Diamond & Related Materials 50 (2014) 97–102

Contents lists available at ScienceDirect

Diamond & Related Materials

journal homepage: www.elsevier.com/locate/diamond

Diamond-like carbon sintered compacts formed by spark plasma sintering

Naomichi Sakamoto [a,*], Shigenari Shida [b]

[a] Department of Science and Technology, Iwaki Meisei University, 5-5-1 Chuodai-Iino, Iwaki 970-8551, Japan
[b] Cooperative Research Center, Iwaki Meisei University, 5-5-1 Chuodai-Iino, Iwaki 970-8551, Japan

ARTICLE INFO

Article history:
Received 1 April 2014
Received in revised form 4 August 2014
Accepted 16 September 2014
Available online 28 September 2014

Keywords:
Diamond-like carbon
Spark plasma sintering
X-ray diffraction
High-resolution transmission electron microscopy

ABSTRACT

A spark plasma sintering (SPS) method was utilized for the novel production of diamond-like carbon (DLC) compacts. Two amorphous carbon powders with different particle sizes (45 μm and 24 nm diameter) were employed as starting materials for the sintering experiments. The carbon powders were sintered using a SPS system at various sintering temperatures and holding times. The structural properties of the sintered compacts were evaluated using X-ray diffraction (XRD) analysis and high-resolution transmission electron microscopy (HRTEM). Disk-shaped compacts were obtained by sintering the powder with a particle diameter of 45 μm, although the compacts were very brittle and easily broken. However, sintering of the 24 nm diameter powder particles at temperatures of 1473 to 1573 K with a holding time of 300 s led to the successful production of sintered compacts without breakage. Reflection peaks related to graphite structure were observed in XRD patterns of the compacts sintered from the 24 nm diameter particles. HRTEM analysis revealed that the compacts sintered at 1473 K with a holding time of 300 s had an amorphous structure and consisted of 34% sp^3 carbon bonding. Evaluation of the structural properties indicated that sintered compacts with DLC structure could be created by the SPS method with 24 nm diameter amorphous carbon particles.

1. Introduction

Diamond-like carbon (DLC) is an amorphous material with excellent tribological properties. The global market for diamond and DLC coatings has been estimated to grow from $782 million in 2009 to $1.7 billion in 2015 [1], which indicates a rapid expected expansion of DLC applications. This immediate development of DLC applications is due to its superior properties such as high hardness, low friction coefficient, high wear resistance and high chemical stability [2,3]. DLC coatings are used in the auto industry for slide members such as pistons and cams, which provide improvement of fuel efficiency [4,5]. Therefore, an increase in the popularity of DLC coatings is expected in the auto industry.

For applications of DLC on slide members, DLC coating films thicker than 10 μm are desirable [6,7]. However, the deposition rate achieved with physical vapor deposition and chemical vapor deposition (PVD/CVD), which are commonly used for DLC coatings, is less than sufficient to deposit thick coatings. PVD systems that employ a pulsed laser can achieve deposition rates in the range from 0.0001 to 0.25 nm/s [8–13]. Different PVD methods such as magnetron sputtering and arc ion plating achieve deposition rates that are less than 0.6 nm/s [14–20]. Many conventional rf/dc plasma enhanced CVD (PECVD) methods provide deposition rates that are less than 1 nm/s [21–29]. Thus, various plasma assisted PECVD systems can result in increased deposition rates. In contrast, dense plasma achieved through the utilization of supermagnetron and high frequency can provide deposition rates of 2.3–2.7 nm/s [29,30]. However, it takes ~10^3 s to deposit DLC films that are more than 10 μm thick, even with the use of these dense plasma systems. Therefore, a novel deposition method with higher deposition rates is required. In addition, the limit of DLC film thickness with conventional vapor deposition methods has been reported to be approximately 1 μm due to internal stress [7,31].

We have focused our attention on a spark plasma sintering (SPS) method to solve such problems such as the low deposition rate and thickness limitation with conventional deposition methods. The SPS method is able to produce sintered compacts by application of a high current to a raw material powder pressed under uniaxial pressure [32]. This method has been expected to be useful not only for the formation of novel materials and treatment processes [33,34], but also for coating processes [35,36]. In addition, the SPS method can produce an amorphous sintered compact from amorphous powders, unlike conventional sintering methods such as hot pressing [37–39]. It is therefore expected that carbon compacts with an amorphous structure could be produced from amorphous carbon powder by the SPS method. The SPS method also has an advantage in the joining of dissimilar materials [40–42]; therefore, it is also anticipated that DLC compacts could be simultaneously joined to an ultrahard base material such as Co–WC alloy

* Corresponding author.
E-mail address: sakamoto@iwakimu.ac.jp (N. Sakamoto).

http://dx.doi.org/10.1016/j.diamond.2014.09.008
0925-9635/

during sintering by the SPS method. However, the production of DLC compacts by the SPS method has not been reported to date. Therefore, an attempt was made in this study to produce DLC compacts by the SPS method with amorphous carbon powder as raw material. In addition, to confirm that the obtained compacts had DLC structure, the structural properties of the compacts were evaluated using X-ray diffraction (XRD) analysis and high-resolution transmission electron microscopy (HRTEM).

2. Experimental procedure

Two amorphous carbon powders with significantly different particle sizes were employed as raw powders for the sintering experiment. The particle diameters of the powders were 45 μm and 24 nm. 3 g of raw powder was placed into a graphitic die/punch assembly; the internal diameter of the cylindrical die and the external diameter of the cylindrical punch were 20 mm. A carbon sheet was inserted between the powder and the die/punch assembly to prevent adhesion. The raw powders in the die/punch assembly were sintered using a SPS system (SPS Syntecs SPS-520). The chamber of the SPS system was evacuated to less than 6 Pa before the sintering process. The raw powder was heated from room temperature up to a preset sintering temperature within 1200 s, where the preset sintering temperatures employed were 1373, 1473 and 1573 K. The holding times at the sintering temperature were 0 and 300 s. The sintering temperature was measured with an emission pyrometer. A uniaxial pressure of 35 MPa was applied to the powder during the sintering process.

