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Microanalytical investigation of sintered SiC

Part 2 *Study of the grain boundaries of sintered SiC by high resolution Auger electron spectroscopy*

R. HAMMINGER, G. GRATHWOHL, F. THÜMMLER
Universität Karlsruhe, Institut für Werkstoffkunde II, Kernforschungszentrum Karlsruhe, Institut für Material- und Festkörperforschung, Postfach 36 40, D-7500 Karlsruhe 1, West Germany

UHV-fracture surfaces of different (B, C)- and (Al, C)-doped pressureless sintered SiC materials are investigated by using high resolution Auger electron spectroscopy (HRAES). The grain boundaries at intergranular fractured regions of (B, C)-doped materials are evidently free of any enrichment of impurity elements or sintering additives. In contrast, the (Al, C)-doped materials reveal the existence of thin Al-containing grain boundary films. Sputtering indicates their thickness to be less than 1 nm. The concentrations of the elements segregated in the grain boundary films are determined.

1. Introduction

The subject of Part 1 of this study [1] was the investigation of the microstructures and compositions of four different (Al, C)- or (B, C)-doped pressureless sintered silicon carbide materials, SSiC I–IV. Evidence was given for all investigated materials that the additives and impurities are distributed in an inhomogeneous manner and a larger number of differently sized inclusions was analysed.

The task of Part 2 of this work is the analysis of the grain boundaries in SSiC. Difficulties arise from the detectability of minimum concentrations of low Z elements and the very small spatial dimensions which have to be analysed. Therefore, special analytical methods with very good lateral and spatial resolutions and detection limits have to be used. Besides HRAES the experimental tools that can provide reliable information on the status of grain boundaries are analytical electron microscopy and diffraction techniques. Although the grain boundaries of SiC were studied in some recent publications, the knowledge about the appearance, purity and microchemical composition remains still doubtful so far.

Especially scanning transmission electron microscopy (STEM) has been used to examine sintered and hot-pressed SiC. Lattice fringe imaging was utilized for the investigation of (B, C)-doped SSiC and the existence of a presumed grain boundary phase (~ 0.8 nm thickness) was discussed [2]. However, it was also concluded from diffraction techniques that a grain boundary phase most probably does not exist in both (B, C)-doped SSiC and hot-pressed SiC. The resolution was indicated as 1.5 nm [3]. Electron energy loss spectroscopy (EELS) and energy dispersive X-ray microanalysis (EDX) have been applicated in conjunction with STEM to identify eventually occurring second phases at the grain boundaries of polycrystalline SiC. It was reported that no amorphous layer exists at the grain boundaries of (B, C)- and (Al, C)-doped SiC [4]. No remnants of a grain boundary phase could be determined in two (B, C)-doped hot-pressed SiC materials by EELS. However, an improved spatial resolution was claimed to be necessary for the unequivocal clarification [5]. The grain boundaries of (Al, C)-doped SSiC and hot-pressed SiC were also examined by a STEM fitted with an EDX spectrometer. Grain boundary segregation of aluminium is claimed to exist in both materials [6, 7]. This statement was given in spite of the fact that only very low X-ray intensities near or below the detection limit have been measured.

From the published data it has to be concluded

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TABLE I Chemical analysis of SSiC V (wt %)

Material	O	N	C_{free}	Si_{free}	Fe	Ca	Mg	Al	B	C_{tot}
SSiC V	0.07	0.29	$\leqslant 1.02$	< 0.2	< 0.1	< 0.05	< 0.01	0.58	< 0.1	31.1

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that today's knowledge about the state of the grain boundaries in SiC is not unambiguous. This may partly be attributed to the early state of development of the investigated materials. On the other side, the methods used were not able to realize the necessary resolution (STEM) and detection limits (EDX, EELS).

In the present work, five high quality SSiC materials with (B, C)- or (Al, C)-additives were investigated by the application of HRAES which has recently become available. Its spatial and lateral resolution enables monolayer-sensitive analytical work on single grain boundaries.

