

Synthesis of Sub-micron/Nano Diamond Powder by Hot Pressing/ Spark Plasma Sintering of Supersaturated Solid Solution of Ni- C_{gr}

Nitika Kundan¹, Biswajit Parida², Anup Kumar Keshri³ and P. R. Soni^{*4}

^{1,2}Department of Metallurgical and Materials Engineering, Malaviya National Institute of Technology, Jaipur, India

³Department of Materials Science and Engineering, Indian Institute of Technology Patna, India

⁴Department of Metallurgical and Materials Engineering, Malaviya National Institute of Technology, Jaipur, India

E-mail: ¹tabbukundan@gmail.com, ²biswajit.parida92@gmail.com,

³anup.kumar.keshri@gmail.com, ⁴prsoni.meta@gmail.com

Abstract—Supersaturated solid solutions (SSSSs) having composition Ni-15wt.%C_{gr}(46.4 at.%), with and without seed nano crystals, were prepared by high energy ball milling of the elemental powders. The SSSSs prepared were degassed for 2 h in vacuum of 10⁻² torr at 200 °C and characterized by SEM and XRD techniques. To estimate the consolidation temperature DSC was performed and accordingly the SSSSs were consolidated under a pressure of 10 MPa at 1000 °C by hot pressing as well as by spark plasma sintering. Raman spectroscopy revealed the formation of diamonds in the hot pressed as well as in SPSed samples. Interestingly in the SPSed samples, formation of SWCNTs also took place. Ratio of I_D/I_G was used to assess the yield of the diamond phase. Synthesized diamond powder was extracted by dissolving the matrix in the boiling acidic solution. TEM micrographs have shown sub-micron and nano size crystallites in the diamond particles synthesized via hot pressing and SPS, respectively.

Keywords: High energy milling; Supersaturated solid solution; Hot pressing; Spark plasma sintering; Raman spectroscopy; Diamond powder.

1. INTRODUCTION

Diamonds are basically categorized into two groups: i) natural, ii) synthetic. Natural diamond is formed due to huge amount of hydrostatic pressure acting upon carbonaceous material within earth mantle whereas synthetic diamond is prepared by three methods; The different processes used for the synthesis are high pressure high temperature (HPHT) [1], chemical vapor deposition (CVD) [2], and detonation synthesis [3].

In HPHT method, conditions similar to those of growth of diamond in earth mantle are created. In this method, the liquid metal having dissolved carbon atoms, along with the tiny diamond seeds, is equi-axially pressurized in the growth cell. The metals used in this technique are from the group of transition elements, e.g. Ni, Fe, Co and their alloys, which act as catalyst. Role of the catalyst here is to minimize the transformation energy needed to convert graphite into

diamond. The combination of high pressure (5-10GPa) and high temperature (1300-2200) causes carbon atoms to deposit on the surface of seeds as diamond [4, 5]. In CVD method, diamond growth takes place due to decomposition of hydrocarbon gas mixture at low temperature (800-1000 °C) and pressure typically under 27 kPa [6] whereas during detonation synthesis process, nano-diamonds are formed by detonation of carbon-based explosives in metal chamber. This explosion provide sufficient temperature and pressure for carbon of explosive to get converted to diamond [7]. Phase transformation diagram (Fig. 1) shows the temperature & pressure requirements for the transformation of graphite (C_{gr}) into diamond [8], in the different processes.

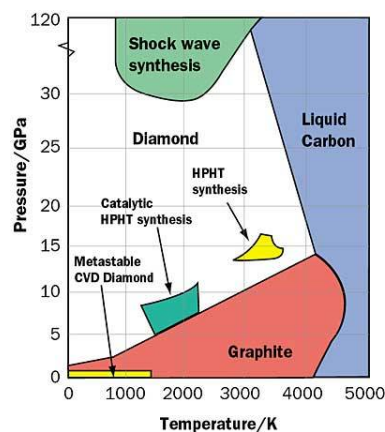


Figure 1. Phase transformation diagram of graphite into diamond

In the recent decades, greater quest has been created in the minds of researchers and scientists towards the diamond synthesis because of its exceptional wear and corrosion resistance [9-12] as well as greater hardness and high refractive index [13, 14] which makes it an ideal material for

making various cutting and polishing applications and other industrial purposes. Recently diamond is entering into numerous novel applications like LED, SAW filters, solar cells, IR detectors, front panel displays [5, 15].

