

Mechanochemical Dispersion of Nanodiamond Aggregates in Aqueous Media

Xiangyang XU^{1,2)†}, Yongwei ZHU²⁾, Baichun WANG²⁾, Zhiming YU¹⁾ and Shengzhong XIE²⁾

1) School of Materials Science and Engineering, Central South University, Changsha 410083, China

2) R & D Center, Changsha Research Institute of Mining and Metallurgy, Changsha 410012, China

[Manuscript received January 12, 2004, in revised form April 26, 2004]

A technology of mechanochemical treatment (MCT) is introduced to modify nanodiamond (ND) surface aiming to obtaining a stable suspension with well-dispersed ND particles in aqueous medium. ND investigated in this paper is a purified product of nanometer-sized diamond synthesized by explosive detonation. As obvious aggregation and sediment were observed when the sample was added into deionized water, it is crucial to conduct deaggregation and dispersion investigations. Amid a series of mechanical treatments, *i.e.* grinding, stirring, ultrasonic and classification, some reagents are introduced to modify the newly created surface during aggregates comminution. For the co-effects of mechanical forces and surfactants, the mean size of particles was reduced and a stable system containing ND with narrow size distribution was prepared. Mechanism of surface reaction and modification are discussed, while AFM, Zetasizer3000HS, XRD, XPS and FTIR are utilized for the analysis. The functional chemical structure of ND particle surface and surface electrical property changed during the modification processes, and the dispersion character and stability of suspension can consequently be improved.

KEY WORDS: Aggregates; Deaggregation; Dispersion; Mechanochemical treatment; Nanodiamond

1. Introduction

Mechanochemistry is a technological research field dealing with physicochemical transformations and chemical reactions of solids induced by mechanical action. As mechanical treatments can activate and intensify the interaction of particulates and chemical reagents during the modification processes, the combined use of it with chemical force was widely introduced in the synthesis, dispersion and modification practices of powder, composite or polymer^[1~5]. Ultrafine Fe powder with a relatively uniform particle size of about 10 nm was synthesized through mechanochemical solid-state reduction of FeCl₃ by Na and subsequent removal of the reaction by-products^[6]. Wollastonite was mechanochemically modified using a jet mill, the surface features of which have been changed from hydrophilicity to hydrophobicity and make wollastonite easy to be combined into polypropylene^[7].

As a newly developed nano-scale material, nanodiamond (ND), obtained from explosive detonation, possesses excellent characteristics such as superhardness, round-shape and nanometer size, and thus has promising application potentials^[8~12]. But, because of its high specific surface energy, ND stays in a thermodynamically unstable state and presents itself as aggregate, so it is crucial to disperse it in a variety of media to actualize its application efficiently^[13,14].

Physical and chemical properties of ND and the investigation on ND dispersion has been carried out synchronously since the beginning of its synthesis research, both in aqueous and in nonaqueous media^[15~21]. Among these researches, the importance of chemical modification of ND surface was emphasized, and ND suspensions, which could be reserved without sedimentation for

hours or couple of days, could be prepared.

Dispersion of ND in aqueous medium was studied in this paper utilizing mechanochemical treatment (MCT), while mechanical forces were used associating with chemical treatments for surface modification of ND particles.

2. Experimental

ND sample used in this work is a purified product of nanometer-sized diamond synthesized by explosive detonation. According to X-ray photoelectron energy spectroscopy (XPS), the main chemical elements on the surface of ND sample are C, O and N, which take 90.65%, 8.09% and 1.14% respectively.

Grinding mill, high-speed shearing emulsification machine and ultrasonic instrument were utilized for comminution and deaggregation, while inorganic electrolytes, surfactants were used in relevant circumstances for chemical stabilization. The whole process can roughly be divided into three stages, named as MCT1, MCT2 and MCT3 sequentially. During MCT1, inorganic electrolyte iron chloride (FeCl₃) and an anionic surfactant which contains large amount of carboxyl and hydroxybenzene groups, were introduced (abbreviated as CHB here). During MCT2, the suspension was modified with the presence of some regulators. During MCT3, medium was regulated further and another anionic surfactant, a disulfonic acid (DSA), was added.

