Conversion of diamond polishing powder to high-density isotropic nano-crystalline graphite through spark plasma sintering

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Abstract

Conversion of diamond polishing powders into graphite nano-crystals and simultaneous densification to high-density graphite were achieved through spark plasma sintering at 2000 °C with 45 MPa pressure. The sintered graphite had a density of 1.84 g/cm³ and hardness of 12.1 ± 0.4 HV. The phase evolution was characterized by X-ray diffraction and Raman spectroscopy. Scanning electron microscopy and transmission electron microscopy revealed that the converted high-density graphite consisted of randomly oriented nano-crystalline grains. The formed graphite was also isotropic in nature.

Keywords Diamond · Graphite · Raman spectroscopy · Electron microscopy · Spark plasma sintering

1 Introduction

Graphite is a material with unique properties that enable it to be utilized in applications ranging from household to aerospace. Many critical applications, like nuclear, aerospace, and military, demand retention of strength at high temperatures, which high-density graphite (> 1.8 g/cm³) can provide [1, 2]. High-density graphite possesses enhanced mechanical properties like compressive, flexural and tensile strength in comparison with low-density graphite (< 1.7 g/cm³) [1]. Production of high density graphite is a time consuming process (several days) [2, 3]. The production of the commercial isotropic graphite involves multiple steps; initially, the carbon precursor is compacted by isostatic pressing followed by carbonization at a temperature near 1000 °C and graphitization at 2500 °C [4]. Generally, precursors like coke, pitch, phenolic resin, and mesocarbon are used in this process [4–6]. This process involves many days mainly due to the slow heating and cooling rates to minimize the thermal stress and to maximize the yield of the carbon during carbonization [4]. In this work, we have demonstrated a facile synthesis

route of high-density graphite from low cost diamond powders that are used in the polishing industry, through spark plasma sintering (SPS) in a single step.

2 Materials and methods

Diamond powders (average size 1 µm) from the polishing industry were filled in a graphite die, with the contact surface of the punch and die cavity covered with graphite foils. The entire die was wrapped with graphite felts to prevent radiation loss. The SPS was carried out at 2000 °C (heating rate of 200 °C/min with a holding period of 10 min) and at 45 MPa pressure in vacuum atmosphere using a SPS machine (HP D25 type, FCT Systeme GmbH, Germany). Sintered pellets of 20 mm diameter and 5 mm height were produced. The phase analysis was carried by WITec Alpha 300 micro-Raman spectrometer (WITec GmbH, Ulm, Germany) and X-ray diffractometer (PANalytical, Almelo, Netherland).

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The dimensions in out-of-plane stacking and lateral directions (L_c and L_a) of the graphite were determined using Eqs. (1, 2) [7].

$$L_c = \frac{0.9\lambda}{\beta_{002} \cos \theta_{002}} \quad (1)$$

$$L_a = \frac{1.84\lambda}{\beta_{100} \cos \theta_{100}} \quad (2)$$

where λ is the wavelength of X-ray (nm), θ is the diffraction angle (degrees), β is the FWHM of the peak of importance (002 or 100).

The degree of graphitization (g) of the sintered product was determined using Equ. (3, 4) [8].

$$g(\%) = \frac{0.3440 - d_{(002)}}{0.3440 - 0.3354} \times 100 \quad (3)$$

$$d_{002} = \frac{\lambda}{2 \sin \theta_{002}} \quad (4)$$

where d_{002} is the inter-planar distance in $\langle 002 \rangle$ stacking direction.

XRD can be utilized for determining isotropy by using Bacon anisotropy parameter given in Eq. (5) [9].

$$B = R^{-(0.406 \pm 0.006)} \quad (5)$$

where $R = I_{\max}/I_{\min}$ of (002) peak in three orthogonal directions.

The microstructures of the samples were observed using the scanning electron microscope (Carl Zeiss SIGMA, Germany) and transmission electron microscope (Libra 200 FE 200 kV, Carl Zeiss, Germany). The density was found on the basis of Archimedes' principle by water immersion technique. The hardness was determined by Vickers hardness tester using a load of 9.8 N. The thermal expansion characteristics of the graphite samples were analyzed in a horizontal dual push-rod dilatometer (TD 5000S, MAC Science, Japan) from 50 °C to 1000 °C.

3 Results and discussion

Figure 1a shows the XRD patterns of the starting diamond powder and the sintered sample, which indicate the total conversion of the diamond powder into graphite. The out-of-plane (L_c) and the lateral (L_a) dimensions of graphite are 10.8 nm and 59.2 nm, respectively as have been determined using Eqs. (1, 2). The degree of graphitization (g) is $81.40 \pm 4.95\%$ which is found by using Eqs. (3, 4).

Figure 1b shows the Raman spectra of the initial diamond powder and the sintered pellet. They indicate

Fig. 1 **a** X-ray diffraction patterns of the starting powder and the sintered sample. **b** Raman spectra of the initial powder and the sintered pellet

complete transformation of diamond powder into graphite. The initial powder shows a peak at 1334 cm^{-1} which is the characteristic peak (D) of diamond due to excitation of sp^3 hybridized bond [10]. The sintered pellets show G peak at 1584 cm^{-1} which is a characteristic peak of graphitic material caused due to excitation of sp^2 hybridized bond [11, 12]. The sintered pellet also has a D peak at 1354 cm^{-1} and 2D peak at 2706 cm^{-1} . D peak is the result of the disorder in graphitic structure and 2D is its overtone [11].