Mechanical alloying (MA) technique has been quite often used for preparation of supersaturated solid solutions (SSSSs) [16, 17]. In the present studies SSSS of graphite in nickel has been prepared using MA technique and the same was consolidated by hot pressing / spark plasma sintering (SPS) for the transformation of graphite into diamond. Aim of the present investigations was to develop a process for transformation of graphite into diamond at lower pressure and temperature, as compared to HPHT process, taking advantage of mechanical activation created by MA processing in the both; solvent (Ni) as well as the solute (C_{gr}).

2. EXPERIMENTAL

In these studies nickel powder (99.8% pure, 14 μ m) and graphite (C_{gr}) powder (99.2% pure, 10 μ m) were used as raw materials. Nano-diamond powder (>97% pure, 4nm, Plasma chem GmbH) were used as seeds. The solid solution, with extended solubility, of C_{gr} (upto 15 wt.%; 46.4 at.%) was prepared using high energy ball milling. Milling was performed in the laboratory attrition mill in nitrogen atmosphere keeping ball-to-powder ratio at 10:1. The milling was continued up to 15 h. For preparing the MA powder sample containing diamond seed crystals, nano-diamond powder (100 ppm level) was added to the elemental powder mixture before the milling.

To identify phase transformation temperature in the milled powder, differential scanning calorimetry (DSC) was performed using a NETZSCH, DSC 404 F1 Pegasus. The heating rate was maintained at 10°C/min for 10mg powder sample.

Both the MA powder samples, with and without seed crystals, were then degassed for 2 h in a vacuum of 10^{-2} torr at 200°C and consolidated by (i) hot pressing and (ii) spark plasma sintering using Dr. Sinter Unit (SPS-625, SPS Syntex Inc., Japan) under a pressure of 10 MPa at 1000 °C for 15 min. Samples of 20mm dia. having 5mm height were prepared.

Surface morphology of as received powder as well as MA powder was investigated using Nova Nano FE-SEM 450 (FEI). The MA powders was characterized for phase analysis using PAN analytical X'pert- Pro diffractometer (45kV, 40mA). Raman Spectroscopy of the consolidated samples was carried out using ALRIX- STR 500 Raman spectroscope.

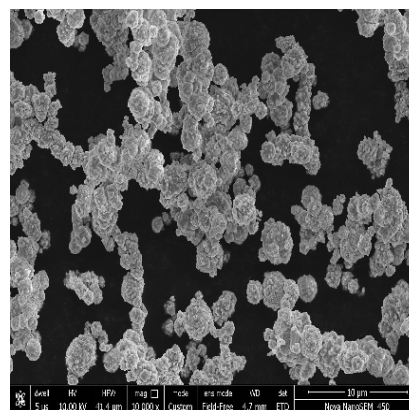
The hot pressed/ SPSed sample were dissolved in the boiling mixture of sulphuric acid and nitric acid (3:1 ratio). The filtrate mixture obtained was washed with distilled water and dried. To remove the carbonaceous material from the diamond surfaces, the powder was heated in oxidative atmosphere. TEM micrographs of the extracted diamond particles were

taken using Tecnai G² 20(FEI) S-Twin transmission electron microscope.

