

# Determination of various impurities in synthetic diamond powder

NAHAR SINGH, RASHMI, A. K. SARKAR

*Materials Characterization Division, National Physical Laboratory, Dr. K. S. Krishnan Road, New Delhi-110012, India*

*E-mail: naharsingh@mail.nplindia.ernet.in*

Impurities in industrial synthetic diamond powder samples were analyzed by X-ray diffraction (XRD) and Flame Atomic Absorption Spectrometry (FAAS). Specimen for FAAS is required in solution form. Diamonds are chemically inert to most acids and alkalis. Carbon was removed as CO<sub>2</sub> on heating and estimated gravimetrically. The remaining residue was fused with di-lithium tetraborate and dissolved in nitric acid. Impurities such as Si, Al, Fe, Ca, Mg, W, Na, Co and Ni were then determined by FAAS. Crystalline phases of major impurities were identified by XRD. © 2004 Kluwer Academic Publishers

## 1. Introduction

Synthetic diamond is manufactured from graphite and solvent-catalyst metal at high temperature and pressure. Synthetic diamond may contain impurities, the degree of contamination and crystal morphology depends upon the temperature [1]. In diamonds grown from Fe and Mn solution, contamination is directly related to the degree of structural compatibility of phases present during crystallization. Ni and Co containing limited amount of carbon, both possess structure, which almost perfectly match to that of diamond. The presence of Si and Al influence the solubility of carbon in the matrix. The color of the diamond depends on the impurities e.g., Al, Ni, Fe and Co give colorless, yellowish green, green and colorless respectively. Diamond is the hardest, stiffest, best thermal conductor and chemically inert to most acids and alkalis. Strength of synthetic diamond grits is reduced by presence of metallic impurities, strength being less in more impure specimen. The expansion coefficient of metals being greater than that of diamond, thermal stress may develop at high temperature [2, 3]. Synthetic diamond is similar to type Ib [3] natural diamond. Iron-carbon and nickel-carbon system at high temperature and pressure forms Fe<sub>7</sub>C<sub>3</sub> and Ni<sub>3</sub>C, enriched in carbon and helps in the formation of diamond [4]. Diamonds grown using nickel or nickel alloy show optical absorption and contain luminescence center and absent in that diamond that do not contain nickel [5]. In synthetic diamond generally, two types of impurities are found. One in which, Fe, Mn and Cr form carbides, while in the other Ni and Co are not prone to form carbides. Iron carbide with highest carbon content observed prior to diamond formation, corresponds to a chemical formula FeC which shows a higher physical hardness and chemical stability than the common carbides of iron e.g., Fe<sub>3</sub>C. The carbides Ni<sub>3</sub>C, Co<sub>3</sub>C and Co<sub>2</sub>C are of poor crystallinity and reactivity and are classified as metastable [6]. The impurities in diamond are detected by a visual discoloration in shades of

yellow, green or brown and quantitative determination could be carried out either by determining degree of magnetism, analytical optical technique, X-ray diffraction [7] electron paramagnetic resonance [8] and neutron activation technique [9].

To study the nature of synthetic diamond, it is important to know its composition accurately for which good analytical method is needed to evaluate the impurities present in it. Fusion technique [10–13] is generally used for the decomposition of silicates and oxides, which are not directly soluble in acids mixture. Synthetic diamond may also contain silica, and some elements in oxide form as well as in carbide form.

In the present investigation, fusion technique has been applied for determination of impurities in synthetic diamond by Flame Atomic Absorption Spectrometry (FAAS). The diamond powder was heated to 850°C up to constant weight to determine total carbon as loss in weight, which is an empirical method for the determination of carbon and remaining residue was fused with di-lithium tetraborate followed by dissolution in nitric acid to obtain a clear solution and the elements such as Si, Na, Al, Fe, Ca, Mg, W, Co and Ni have been determined by FAAS. The validity of the method has been established by analyzing same samples by titrimetric method for Fe [14] and gravimetric method for silica [15]. Crystalline phases of major impurities are determined by X-ray diffraction (XRD).

## 2. Experimental

### 2.1. Samples

Nine samples of industrial synthetic diamond powder provided by D-Tech India, Delta Exports and Gem diamond products have been analyzed in this investigation. Some of the samples were of light color whereas others were of dark gray color. One of the samples was a mixed phase with major amounts of Alumina and Silica.