2. Materials

The (Al, C)- and (B, C)-doped SSiC materials investigated in this work were characterized as described in Part 1 of this paper [1]. SSiC I is an Al-doped material, whereas SSiC II–IV are B-doped. Both transgranular and intergranular fracture modes were observed in all materials. SEM studies gave evidence, that a higher degree of intergranular fractured regions was found in Al-doped materials than in B-doped samples. Additionally, a material SSiC V containing AlN and carbon as intentional sintering additives was investigated. This material has an average grain size of 3.5 μm, a density of 3.09 g cm^{-3} (corresponding to 96.5% theoretical density) and the chemical analysis given in Table I.

3. Experimental details

Grain boundaries of SSiC were investigated by imaging HRAES in combination with an ultra high vacuum fracture equipment (liquid N_2-cooled) to avoid any detectable contamination. The chemical composition of grain boundaries or of eventual intergranular layers has been measured on freshly generated intergranular fracture surfaces. Similarly the local composition in single grains has been determined on cleavage surfaces.

The analyses were performed in a Perkin Elmer* equipment fitted with an analyser of the cylindrical mirror type. An acceleration voltage of the primary electrons of 10 kV was chosen at vacuum conditions better than 10^{-9} torr. Sputtering with argon ions enabled the evaluation of the thickness of segregation films, based on the comparison with standards of Ta_2O_5 and steel. During sputtering of SSiC no selective attack was found to take place as is also proclaimed elsewhere [8].

Reducing the primary electron beam diameter, the lateral resolution of HRAES has now been minimized to areas as small as about 50 nm. Analysis depth, typically 0.5 to 2 nm, is determined by the escape depth of the Auger electrons allowing detection and identification of all elements with the exception of hydrogen and helium which do not make Auger transitions. The detection limit can be considered to be as small as 0.1 at % of the analysed layer [9, 10].

The Auger spectra contain both qualitative and reliable quantitative information and in many cases the status of the chemical bonding is distinguishable. Quantification is usually done by using known elemental sensitivity factors [11]. Due to the neglection of the variation of the backscattering factor and of the escape depth in different materials a semi-quantitative analysis is then possible. The advantage of this method can be seen in the insensitivity to surface roughness because all Auger peaks are uniformly affected by surface topography.

4. Results and discussion

Neither boron nor any traces of impurity elements were found at the grain boundaries of three B-doped materials. Within the monolayer-sensitive resolution of HRAES these grain boundaries are claimed to be absolutely free of any segregation. Fig. 1 presents one typical grain boundary spectrum, e.g. from SSiC II which is identical with the point analyses of transgranular fractured regions, not shown here. The given spectrum is also identi-