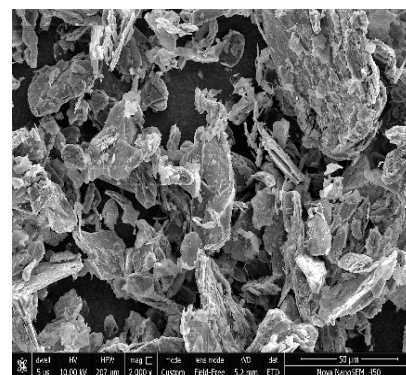
3. RESULTS & DISCUSSION

3.1 Formation of SSSS

SEM of as-received and 15 h milled powder samples are shown in Fig. 2 and Fig. 3, respectively. XRD patterns of the samples, having progressively dissolved C_{gr} in nickel lattice during the high energy milling, are shown in Fig. 4. The absence of the C_{gr} peak (002) in the XRD pattern of the 15 h milled powder indicates complete dissolution of C_{gr} in the nickel lattice. The nickel grain size in 15 h milled powder, as calculated by Scherrer's equation is found to be 43 nm. Detailed discussion on synthesis and characterization of SSSS of Ni-15wt.% C_{gr} can be referred in our other publication [18].



(i) Nickel



(ii) Graphite

Figure 2: SEM micrographs of as- received powders

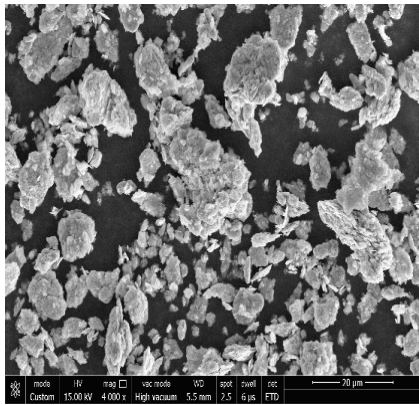


Figure 3: SEM micrographs of MA powders milled for 15 h

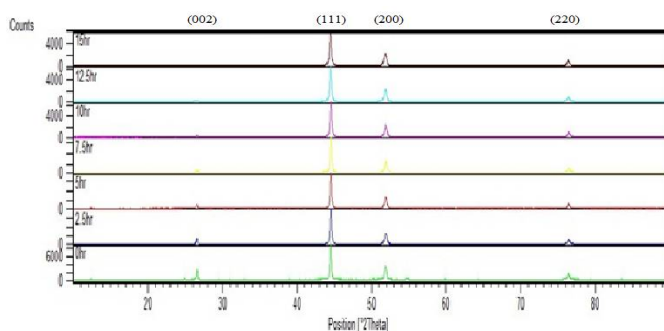


Figure 4: XRD patterns of Ni-15wt% C_{gr} milled for different milling duration

3.2 Differential Scanning Calorimetry

The DSC curve of the supersaturated solid solution is shown in Fig. 5. It indicates that milled powder has undergone an endothermic reaction at 1080 °C. During the DSC analysis, the nickel lattice got annealed by absorbing the heat energy and precipitation of excessive graphite dissolved started at this temperature. This could be a good guideline for the selection of hot pressing/ SPSed temperature, as the basic purpose of carrying out the consolidation in these studies is to precipitate the graphite in the nickel lattice under low pressure and low temperature. Transformation of graphite into diamond basically takes place during this precipitation, along the dislocation surface rupture plane (111) [19].

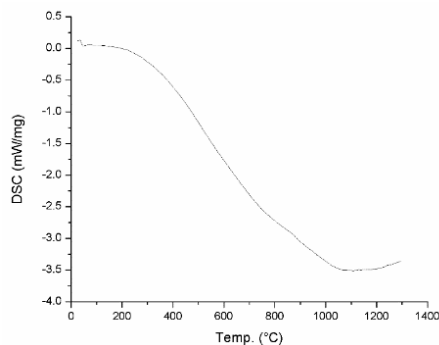
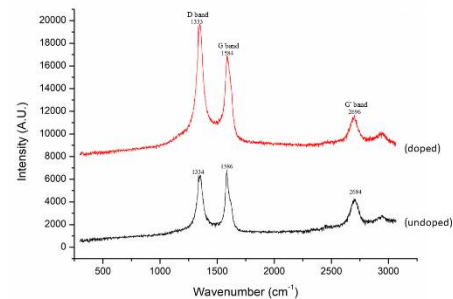


