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Keywords

mechanical, assisted, discharge, electric, sic, carbide, silicon, milling, cubic, rapid, hexagonal, transformation

Disciplines

Engineering | Science and Technology Studies

Publication Details

Aisyah, I. S., Wyszomirska, M., Calka, A. & Wexler, D. (2016). Rapid transformation of hexagonal to cubic silicon carbide (sic) by electric discharge assisted mechanical milling. *Plasma Chemistry and Plasma Processing*, 36 1177-1186.

Rapid Transformation of Hexagonal to Cubic Silicon Carbide (SiC) by Electric Discharge Assisted Mechanical Milling

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Abstract

Silicon Carbide powder was successfully transformed from hexagonal SiC into cubic SiC using the Electric Discharge Assisted Mechanical Milling (EDAMM) method. The milling process was conducted in nitrogen plasma at atmospheric pressure. The effects of pulsed Alternating Current (AC) and Direct Current (DC) discharge on product formation were investigated. Products were characterized by X-ray Diffractometry (XRD), Scanning Electron Microscopy (SEM), Transmission Electron Microscopy (TEM) and Nanohardness. It was found that hexagonal SiC can be transformed into cubic SiC under EDAMM processing, near complete transformation occurring within 5 min when applying AC mode electrical pulses, and within 10 min when applying DC mode discharges.

Keywords: silicon carbide, electric discharge assisted mechanical milling, spark plasma.

1. Introduction

Silicon Carbide is a well-known refractory structural ceramic with a history going back to the 19th century. It is widely used in industrial applications as abrasives, cutting tool elements, heating elements, thermal barriers for aeronautic or aerospace applications. It is relatively inexpensive with high hardness, high strength, low bulk density, good wear, corrosion and oxidation resistance and excellent thermal stability. These properties, combined with its high breakdown field and wide band gap make it a promising semiconductor for high temperature, high frequency and next generation high power devices applications [1]. Specific crystallographic polymorphs of SiC powder are synthesised via a range of methods, often requiring long processing times or complex processing procedures. These include; mechanochemical processing and hot consolidation [1,2], chemical vapour deposition [3], carbothermic reduction [4,5], carbothermal reduction [6], aerosol assisted synthesis and DC thermal plasma synthesis [7]. Cubic SiC is attractive as it exhibits high thermal conductivity and refractoriness, low thermal expansion and outstanding abrasion/erosion resistance. It also has a low background current, good electrochemical activity and can be n- or p-doped reaching up to high electrical conductivities [8]. The properties of the final product vary depending on the purity of the ceramic and its crystallographic structure. Within the most commonly used SiC crystallographic structures we can distinguish between α phases corresponding to the hexagonal structures and β phases corresponding to the cubic phase. Commonly used nomenclature to further distinguish in between the polymorphic structures of these phases is 4H and 6H SiC for hexagonal and 3C for the cubic ones.

Silicon carbide experiences a hexagonal/cubic crystal structure transition which was proven in late 60's [9] to be triggered by not only high temperature (in the range of 2000-

2300°C) and pressure but also impurities and defects. The literature review reveals that the study concentrated mainly on the cubic to hexagonal transformation rather than the reverse one and so the experimental results in this work will be able to complement the knowledge on this transition in pulsed plasma conditions which hasn't been reported before. Research in this area of is even more important as the thermal stabilities of the 6H and 3C SiC polymorphs suggest that heating will naturally promote formation of the hexagonal crystal structure which is stable above 1700°C. Reverse transformation on the other hand is relatively hard to achieve as the structure has to rearrange itself from an already stable form and cannot be achieved by simply decreasing the temperature of the process.