TABLE I Details of instrument and standard setting for FAAS measurements

Equipment		Varian spectr AA-10 atomic absorption spectrophotometer (flame) wavelength range 190–900 nm		
Element	Lamp make	Wavelength (nm)	Slit width (nm)	Flame conditions (liter min <sup>-1</sup> )
Iron	Varian	248.3	0.20	Air /Acetylene 5.0/0.8–1.0
Aluminum	Varian	309.3	0.50	Nitrous oxide/Acetylene, fuel rich 5.0/4.5–5.0
Silicon	Varian	364.3	0.50	Nitrous oxide. Acetylene, fuel rich 5.0/4.5–5.0
Calcium	Varian	422.7	0.50	Air/acetylene 5.0/0.9–1.1
Magnesium	Varian	285.2	0.50	Air/acetylene 5.0/0.9–1.1
Manganese	Varian	279.5	0.20	Air/Acetylene 5.0/0.8–1.0
Sodium	Varian	589.0	0.50	Air/Acetylene 5.0/0.8–1.1
Nickel	Varian	232.0	0.20	Air/Acetylene 5.0/0.8–1.0
Cobalt	Varian	240.7	0.20	Air/Acetylene 5.0/0.8–1.0

Sample intake rate 5 mL/min.

Inbuilt spray chamber of Varian Spectr AA-10.

## 2.2. XRD

XRD patterns were recorded on a Bruker AXS D8 Advance diffractometer (with DIFFRAC plus software) using Cu K $\alpha$  radiation (0.15418 nm), secondary beam curved graphite monochromator and a scintillation detector. The patterns were recorded in the  $2\theta$  range 10° to 95° at a scan speed of 0.02°/s and tube rating 35 kV/30 mA.

## 2.3. Carbon determination by gravimetry

The synthetic diamond samples were dried in an oven at 110°C for 2 h. Ten weighing of 1.0 gm of sample nos. 1, 2, 4, 5, 9 and 0.5 gm of sample nos. 3, 6, 7 and 8 were taken in a preweighted platinum dish (cleaned by KHSO<sub>4</sub> before experiment). The platinum dish was heated in a muffle furnace at 850°C up to constant weight. The procedure of heating, cooling and weighing was repeated until constant weight is obtained. The total carbon is thus determined gravimetrically assuming total weight loss was due to carbon.

## 2.4. FAAS

### 2.4.1. Instrumental details

Details of equipment and standard setting for FAAS measurements are given in Table I. Calibrated volumetric flasks, pipette and burette of Borosil Glass India were used.

### 2.4.2. Reagents

Nitric acid 69% E. Merck (India), which was further, purified by sub-boiling point distillation in a quartz device and di-lithium tetraborate 98% E. Merck (Germany) were used. De-ionized water (18 mega ohm resistivity) prepared from Millipore milli-Q water purification system, USA was used. The standard stock solution of 1000 ppm of all the elements were prepared from high purity metals (99.99%) procured from J. Matthey, England in sub-boiled nitric acid or sub boiled hydrochloric acid as per ASTM procedure, and final volume was made by de-ionized water. Subsequent dilutions have been done from stock solution to get the working range solution. These solutions were used for calibration graph of each element.

### 2.4.3. Procedure for sample dissolution

The remaining residue after the determination of carbon was fused with double quantity of di-lithium tetraborate at 1250°C for 20 min. The melt was cooled and dissolved in (1:1) 15 mL nitric acid. The volume made up to 25 mL by de-ionized water and subsequent dilutions were made to get the desired concentration range. The elements viz Si, Al, Fe, Ca, Mg, W, Ni, Co and Na were measured in the solution by FAAS using respective standards for each element. Reagent blank was also prepared with the sample and correction applied wherever required. Mean absorbance values of ten replicates of each sample were taken in to consideration for calculation of each analyte element. Details of measurement are given elsewhere [16].

### 2.4.4. Calibration

The calibration of the FAAS instrument was carried out with standard solutions covering the desired concentration range of the analyte in the sample. The standard solutions required for calibration of FAAS for different elements were prepared as mentioned in ASTM procedure for coal and coke ash [17]. Standard addition of Al and Fe in required proportion was added to the standard to match the sample solution to avoid the interference of Al and Fe in their analysis, di-lithium tetraborate was added in all the standard as per requirements.