Figure 5: DSC curve of 15 h milled powder

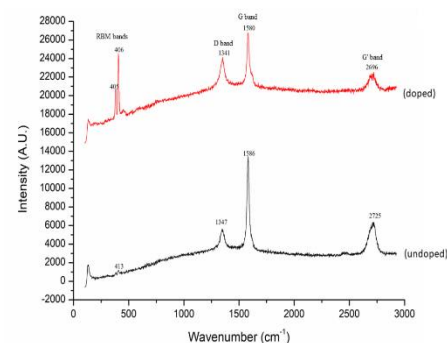
3.3 Raman Spectroscopy

Raman Spectroscopy is well suited to molecular morphology characterization of carbon materials. Every band in the Raman spectrum is very specific to the vibrational frequency orientation, and the weight of the atoms at the ends of the bonds. As per the ample literature available in this regard [20-24], the Raman spectra obtained for all the samples have been labelled and shown in Fig. 6. The ratios of I_D/I_G peaks are shown in Table 1.

As per the Fig. 6, formation of diamond has taken place in hot pressed/SPSed samples, but the D-peak is more prominent in the doped samples due to readily available seed nuclei which facilitated the diamond growth. This is also reflected by the increase in ratio of (I_D/I_G) (Table 1). Also, presence of radial breathing mode (RBM) bands in the spectra of SPSed samples indicate the formation of single walled carbon nanotubes (SWCNTs), which have quite likely formed due to the successful efforts of the graphene sheets to achieve the stable state by lowering the activation energy by joining the edges. The direct heating i.e. joule heating must have been a helping factor in this process. The diameter of these SWCNTs appear to be smaller than 1nm as indicated by the shift of RBM bands towards the higher wavenumber (cm⁻¹) [24].



(i) Hot pressed



(ii) SPSed

Figure 6: Raman spectra of Ni-C_{gr} consolidated samples

Table 1: Comparison of I_D/I_G peak ratio

S. No	Sample	ID/IG	
		Hot pressed	Spark plasma sintered
1	Ni-15wt% Cgr	0.68	0.41
2	Ni-15wt% Cgr (doped)	0.76	0.78

3.4 Transformation Mechanism

High energy milling of Ni-15wt.%C_{gr} resulted in dissolution of graphite as interstitial, along the dislocation lines in the form of chains, and at nano-grain boundaries [18]. During high energy milling high dislocation density and strains were created in the nickel lattice, and also activation of the graphite took place. All these factors resulted in increase in catalytic activity of the system many fold. During hot pressing/ SPSed of the SSSS, the applied pressure and the temperature forced the dissolved graphite atoms to squeeze out. During this squeezing, the graphite and the nickel came in intimate contact to the atomic proximity and transformation of hexagonal graphite (sp^2) to cubic diamond (sp^3) happened. The mechanical activation of nickel lattice as well as of graphite made the transformation possible at lower pressure of 10 MPa and the temperature 1000° C. The schematic of the graphite transforming into various carbon allotropes is shown in Fig. 7.

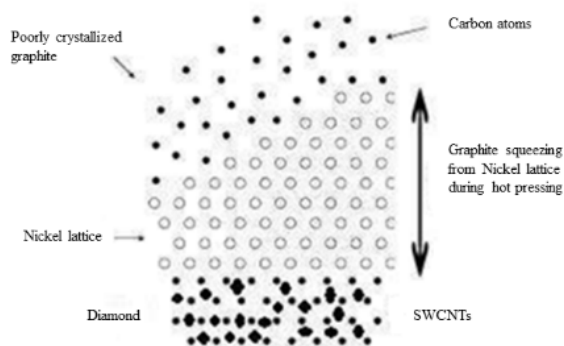
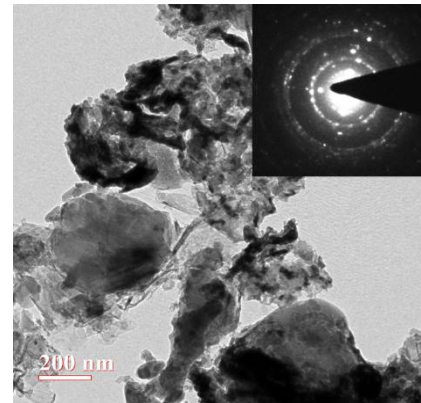