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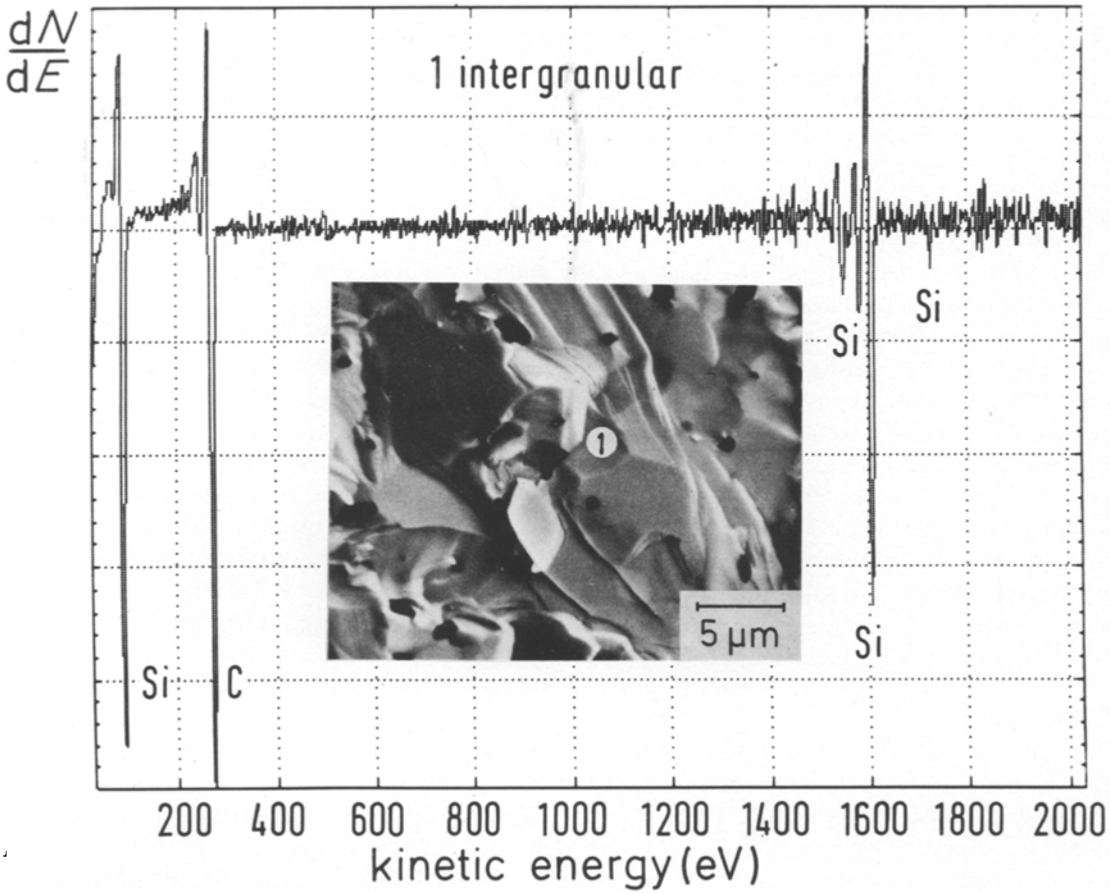
*Perkin Elmer, Physical Electronics Div. Europe, Bahnhofstr. 30, D-8011 Vaterstetten, Germany.



cal with the grain boundary spectra of SSiC III and SSiC IV and seems to represent a general characteristic for the B-doped materials.

Boron could be detected in the matrices of SSiC II, SSiC III and SSiC IV by taking up differently sized area analyses of transgranular fractured regions. Quantitative measurements revealed a boron content of the matrices which is in reasonably good agreement with the chemical analyses [1]. This result can be interpreted as a solid solution of boron in the bulk materials [12].

In contrast to the results received from B-doped materials the grain boundaries of the Al_4C_3- and AlN-doped materials were found to be enriched with aluminium. These enrichments of the sintering additive aluminium are generally accompanied by boron; the boron content was also measured in the Al-doped materials by chemical analysis (see Table I). A representative example for these results is shown in Fig. 2 for the Al_4C_3-doped SSiC I. The grain boundary spectrum of this figure was taken from the intergranular fractured region at Point 1 of the appropriate secondary electron image.

Slight sputtering treatments with argon ions gave quick evidence about the extremely small spatial extension of the indicated grain boundary films. This fact is discussed in the next figures showing some expanded spectra. Fig. 3a presents again the grain boundary analysis of SSiC I belonging to Point 1 of the secondary electron image of Fig. 2. The aluminium and boron content is clearly revealed. After sputtering which removed a film of about 0.6 nm thickness (30 sec, 1 kV) these elements have nearly vanished, as shown in Fig. 3b. The Al-, B-depressed low energy Si-peak has increased and the stoichiometric C/Si ratio of the matrix was re-installed. For comparison the spectrum from Fig. 3c was taken from a transgranular fractured region at Point 2 of Fig. 2. The identity of both the sputtered intergranular and the transgranular spectrum is clearly demonstrated.