Taking into account solely the 6H→3C transformation there are only a few records on the successful reaction. Turan and Knowles [10] studied the influence of the secondary phase on the hexagonal-cubic so-called “reverse” phase transformations, in Si₃N₄ reinforced 6H-SiC composite. The phase transformation occurred to a low extent even though the Hot Isostatic Pressing was used at the temperature of 2100°C and pressure of 200 MPa in argon. It was then recently reported by Limeng et al. [11] that this phase transformation can occur fast and to a greater extent when the additional Al₂O₃, Y₂O₃ and AlN are included in the composite. Spark Plasma Sintering was able to facilitate this transformation in a much lower temperature of 1700°C, pressure increasing from 5 to 30 MPa in time as short as 30s. Additionally, the Liquid Phase Sintered method reveals, that nitrogen atmosphere together with the Al₂O₃ and Y₂O₃ additives suppresses the 6H→3C transformation which otherwise is completed in argon atmosphere. More importantly though the authors state that the nitrogen atmosphere leads to its incorporation in the intergranular phase which increases the hardness of the SiC in higher temperatures [11]. For the above reasons, the reasonable step taken was to use the EDAMM process to attempt on the phase transition in the nitrogen atmosphere.

It should be noted that none of the above methods were previously reported to be successful in that kind of phase transformation without any additives. Pure SiC powder processed by the High Energy Ball Milling (mechanosynthesis) method was only able to produce the 3C-SiC and no phase transformation was recorded [12]. No β→α transformation was also noted in [13] where ball milled powder was subjected to Spark Plasma Sintering process in the temperature range of 1650-2220°C and up to 150 MPa pressure.

Here, we present Electric Discharge Assisted Mechanical Milling (EDAMM) as a synthesis and processing method demonstrated to promote rapid transformations allowing reaction between freshly fractured particles and ions associated with the generated dusty plasma [15]. In comparison to the previously described methods, EDAMM holds an advantage of promoting the interface rather than the diffusional transformation. Because of that fact, when the pressure as low as 90kPa is applied and only localised temperature occurs with additional milling, the phase transformations can occur in much lower temperatures. We decided to investigate EDAMM processing of hexagonal SiC in nitrogen rich plasma to determine if the method could be applied to promote the transformation to refractory cubic SiC. The investigation of phase transformations in hexagonal SiC induced by EDAMM was performed using both AC and DC discharges.

2. Materials and methods

The starting powder was hexagonal SiC obtained from Aldrich (product number 357391) with a particle size of 400 mesh and 97.5% purity. As advised by Aldrich, the SiC was synthesized by high temperature reduction of silica with coke (salt was used as flux) in an electric furnace. EDAMM was performed in a modified vibratory laboratory rod mill. The mill

was designed to produce a milling mode combining a repeated impact of a curved stainless steel rod end on powder particles, placed on a vibrating hemispherical stainless steel container under electrical conditions of pulsed discharges (Figure 1). During milling, pulsed discharges are initiated at the tip of the rod, travel through the milling atmosphere and powders, terminating in the base at the centre of the hemispherical milling cell. The power supply unit is custom built specifically for discharge milling, yielding a discharge current of 3.12A with the averaged voltage of 100V for alternating current and a peak voltage of 600V for the direct current. It should be noted that no phase transformation occurs with the discharge switched off. More specific information is given in Table 1 with comparison to the traditional planetary ball milling.

Fig. 2 shows oscilloscope voltage vs time images of the discharges. In AC mode the detected pulsed waveform (high voltage low current) is relative to a base of zero voltage and current while in DC mode the pulsed waveform is applied on top of a negative discharge voltage and constant current. The EDAMM experiments were carried out under atmospheric pressure of nitrogen, using AC and DC milling modes. The average gap between electrodes was 6 mm. It has to be born in mind that the experimental procedure and conditions of processing were both based on the fact that no phase transformation was occurring when the discharge was switched off and so the impact on the particles within the same time frame is not causing any chemical reactions or diffusion on the atoms.