Figure 7: Schematic of graphite squeezing from nickel lattice during hot pressing/ SPS

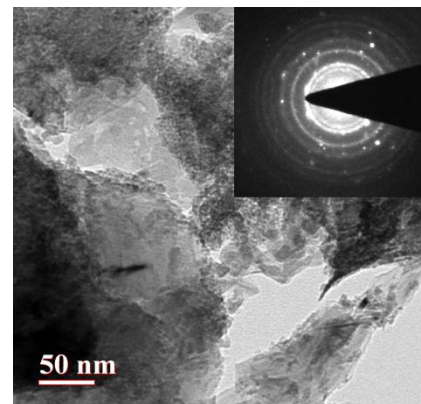
3.5 Synthesized diamond powder

TEM micrographs of synthesized diamond particles by hot pressing/ SPSed are shown in Fig. 8. The insets are the SAED patterns. It can easily be interpreted that the diamond particles synthesized via hot pressing have sub-micron size crystallites. While the others obtained by SPS have nano and ultra-nano size crystallites. It can be an attribute of high local temperature present in the sparks, during the initial sintering period, which must have created large number of diamond nuclei to grow (The SPS is based on three main stages: plasma heating, joule heating and plastic deformation. In the initial stage powder particles are locally and momentarily heated up to high

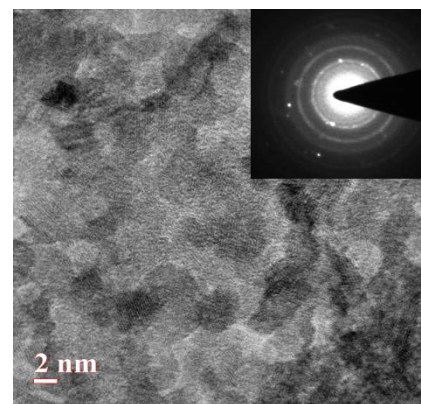
temperatures due to electrical discharges, and thereafter the joule heating starts.). However, to know morphology, size and size distributions, inclusions, etc. in the synthesized diamond particles needs further research.



(i) Hot pressed



(a) Nanocrystalline diamonds



(b) Ultra Nanocrystalline diamonds

(ii) SPSed

Figure 9: TEM micrographs of diamonds synthesized via (i) hot pressing (ii) SPS

4. CONCLUSIONS

SSSSs having the composition Ni-15 wt.% C_{gr}, prepared using MA technique, and their subsequent compaction, under a pressure of 10MPa and temperature of 1000 °C, resulted in formation of diamond powder as detailed below;

- i. Diamond particles having micron size crystallites formed when consolidation was done by hot pressing.
- ii. Diamond particles having nano/ultra nano size crystallites, and SWCNTs were obtained when consolidated by SPS.

Thus, sub-micron and nano /ultra nano size crystallized diamond particles have been prepared firstly through powder metallurgy route, and at much lower pressure and lower temperature as required in HPHT technique.