DLC is defined as an amorphous material; therefore, the crystallinity of the obtained compacts was investigated using XRD (Shimadzu XRD-6100) in θ–2θ mode with a Cu Kα source and a scan range from 10 to 80°. The X-ray tube voltage and current were 40 kV and 20 mA, respectively.

The microstructures of the sintered compacts were analyzed using HRTEM (FEI Tecnai 30S-Twin). The crystallinity of the compacts was also examined by measuring selected area diffraction (SAD) patterns. In addition, the carbon bonding states were evaluated using electron energy loss spectroscopy (EELS) with a transmission electron microscope. Two characteristic peaks are observed at the carbon K-edge region in the EELS spectra of the DLC; one peak located at ca. 285 eV corresponds to transmission from the 1s to π^* antibonding states and another located at ca. 296 eV is attributed to transmission from the 1s to σ^* antibonding states. The fraction of sp^3 carbon bonds can be estimated from the integrated intensities of the π^* and σ^* peaks, denoted as $I_{u\pi^*}$ and $I_u(dE)$, respectively [43–46]:

$$sp^3 \text{ fraction} = 1 - \frac{I_{u\pi^*}}{I_{g\pi^*}} \frac{I_g(dE)}{I_u(dE)} \quad (1)$$

where $I_{g\pi^*}$ and $I_g(dE)$ are appropriate integrals for reference graphite (sp^3 fraction = 0%). The EELS spectrum of graphite was obtained from graphite powder (Nippon graphite CPB-S) with 99.99% purity.

Martens hardness of the obtained compacts was evaluated by a dynamic ultra micro-hardness tester (Shimadzu DUH-211). A Berkovich diamond pyramid was used as the indenter. Measurements were made by increasing the loading force with a load rate of 4.4413 mN/s, to a maximum force of 20 mN, followed by decreasing the loading force with the same rate.

3. Results and discussion

3.1. Dependence of sintering on the particle size of raw powders

Fig. 1 shows photographs of the compacts obtained from the raw powder with a particle diameter of 45 μm that were sintered at 1373 to 1573 K for holding times of 0 and 300 s. The photographs show that disk-shaped compacts with various sizes were obtained. However, all of the compacts were particularly brittle and were easily broken into powdered fragments. Therefore, the raw powder with a particle diameter of 45 μm was not suitable for the formation of compacts without breakage under the SPS conditions used.

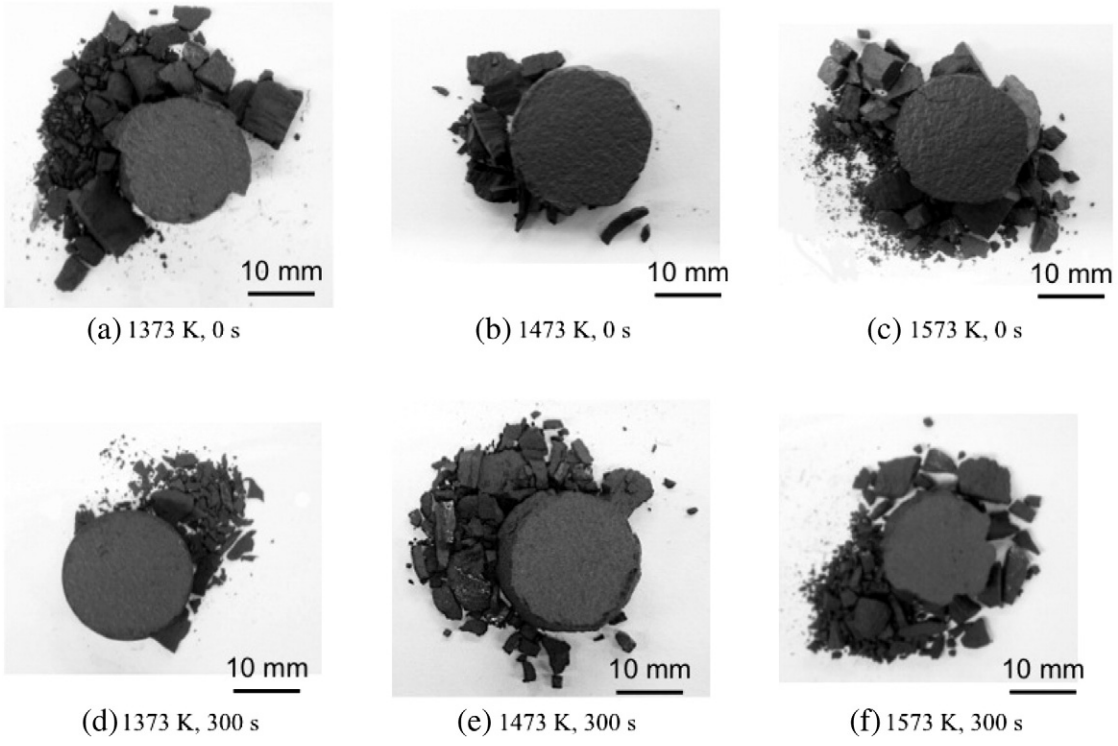

Fig. 1. Photographs of compacts sintered from raw powders with a particle diameter of 45 μm at 1373, 1473 and 1573 K for holding times of 0 and 300 s.