X-ray diffraction analysis of starting and milled powders was performed using a Philips Diffractometer with Cu K α radiation and graphite monochromator. Diffractometer output was analysed using Traces Version 5.1.0 software. Phase identification was carried out using the International Centre for Diffraction Data (JCPDS-ICDD 2000) Powder Diffraction Files (PDF). Powder morphologies were characterized using a JOEL 7001 FEGSEM scanning electron microscope (SEM). Elemental composition was also performed using energy dispersive spectroscopy (EDS) using a Bruker EDS detection system running in semi-quantitative standardless analysis mode. Transmission electron microscopy (TEM) was performed using a JEOL 2011 200 KeV high resolution analytical instrument. TEM samples were prepared by dispersion of SiC powders onto holey carbon support grids. Polished powder samples were prepared by hot mounting machine under 4200 kPa at 150 °C for 8 minutes. The nanohardness measurements were carried out by UMIS nanoindenter and the Vickers hardness test was performed with hardness tester machine LECO M-400-H1 with 50g load imposed for 5 sec. An average value gained from the measurements was taken from 8 indentations.

3. Results and discussion

Following a series of trials during which the applied power during EDAMM processing was varied the highest reaction rates of the as-received powders were found when the averaged discharge power was around 0.54 kW. Higher discharge powers, of up to 3 kW, were found to cause excessive powder particles agglomeration which generally slows down transformation rates.

3.1 Phase identification.

There are more than 250 different polymorphic crystal structures of SiC whose electromagnetic properties may differ significantly. Within that group we can distinguish so-called polytypes which are characterized by a unique shift in the bilayer lattice between the SiC unit cells otherwise called bilayer stacking. Because of the relatively easier manufacturing of a single type SiC 4H, 6H and 3C types are of the most interest. In case of a 3C cubic and the 4H and 6H hexagonal structures, differences in stacking sequence do not alter the distance between those atom planes which give rise to the most intense lines of the x-ray diffraction patterns. For

this reason it can be difficult to distinguish between polytypes on the basis of XRD results alone [17], when a mixture of cubic and hexagonal phases are present. Therefore in this study we combined x-ray analysis with TEM and electron diffraction.

X-ray diffraction revealed structures present in the starting powder (Fig. 3(a)) to be consistent with a mixture of the hexagonal 4H structure (PDF Card, 02-1463; $a = 0.30730$ nm and $c = 1.0053$ nm) and the hexagonal 6H α structure (PDF Card 42-1360; $a = 0.30730$ nm and $c = 1.511$ nm). Starting powders were processed under EDAMM for 5 and 10 min in both DC and AC modes to observe effects of processing parameters on product formation. In Fig. 3 X-ray diffraction patterns obtained from samples after EDAMM for 5 and 10 min in DC mode are presented. Note that XRD peaks related to the Hexagonal SiC phases alone show much lower intensities and only those hexagonal SiC peaks, which overlap with the 3C-SiC, show the same or higher intensity, a result consistent with the formation of a significant proportion of 3C-SiC. XRD results from the sample after 10 min of EDAMM show a set of peaks that can be indexed to 3C-SiC (PDF 02-1050; $a = 0.4349$ nm). Fig. 4(b) and (c) show x-ray diffraction patterns obtained from samples after EDAMM for 5 and 10 min in AC mode. In this case a full set of 3C-SiC peaks is seen after 5 min of EDAMM (Fig. 3(b)). Prolonged milling for 10 min results in formation of additional peaks corresponding to a non-stoichiometric $\text{Fe}_{0.42}\text{Si}_{2.67}$ phase (PDF 41-122). This phase is believed to have formed as a result of a processing induced reaction between the steel (plunger and milling base) and silicon after partial decomposition of the SiC.

Transmission electron microscopy was used to investigate the morphology and structure of EDAMM processed samples. Fig. 5 shows TEM results obtained from the sample processed for 10 mins under DC mode. The nanostructural morphology of the agglomerates formed was confirmed, with a mixed nanocrystalline size, as indicated in (Fig. 5(a)). The 3C-SiC cubic structure of the sample was confirmed by electron diffraction of the selected area (Fig. 5(b)), while dark field imaging (Fig 5(c)) confirmed that the nanostructural particles were distributed throughout the particle's agglomerates. In contrast to the EDAMM processed samples, the starting powder was coarse. Fig. 5(d) shows a starting powder particle, the top end producing HRTEM contrast consistent with that of a faulted hexagonal SiC phase.