## 3. Results

### 3.1. XRD

Fig. 1a shows XRD pattern of sample no. 1, which shows only diamond phase (PDF No. 6-675). The XRD pattern of sample no. 2 is similar to that of Fig. 1a. Fig. 1b shows XRD pattern of sample no. 3. Besides the sharp diffraction peaks of diamond, some low intensity broad peaks are also observed. These were identified with  $\alpha$ -iron phase (PDF No. 6-696). The XRD pattern of sample no. 4 and 5 were similar to that of sample no. 1 as shown in Fig. 1a. Sample no. 6 also has  $\alpha$ -iron phase present in small amounts and the pattern is similar to that of Fig. 1b. Sample no. 7 has diamond and corundum (PDF No. 46-1212) as major phases as revealed in its XRD pattern, Fig. 1c. The XRD pattern of sample no. 8, Fig. 1d, shows presence of corundum, almandite (PDF

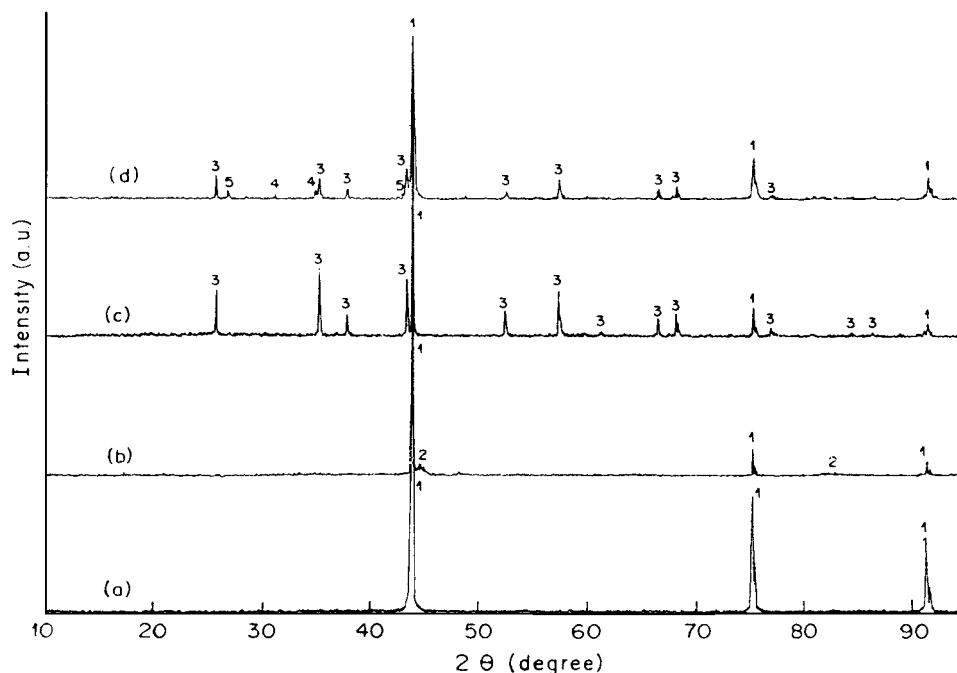


Figure 1 XRD patterns of diamond powder samples. The phases have been marked as: 1-diamond; 2- $\alpha$ -iron; 3-corundum; 4-almandite; 5-graphite. (a) Sample no. 1; (b) sample no. 3; (c) sample no. 7; (d) sample no. 8.

No. 9-427) and probably graphite (PDF No. 25-284) in addition to the diamond phase. The sample no. 9 did not show any impurity phase. The results of XRD crystalline phase analysis are compiled in Table II for quick reference.

### 3.2. FAAS

A new approach of sample dissolution for synthetic diamond powder has been developed, in which carbon is removed on heating and determined quantitatively. This is an empirical method for carbon determination as the loss in weight during heating is presumed to be purely due to carbon. The results are mentioned in Table III. Carbon the major constituent of synthetic diamond is removed as  $\text{CO}_2$  and remaining residue is fused with di-lithium tetraborate in the ratio of 1:1 with respect to sample weight and hence salt concentrations reduces and also the blank values. The melt obtained after fusion with di-lithium tetraborate dissolved in dilute nitric acid gives a clear solution, even after keeping it for several days, analysis can be carried out without any significant change in the values obtained earlier. The results obtained for major and minor constituents are

TABLE II Crystalline phase analysis by XRD

Sample no.	Main phase	Other phase
1	Diamond	—
2	Diamond	—
3	Diamond	Alpha iron
4	Diamond	—
5	Diamond	—
6	Diamond	Alpha iron
7	Diamond	Corundum
8	Diamond	Corundum, almandite, graphite (probable)
9	Diamond	—

mentioned in Table III while the results obtained for major constituents like silica and iron by gravimetry and titrimetry are mentioned in Table IV along with proposed method. The standard deviation is calculated by the ten measurements of ten replicates of each sample. Blank level has been found to be very low for the elements reported. All the reported data have been corrected for the blank.

