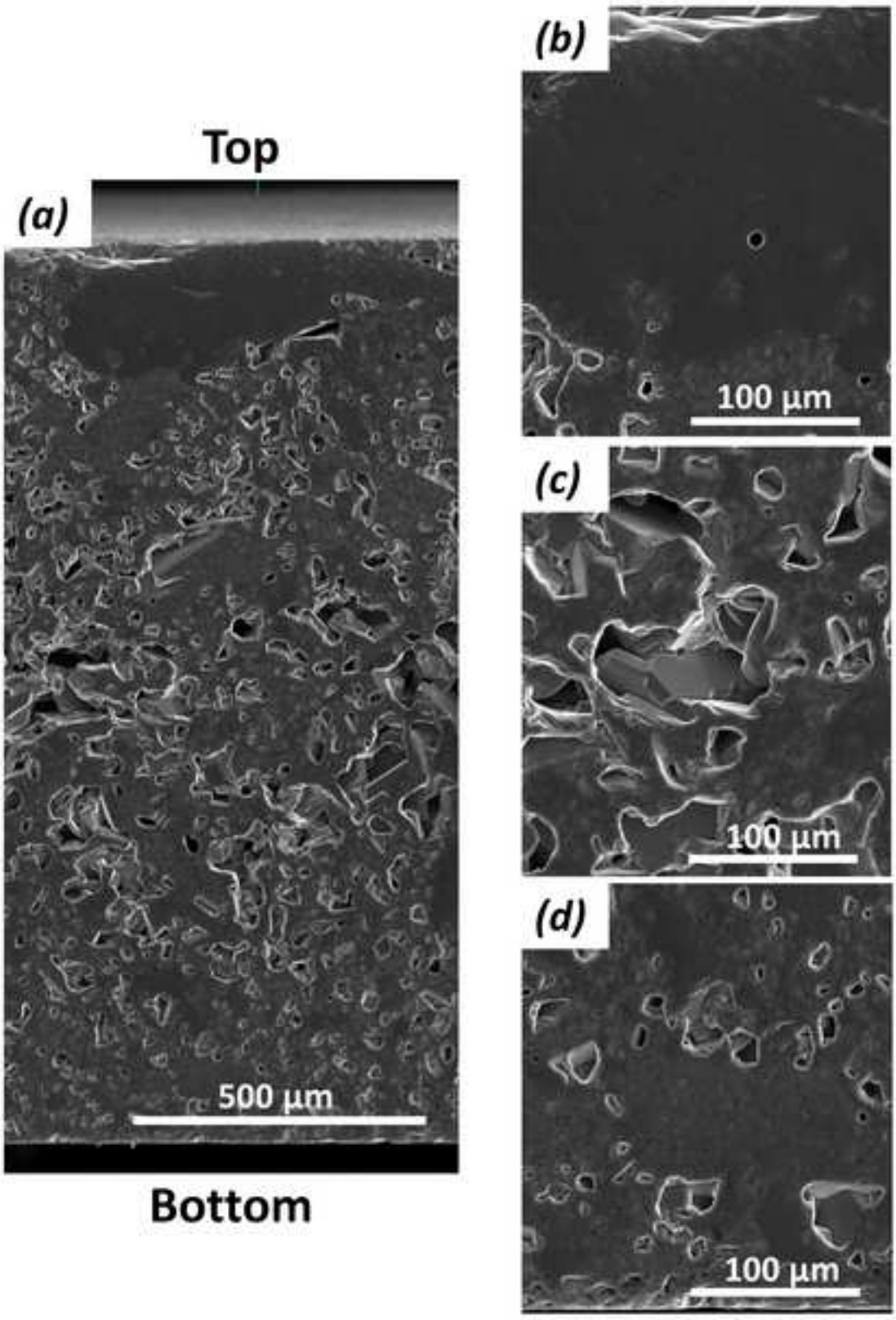

Figure 4

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