Small angle X-ray scattering (SAXS), Zetasizer-3000HS and atomic force microscope (AFM) were adopted for size distribution measurement, while Zetasizer3000HS was used to measure the surface zeta (ζ)-potential as well. The crystal structures of ND were studied using X-ray diffraction (XRD) diffractometer D/max-rA, and infrared spectra were obtained using the standard technique of KBr-pellet with Nexus 470. Samples

† Ph.D. candidate, to whom correspondence should be addressed, E-mail: xiangyang.xu@sohu.com.

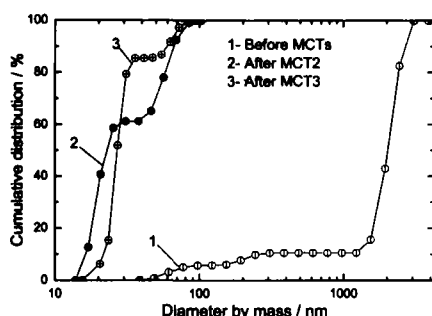


Fig.1 Size distribution after MCT modifications

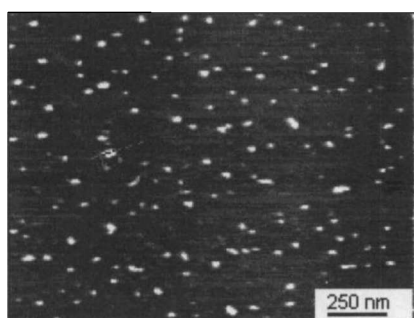


Fig.2 AFM image of ND suspension after MCT2

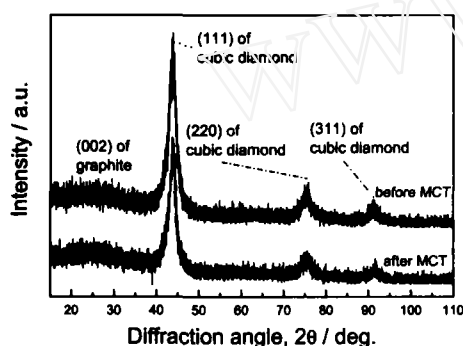


Fig.3 XRD patterns of ND before and after MCTs

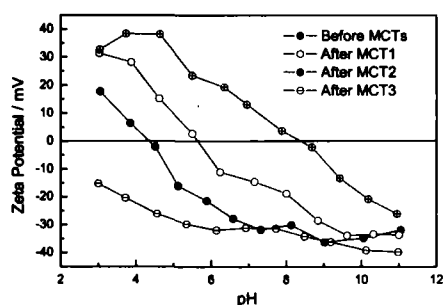


Fig.4 Surface electrical property of ND during MCTs

used for FTIR analysis were washed for 5 times in order to eliminate the influence of ions in suspension or physically adsorbed on ND surface.

3. Results and Discussion

3.1 Properties influenced by MCTs

3.1.1 Size distribution The size distribution of ND sample was measured using SAXS, while particulates have a

primary dimension smaller than 60 nm with the average size of 12 nm. Obvious flocculation and sedimentation were observed when this powder was added into deionized water. Zetasizer3000HS was used to measure the size of ND particles in water, see Fig.1. Before treatment, the size distribution of ND takes a quite broad range, and the diameter of most particles is over 2000 nm, while no more than 6% particles are smaller than 100 nm. So, it is crucial to conduct a surface modification to achieve the stable dispersion of ND particles in aqueous medium. After MCT2 and a classification process, significant reduction of particle size was observed, as all the particles in the suspension are less than 100 nm. Size distribution of ND remains quite narrow after MCT3. ND diameter after MCT2 was also examined using AFM (Fig.2). It testified the small size and dimensional uniformity (with an even shape and size) of ND particles.

3.1.2 Crystal structure XRD patterns were investigated to check the quality of ND after these MCT processes (Fig.3). No obvious change of particle crystal structure was found. When the scan angle 2θ ranging from 20° to 110° , typical intense diffraction lines of diamond are observed for both the samples before and after MCTs with 2θ angles of 44° , 76° and 92° , which agree well with the crystal faces of {111}, {220} and {311} respectively. As no trace of graphitization of ND was detected, it can be concluded that the characteristics of ND remain uninfluenced during MCTs.