REFERENCES

- [1] J. P. Boudou, P. A. Curmi, F. Jelezko, J. Wrachtrup, P. Aubert, M. Sennour, G. Balasubramanian, R. Reuter, A. Thorel, E. Gaffet, "High yield fabrication of fluorescent nanodiamonds", *Nanotechnology*. 20 (2009) 235602-13.
- [2] M. Frenklach, W. Howard, D. Huang, J. Yuan, K. E. Spear, and R. Koba, "Induced nucleation of diamond powder", *Appl. Phys. Lett.* 59 (1991) 546-548.
- [3] V. Yu. Dolmatov, A. Vehanen, V. Myllymäki, K. A. Rudometkin, A. N. Panova, K. M. Korolev, T. A. Shpadkovskaya, "Deep purification of detonation nanodiamond material", *Journal of Superhard Materials* 35 (2013) 408–414.
- [4] A.S. Osipov, S. Nauyoks, T.W. Zerda, O.I. Zaporozhets, "Rapid sintering of nano-diamond compacts", *Diamond & Related Materials* 18 (2009) 1061–1064.
- [5] J. C. Yung, J. Ji. "Diamond Nanotechnology: Syntheses and Applications", Pan Stanford Publishing Pte. Ltd., 2010.
- [6] S. Koizumi, C. E. Nebel, M. Nesladek, "Physics and Applications of CVD Diamond", Wiley-VCH Verlag GmbH & Co. KGaA, 2008.
- [7] P. Decarli, J. Jamieson, "Formation of diamond by explosive shock". *Science*. 133 (1961) 1821–1822.
- [8] F. P. Bundy, "The P, T phase and reaction diagram for elemental carbon" *Journal of Geophysical Research: Solid Earth* 85 (1980) 6930–6936.
- [9] Q. Wei, Z. M. Yu, M. N.R. Ashfold, L. Ma, Z. Chen, "Fretting wear and electrochemical corrosion of well-adhered CVD diamond films deposited on steel substrates with a WC–Co interlayer", *Diamond & Related Materials* 19 (2010) 1144–1152.
- [10] A. Erdemir, C. Donnet, "Tribology of diamond-like carbon films: recent progress and future prospects", *J. Phys. D: Appl. Phys.* 39 (2006) 311–327.
- [11] M. D. Fries, Y. K. Vohra, "Properties of nanocrystalline diamond thin films grown by MPCVD for biomedical implant purposes", *Diamond and Related Materials* 13 (2004) 1740 – 1743.
- [12] Q. Wei, Z.M. Yu, M. N.R. Ashfold, Z. Chen, L. Wang, L. Ma, "Effects of thickness and cycle parameters on fretting wear behavior of CVD diamond coatings on steel substrates", *Surface & Coatings Technology* 205 (2010) 158–167.
- [13] P. Koidl, C. P. Klages, "Optical applications of polycrystalline diamond", *Diamond and Related Materials*. 1 (1992) 1065-1074.
- [14] C.R. Lin, D.H. Wei, C.K. Chang, W.H. Liao, "Optical properties of diamond-like carbon films for antireflection coating by RF magnetron sputtering method", *Physics Procedia* 18 (2011) 46–50.
- [15] D. M. Gruen, "High efficiency diamond solar cells", US Patent, 7368658 B1, 2008.
- [16] C. Suryanarayana, "Mechanical alloying and milling", *Prog Mater Sci*, 46 (2001) 1-184.
- [17] P.R. Soni, "Mechanical alloying- fundamentals & applications", Cambridge Int. Science Publishing, 2001.
- [18] N. Kundan, B. Parida, A. K. Keshri, P.R. Soni, "Preparation of the supersaturated solid solution in nickel-carbon system by mechanical alloying", *Int. Journal of Minerals, Metallurgy and Materials*, 2018 (under review).
- [19] R. Sinclair, T. Itoh, R. Chin, "In situ TEM studies of metal-carbon reactions", *Microsc. Microanal.* 8 (2002) 288–304.
- [20] R. F. Davis, "Diamond films and coatings: development, properties, and applications", William Andrew Publishing, 1994.
- [21] S. Costa, E. Borowiak-Palen, M. Kruszynska, A. Bachmatiuk, R. J. Kalenczuk, "Characterization of carbon nanotubes by Raman spectroscopy", *Materials Science-Poland*. 26 (2008) 433–41.
- [22] D. S. Knight, W. B. William, "Characterization of diamond films by Raman spectroscopy" *Journal of Materials Research*. 42 (1989) 385-393.
- [23] M. S. Dresselhaus, A. Jorio, R. Saito, "Characterizing graphene, graphite, and carbon nanotubes by Raman spectroscopy." *Annu. Rev. Condens. Matter Phys.* 1 (2010) 89-108.
- [24] J. Hodkiewicz, "Characterizing carbon materials with Raman spectroscopy", Thermo Fisher Scientific, 2010.