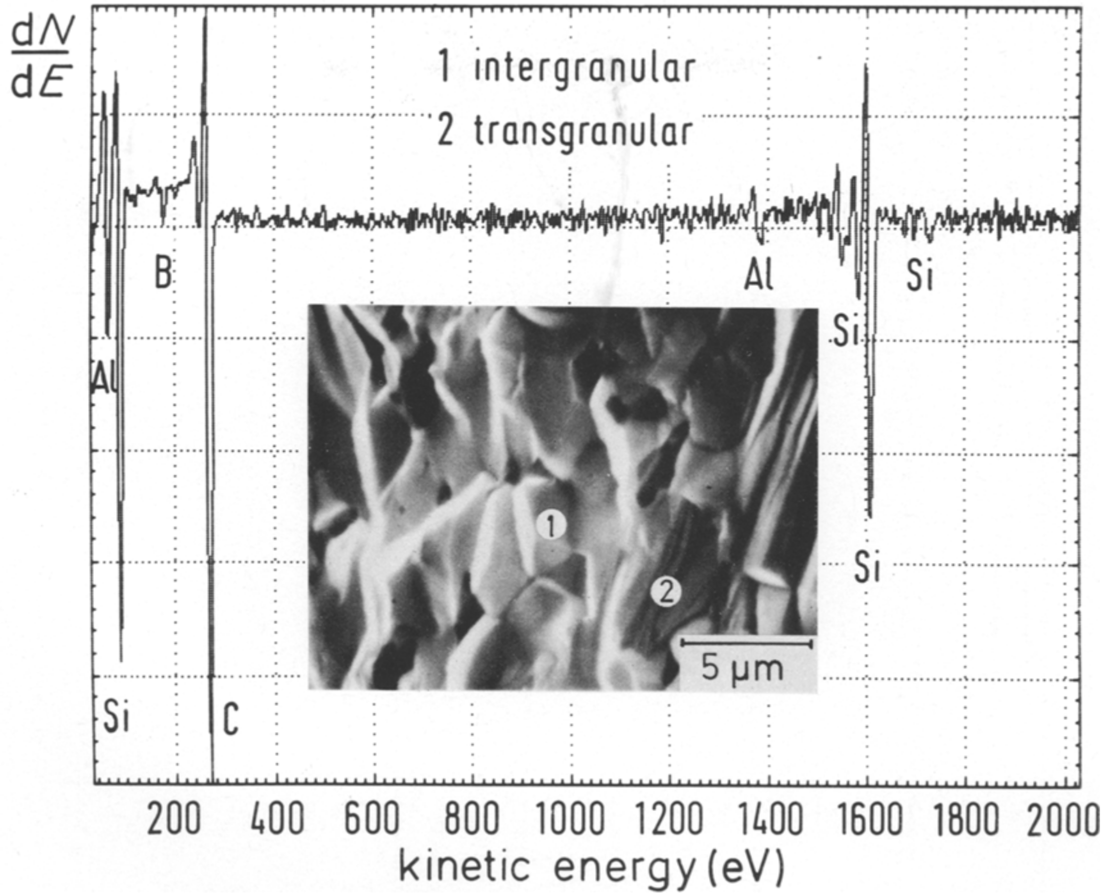


Figure 2 Grain boundary spectrum of SSiC I (Point 1).

Similar results were found for the AlN-doped SSiC V. In addition to the aluminium and boron content the grain boundaries of this material contain also some nitrogen which is referable to the used sintering aid. Grain boundary spectra of SSiC V are given in Fig. 4; the enrichment of aluminium and boron is again clearly revealed by a survey-spectrum (Fig. 4a). The expanded spectra of Fig. 4 before (Fig. 4b) and after (Fig. 4c) sputtering of about 0.6 nm give again strong evidence for the extremely small thickness of the enrichments.

Using elemental sensitivity factors the concentration of the elements in the analysed layer can be determined quantitatively. This procedure leads to values of about 5 at % and 4.5 at % Al at the grain boundaries of SSiC I and SSiC V, respectively. The boron content of the segregation films was determined to be about 4.0 at % for both materials, whereas the grain boundaries of SSiC V contain also about 1.5 at % N. However, one has to keep in mind that the total analysis depth is larger than the extremely small extension of the indicated grain boundary layers (2 to 3 nm and 0.6 nm, respectively). Thus, the aluminium, boron and nitrogen concentration values in the segregation films are thought to be higher than the values resulting from the total analysis depth. While nearly half of the intensity of the Auger signal is obtained from the outermost atomic layer, a multiplication factor not higher than 1.5 may be suggested.