3.1.3 Surface electrical property Figure 4 shows the influence of MCTs on ND surface electrical property. Four curves reflect respectively the relationship of surface ζ -potential of untreated ND particles and samples after the three MCT stages vs pH value of the aqueous medium. As the existence of Fe (III) ions in MCT1 and the removing and substitution of Fe (III) and CHB in the suspension and on ND surface by other cations, the ζ -pH curve moves stepwise upwards, and the isoelectric point (IEP) moves rightwards from 4.3 to 5.6 and 8.4. After MCT2, ND particles were positively charged with electricity in a wide range of pH value, of which a considerable high absolute value of ζ -potential was achieved while the medium pH value ranging from 3 through 5. And a relatively stable dispersion can thus be realized. When anionic DSA was added in MCT3, no IEP was observed, and particles were negatively charged, while comparatively high absolute value can be measured in alkaline medium.

3.1.4 Surface functional groups FTIR-spectrum of ND sample before MCT (Fig.5(a)) consists of absorption bands with the peak of 3433.76 cm^{-1} (stretching O-H and N-H vibration), 1764.89 cm^{-1} (stretching C=O vibration in carbonyl, carboxyl groups) and 1629.29 cm^{-1} (deformation NH vibration). In addition, absorption bands of stretching C-H vibrations are observed at 2923.16 and 2855.02 cm^{-1} (representing asymmetric and symmetric vibration, correspondingly), and the broad band with the peak of 1117.43 cm^{-1} may connect with the stretching C-OH vibration of hydroxyl groups and stretching C-O vibration of carboxyl groups.

After MCT1 (Fig.5(b)), an obvious change of spectrum is the disappearance of absorption band of stretching C=O vibration of carbonyl, carboxyl groups, which is substituted by absorption bands of carboxylic acid anions

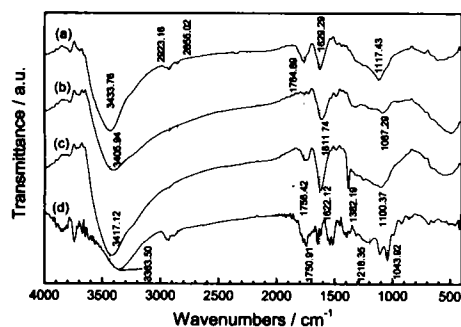


Fig.5 FTIR spectra of ND during MCTs, (a) before MCTs, (b) after MCT1, (c) after MCT2, (d) after MCT3

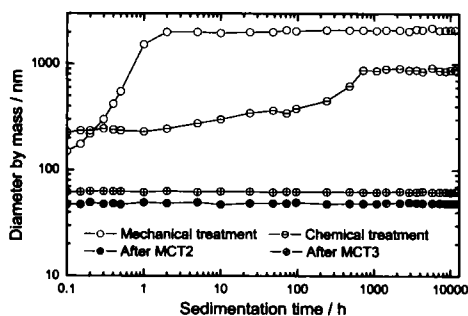


Fig.6 Stability of dispersed systems after different treatments

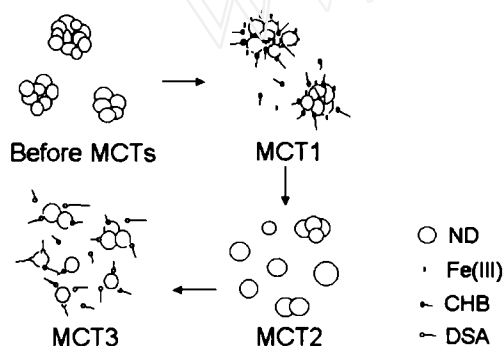


Fig.7 Schematic depiction of MCT processes

with the peaks of 1611.74 and 1324.48 cm^{-1} (asymmetric and symmetric vibration, respectively). This may be originated from the transformation of carboxyl groups to carboxylate during MCT1 as a result of reaction on ND surface and the formation of ferrite carboxylate. Another phenomenon is that the peaks of stretching O-H, N-H vibration, peaks of stretching C-OH vibration of hydroxyl groups and stretching C-O vibration of carboxyl groups move towards lower wavenumbers, to 3405.94 and 1087.29 cm^{-1} respectively, which may be due to the bonding between functional groups like hydroxide, carboxyl or amine and surfactants during surface modification. According to FTIR spectra, the adsorption of CHB on ND surface is not so apparent comparing with the influence of iron ions, as no apparent absorption of aromatic groups was detected, and its contribution to particle dispersion may lie in the abundance of hydrophilic hydroxybenzene groups in its structure.