Figure 2a and b show the XRD patterns and the Raman spectra of three sintered samples indicating the consistency in transformation. The graphitization of the diamond powders takes place because diamond is a metastable phase whereas graphite is the equilibrium phase. The conversion of diamond to graphite takes place as it is

Fig. 2 **a** X-ray diffraction patterns. **b** Raman spectra of three pellets sintered at 2000 °C (heating rate of 200 °C/min with a holding period of 10 min) and 45 MPa pressure

thermodynamically feasible as shown by the free energy values (at 298 K) given below in Table 1 [13]:

The SPS temperature of 2000 °C provides the required energy of 732 kJ/mol to overcome the activation barrier of diamond along {110} plane to convert to graphite [14]. The graphitization rate follows the Arrhenius equation and the rates at various temperatures are shown in Fig. 3. The graphitization rate at the sintering temperature

Fig. 3 Arrhenius plot indicating the graphitization rate of diamond at various temperatures (re-plotted based on data from Davies et al. [14])

(2000 °C) is sufficient for the completion of graphitization at the utilized holding time (10 min).

The TEM micrographs (Fig. 4a) reveal the sheets of graphite with a layered structure in the nanocrystalline range. The graphene sheets of graphite are non-wrinkled and the high resolution image (Fig. 4a inset) shows an inter-planar spacing of ~0.33 nm. The orientation of the graphitic grains was determined using image analysis software Image J with Orientation J [15] plug-in from SEM images (Fig. 4b). The graphitic grains are nanocrystalline and randomly oriented. The polar plot (Fig. 4c) generated by orientation J shows the orientation distribution of the graphitic grains with respect to the horizontal orientation of the image which indicates no preferred orientation.

The formed graphite in the form of a sintered pellet has a density of 1.84 g/cm³ as measured using the Archimedes principle. The hardness of the sintered pellet is 12.1 ± 0.4 HV.

The usage of graphite in certain applications, like nuclear application requires isotropic nature [16]. Isotropy of 1.05 is required for sustaining fast neutron in reactors [16]. Bacon isotropy parameter of 1.02 was obtained which suggested good isotropic property. Values similar to this have been obtained for commercial nuclear grade isotropic graphite [17].

The values of thermal expansion of the graphite in the radial and the axial directions are given in Fig. 5. The ratio of coefficients of thermal expansion (CTE) in two perpendicular directions can be used as a criterion for quantifying the isotropy in graphite [18]. The ratio of CTE of 1.036 was obtained in these samples. Values between

Table 1 Thermodynamic properties of graphite and diamond at 298 K

	Standard enthalpy of formation (kJ/mol)	Standard molar entropy (J/mol/K)	Standard Gibbs energy of formation (kJ/mol)
Graphite	0	+5.740	0
Diamond	+1.895	+2.377	+2.900

Fig. 4 **a** TEM micrographs of a sintered pellet. **b** SEM of the sintered pellet with orientation mapping of grains and **c** Polar plot for distribution orientation of graphite grains

Fig. 5 Thermal expansion of the graphite sample in different directions

1 to 1.05 have been obtained for isotropic commercial nuclear grade graphites given in the literature [18].

The densification curve during SPS is shown in Fig. 6. The densification of the sample during SPS was observed through the ram movement of the SPS instrument. Initially, the sample underwent densification which was mainly due to the particle rearrangement on the application of the load. As the temperature was raised the density decreased. This could be attributed to the thermal expansion of the sample and die. At high temperatures around ~ 1600 °C slope change was observed in the densification curve which indicated the onset of the graphitization process. Density started increasing again in holding temperature which could mainly be due to the graphitization.

Fig. 6 Densification curve of the sample obtained through ram movement of SPS

Fig. 7 Power variation during the SPS process

Figure 7 shows the variation of power consumption during the SPS process. It can be observed that the power consumption dropped drastically at high temperatures (beyond 1600 °C) which could be due to the transformation of the insulating diamond to conducting dense graphite.

The graphitization temperature (2000 °C) of the current process as observed by the pyrometer is lower compared to the conventional manufacturing process (> 2500 °C). This may be due generation of very high localized temperature due to plasma formation between the powder particles [19] during SPS. Geuntak et al. [20] has also shown that the interior of SPS die is significantly hotter than the surface where temperature measurement is taken. In our case, the pyrometer readings were measured on the die surface which was 5 mm away from the surface of the sample. Hence even though the pyrometer showed the

temperature of 2000 °C, the actual temperature inside the sample could be significantly higher causing effective graphitization.

4 Conclusions

We could convert the low cost diamond polishing powders into high-density sintered graphite using SPS in a single step. The temperature (2000 °C) and time (30 min) utilized in SPS were significantly lower than that of the commercial production of highly dense graphite that requires temperature above 2500 °C and several days for completion. XRD patterns and Raman spectra confirmed 100% conversion of diamond into graphite. The grains were nano-crystalline in nature with random orientation. A density of 1.84 g/cm³ with a hardness of around 12.1 ± 0.4 HV could be achieved. XRD and dilatometer data depicted isotropy in the samples. The process may be useful for producing small-sized high-density graphite pellets for different applications.

Compliance with ethical standards

Conflict of interest The authors claim that there is no conflict of interest.

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