On the basis of the XRD and TEM results we can conclude that the rate of 3C-SiC formation under AC mode discharge milling is faster than under DC mode. This phenomenon possibly relates to the different kinetic conditions during EDAMM, and the transport of particles to the centre of the milling cell. It has been established from previous investigations that under DC mode processing localized Joule heating of particles occurs in the vicinity of the electrical discharges as they pass through the powder. This would imply that the hexagonal SiC particles at the centre of the cell experience a higher maximum temperature than those located at the edges of the cell. On the other hand, under AC mode the discharge is less localized and covers much wider area, thus the particles at the centre and at the edges are more equally heated to a maximum temperature where reaction is most rapid. The mechanical milling action of the stainless steel rod facilitates mixing during EDAMM and combined with the more even temperature distribution associated with milling for 5 minutes in AC mode results in an overall effect, where more particles experience the maximum temperature under AC mode consistent with the observed increase of the transformation rate compared to DC mode.

As seen in the experimental work above, the reverse transformation occurs both in the AC and DC plasma in Nitrogen atmosphere. It should be noted that N_2 plays an important role as an energy carrier which in comparison to Argon is a diatomic gas subjected to first dissociation and ionization. Because of that reason, N_2 is able to supply much higher energy content in a

lower temperature than monoatomic gases and force the thermodynamically unfavorable transformation.

The speed of any phase formation is related to the type of the transformation process like diffusional or interface. In processes like grain growth that do not involve a composition change but only interface motion, the boundary migration kinetics involve local atomic rearrangements as atoms jump from one grain to their neighbour. Such process is generally considered as interface controlled. Often, interface-controlled motion occurs at constant velocity and it is found to be linear in time.

3.2 Size and morphology trends with processing and Hardness Measurements

Fig. 6 compares SEM images obtained from the hexagonal SiC starting powder; (a) with products formed after discharge milling in nitrogen under AC mode (Fig 6 (b) and (c)) and DC mode (Fig. 6(d-f)). The SiC starting powder (Fig. 6(a)) comprised large irregular particles with diameters ranging in between 20-40 μm and a fraction of smaller particles below 20 μm . After 5 minutes of discharge milling under AC mode (Fig. 6(b)) the average particle size is reduced and agglomerations of small particles are present. During the first 5 minutes of milling the relatively large powder particles undergo fragmentation, presumably caused by ion surface bombardment and mechanical action of the plunger, while very small powder particles produced are believed to agglomerate under the influence of strong electrostatic forces. Fig. 6(c) shows the powder morphology after 10 minutes of milling, which comprises predominately clumps of $\sim 1\text{-}5\text{ }\mu\text{m}$ in size, of very small particles which have agglomerated. Similar trends in particle size reduction and agglomeration were observed in the sample milled under DC mode for 5 (Fig. 6(d)) and 10 min (Fig. 6(e)), with indication of a less uniform particle size distribution in the samples milled for 10 min.