5. Conclusions

The results on the status of the grain boundaries of SSiC are based on a large number of investigated samples. The grain boundaries of three B-doped materials were always found to be free of any intergranular enrichment. This probably represents a characteristic feature of B-doped SSiC. On the other hand, all investigated Al-doped materials exhibit aluminium and boron segregations on the

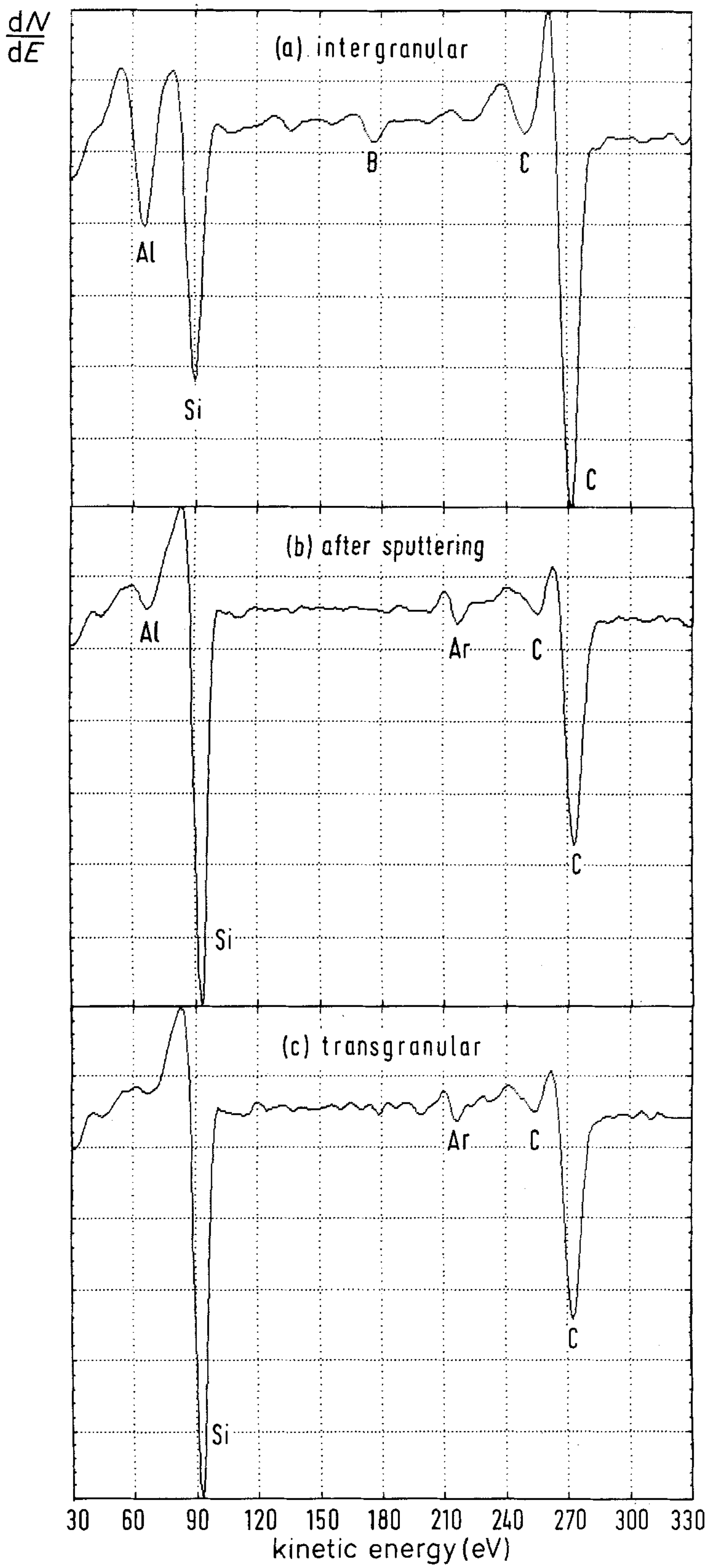


Figure 3 Expanded spectra of SSiC I: (a) grain boundary (Point 1 in Fig. 2), (b) grain boundary after sputtering about 0.6 nm, (c) transgranular region (Point 2 in Fig. 2).