### 4. Discussion

Analysis of impurities in industrial diamonds is important as they affect the properties. Impurities in diamonds have not been analyzed by FAAS so far, mainly because of two reasons. Firstly, FAAS requires specimen in solution form whereas diamond is chemically inert and secondly, diamond being precious material, non-destructive testing is obviously preferred. But FAAS has another advantage that the impurities present in trace level can be identified by good precision and it is also cheap in comparison to other instruments which is generally used for the identification of impurities in diamond.

The major impurities of synthetic diamond like iron and silica were further verified by analyzing same samples by titrimetry and gravimetry, as can be seen from Table IV, all the results are comparable obtained by classical method and by proposed method.

Metallic impurities in synthetic diamond arise from the solvent-metal catalyst used for synthesis [18]. Impurities such as almandite are from the pyrophyllite alteration zone [19]. The solvent-catalyst metal may be trapped as inclusion or may be in the form of carbides [18–20]. It was noted that the sample nos. 1, 2, 4, 5 and 9 free from major impurities, were light colored powder. Sample no. 7 which has major amount of corundum was also of light color. Sample nos. 3, 6 and 8 were of dark gray color.

TABLE III Results of Carbon content and major and minor impurities

Sample no.	wt. (%)				wt. (mg/kg)						
	Carbon	Iron	Si	Al	Ni	Ca	Na	Mg	W	Co	
1	99.82 ± 0.11	0.03 ± 0.008	—	—	16.0 ± 1.2	37.0 ± 2.4	20.0 ± 1.3	8.73 ± 0.8	—	—	
2	99.82 ± 0.11	0.044 ± 0.006	—	—	15.0 ± 1.1	44.0 ± 2.5	160.0 ± 3.3	18.0 ± 1.3	0.37 ± 0.07	—	
3	82.6 ± 0.11	5.98 ± 0.20	1.27 ± 0.20	0.11 ± 0.07	310.0 ± 3.3	56.0 ± 1.6	76.0 ± 2.0	120.0 ± 2.3	0.37 ± 0.09	2.4 ± 0.3	
4	99.86 ± 0.10	0.015 ± 0.005	—	—	30.0 ± 1.7	260.0 ± 4.2	60.0 ± 2.8	30.0 ± 1.3	0.25 ± 0.04	4.2 ± 0.5	
5	99.84 ± 0.10	0.015 ± 0.008	—	—	30.0 ± 1.6	250.0 ± 3.7	40.0 ± 2.5	30.0 ± 1.3	0.25 ± 0.04	—	
6	82.65 ± 0.10	8.03 ± 0.25	0.71 ± 0.15	—	2040.0 ± 15	130.0 ± 1.4	220.0 ± 3.9	130.0 ± 1.4	0.94 ± 0.08	1.6 ± 0.3	
7	40.92 ± 0.25	0.59 ± 0.10	5.00 ± 0.09	21.80 ± 0.9	95.4 ± 3.8	75.4 ± 2.4	105.4 ± 3.6	95.4 ± 2.6	0.85 ± 0.06	3.6 ± 0.6	
8	85.27 ± 0.08	0.32 ± 0.04	0.73 ± 0.18	5.08 ± 0.38	45.1 ± 2.3	63.3 ± 2.6	85.4 ± 2.6	105.0 ± 2.0	0.33 ± 0.08	1.7 ± 0.3	
9	99.82 ± 0.10	0.06 ± 0.02	—	—	15.0 ± 1.1	53.2 ± 2.6	46.6 ± 2.1	95.0 ± 2.8	—	—	

(±) Standard deviation of ten replicates of each sample.

(—) Element not analyzed.

TABLE IV Analysis of Silica by gravimetric and Iron by titrimetric method

Sample no.	Silica (%)		Iron (%)	
	Gravimetric method	Proposed method	Titrimetry method	Proposed method
3	2.51 ± 0.18	2.71 ± 0.20	5.65 ± 0.20	5.98 ± 0.20
6	1.43 ± 0.21	1.51 ± 0.15	7.80 ± 0.15	8.03 ± 0.25
7	10.4 ± 0.27	10.7 ± 0.17	—	—
8	1.36 ± 0.22	1.56 ± 0.18	—	—

(—) Not analyzed.

## 5. Conclusions

Quantitative analysis of impurities in industrial synthetic diamond samples have been done by FAAS. Fusion method has been applied to prepare specimen solution for absorbance measurement. Crystalline phase analyses of major impurities have been identified by XRD.

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