As mentioned in at the start of this Section, the usage of discharge power up to 3 kW causes excessive powder particles agglomeration. This phenomenon can be applied to form fully sintered, high density particles of sufficient size to perform nanohardness test on, for example, the particle shown in Fig. 6(f). To achieve such morphology the EDAMM process is performed in two stages where; (i) low power EDAMM, up to 0.54 kW, is used for up to 10 min to allow transformation from hexagonal to cubic SiC and then (ii) additional EDAMM is performed for about 2 min, with 3 kW power to form large particles. Nanoindentation test was performed yielding the value of 24.4 GPa with the standard deviation of 4 GPa which, according to the literature [16], should give a value higher than the standard Vickers test by 10-30%. Additionally, the measurement enabled a Young Modulus estimate. A wide range of SiC Young's moduli are reported in the literature. The highest value was reported in Gmelin's Handbook, 8th edition (1959), which listed 748 GPa for cubic-SiC in the [100] set of directions. While directionality of polytype is not expected to affect the number greatly, defects are, and annealing and other treatments can produce widely different results for the same specimen. Later versions of Gmelin's (1984) [18] report values of Young's modulus in the range of 400–500 GPa. On the other hand, [19] reported a value of 302.8 GPa while in [19] the reported value is 240 GPa. In our samples the Young's modulus value was found to be 209.6 GPa which is a typical one for the recrystallized state of commercially produced SiC [21]. During extended EDAMM processing powders are subjected to localized intensively heated areas by the formation of the electric discharge. This condition is believed to be favorable for formation of microstructures similar to those associated with recrystallized states.

4. Conclusions

Hexagonal Silicon Carbide was transformed into to cubic form by application of the Electric Discharge Assisted Mechanical Milling (EDAMM) in a nitrogen atmosphere. It was found that the transformation takes place in as little as 5 min of milling under the AC mode and 10 min using the DC discharges what is a result of the different heat distribution during the process. Prolonged milling times of 10 min in AC mode and above result in significant increase in contamination from the milling media, and formation of Iron Silicon phase.

It was proven, in comparison to the previous research, that it indeed is possible to transform the Hexagonal SiC into its Cubic polytype without the additives such as Al_2O_3 , AlN or Si_3N_4 to facilitate the reaction and stabilize the cubic structure. Thus, not only is the method one-step, quick and effective but it also gives a new insight on the way the transformation takes place. Above results suggest that in the case of EDAMM, the transformation is related to the heat distribution through the particles being possibly facilitated by the Nitrogen atmosphere.

Acknowledgements

This work was supported by funding from the Australian Research Council Discovery Grant no DP130101390. Electron microscopy equipment used was funded by Australian Research Council grants LE 0882813 and LE 0237478 and located at the UOW Electron Microscopy Centre.

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Table 1 Standard Ball Milling Device specifications comparison with the EDAMM device.

Specification	Retsch and Fritsch planetary mill [16]	EDAMM
Discharge current	-	3.12A
Averaged voltage	-	100 V
Max voltage in peak	-	600V
Impact force	33.3 g (G force on ball)	0.04 N
Velocity before impact	4.427 m/s	0.313 m/s
Impact kinetic energy	0.3234 J	0.004 J

Figure 1 Schematic representation of the EDAMM method.

Figure 2 Oscilloscope images showing differences in high frequency AC mode (top) and lower frequency DC mode (bottom) pulsed electrical discharges, as detected during EDAMM processing.

Figure 3 XRD of a) starting powders and powders processed in Nitrogen by EDAMM for b) 5 and c) 10 min using DC mode.

Figure 4 XRD of a) starting powders and powders processed in Nitrogen by EDAMM for b) 5 and c) 10 min using AC mode.

Figure 5 TEM Observations: (a)-(c) Sample EDAMM processed for 10 mins under DC mode. Bright field image (a) shows variation in crystallite size. Inset diffraction associated with region shown in (b) is indexed according to cubic SiC, (c) a higher magnification dark field image of (b), with aperture centered around (111) and (200) diffraction rings; structure. Image (d) is of the starting powder. HRTEM contrast from the top of this particle is consistent with a structure comprising faulted hexagonal SiC phases.

Figure 6 SEM results: Secondary electron images of (a) dispersed starting powder; product after 4 kW EDAMM under AC mode for (b) 5 min and (c) 10 min; product after EDAMM under DC mode for (d) 5 min and (e) 10 min. (f) Higher magnification backscattered image agglomerated product, polished and sectioned. The sample shown in (f) was prepared by EDAMM processing of sample (e) for an additional 2 mins at high power (3 kW).