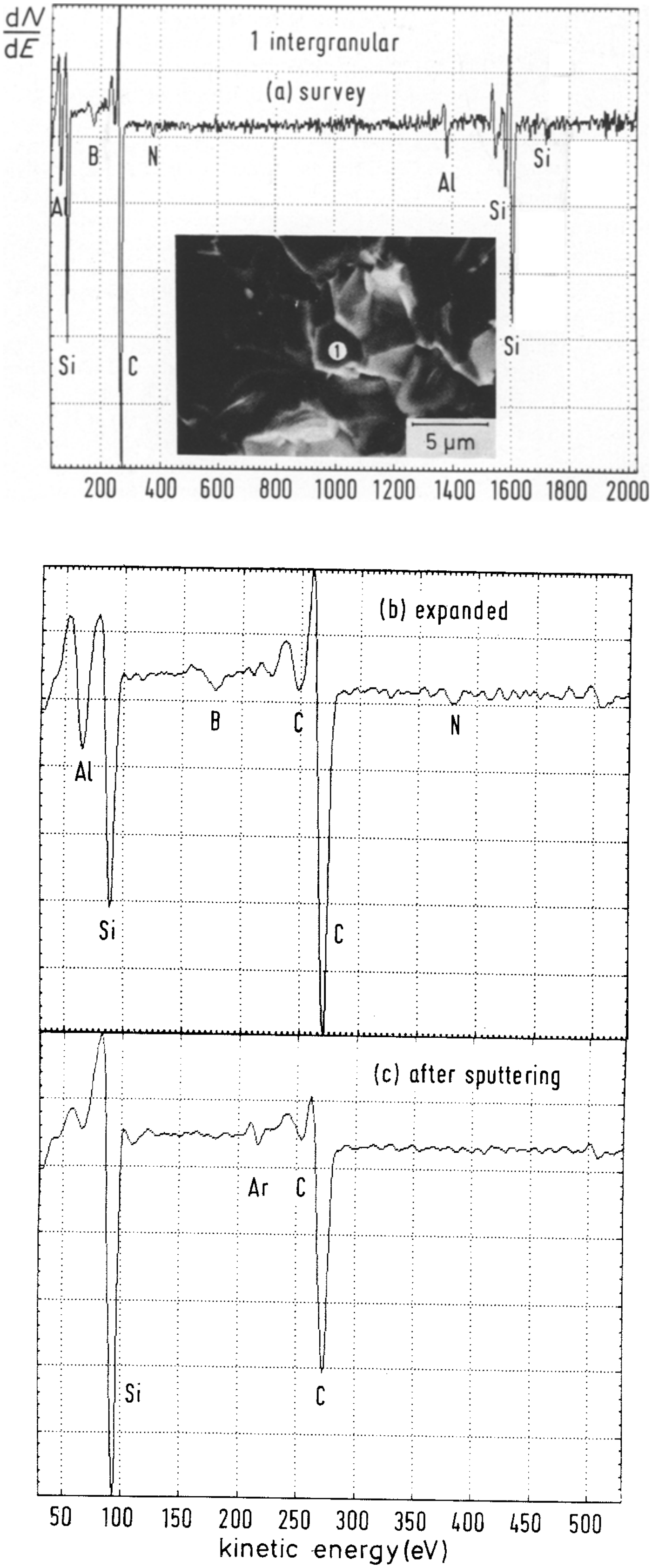


Figure 4 Grain boundary spectra of SSiC V: (a) survey, (b) expanded, (c) after sputtering about 0.6 nm.

grain boundaries. Although specified as Al-doped SSiC, these materials are obviously not free of any boron. The thickness of these segregations is limited to less than 1 nm.

The grain boundaries of the B-doped SSiC can be considered to be in an optimum state with respect to the high temperature long term properties [13], while these properties of Al-doped SSiC may be influenced by the measured grain boundary segregation.

The O-free status of the grain boundaries in both types of materials as well as the oxide-containing large inclusions, mentioned in Part 1 [1], are pointing out to desoxidation processes being highly effective in the presence of the additives during sintering, as supposed earlier [14].

Acknowledgements

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