Absorption bands of carboxylic acid anions disappear after MCT2, and those of carbonyl, carboxyl groups present themselves again (Fig.5(c), 1756.42 cm^{-1}), as a result of the disassociation of carboxylate and the removal of iron chloride and CHB, and as hydrolysis and ionization of carboxyl groups are restricted because of medium modification. The adsorption of hydrophilic groups like carboxyl and hydroxyl are strengthened, which may contribute to the hydrophilicity and stability of particles.

After MCT3, bands of stretching O-H and N-H vibration moved to 3383.50 cm^{-1} after DSA was added, and asymmetric and symmetric vibration absorption bands with peaks of 1218.35 and 1043.92 cm^{-1} of functional group -SO_2 were observed (Fig.5(d)), which indicated the chemical adsorption of DSA on ND surface.

3.2 MCT process illustration

While mechanic forces are introduced to crush the aggregate, surfactants and inorganic electrolytes are added to modify the newly created surface. Through this way, an instant surface coating can increase the electrostatic repulsion among particles and improve the hydrophilicity. Stability of systems from different treatments was investigated by consecutive measurement of particle diameter (Fig.6). When mechanical treatment was introduced solely, the size of ND climbed rapidly although initially the agglomerates can be smashed into small pieces. Suspension with the presence of surfactant (only chemical treatment conducted) can be somewhat more stable, but ND particles were still coarse. Only after MCT modification considerable stable system can be prepared, as average size of ND remained almost unchanged for more than one year, and, absolutely, no sediment was detected.

MCT procedure can be illustrated as Fig.7. During MCT1, iron chloride and CHB adsorbed on and reacted with ND surface, but after MCT2, they were removed, which has been testified by chemical analysis and XPS analysis as well. As what has been proved in FTIR analysis, the spectra before MCTs and after MCT2 are quite alike notwithstanding particle size reduction. The reaction mechanism of Fe (III) and CHB may be classified as catalysis. After MCT3, anionic DSA attached on ND surface, just as what was observed in ζ -pH relationship, an electrostatic repulsion state was reached.

4. Conclusions

(1) During MCT process, surface modification of ND was accomplished, and the stable dispersion of ND in aqueous medium was realized. Suspension with a narrow, even particle size distribution and excellent stability can be prepared, while all ND particles are less than 100 nm , and no obvious change of ND crystal structure occurred in MCTs.

(2) Surface ζ -potential of ND shifts accordingly when different reagents were presented during MCTs, and electrostatic stabilization plays an important role in dispersion practice.

(3) Composition of surface functional groups changes according to MCTs. Hydrophilic carboxyl and hydroxyl groups, intensified after the modification, may contribute

to the improvement of dispersion and stability.

REFERENCES

- [1] M.Suzuki, H.Iguchi and T.Oshima: in *Proc. of The 4th JAPAN-RUSSIA Symp. on Mechanochemistry*, Nagoya, 1992, 173.
- [2] F.Garcia, N.Le.Bolay and C.Frances: *Powder Technol.*, 2003, **130**(1-3), 407.
- [3] A.Frendel, M.Drache, G.Janke and G.Schmidt-Naake: *Chem. Ing. Technol.*, 2000, **72**, 391. (in German)
- [4] C.Frances and C.Laguerie: *Powder Technol.*, 1998, **99**, 147.
- [5] M.Hasegawa, M.Kimata, M.Shimane, T.Shoji and M.Tsuruta: *Powder Technol.*, 2001, **114**(1-3), 145.
- [6] J.Ding, W.F.Miao, P.G.McCormick and R.Street: *Appl. Phys. Lett.*, 1995, **67**, 3804.
- [7] Zhen LI, Shangyue SHEN, Jirong PENG and Chunrong YANG: *Key Eng. Mater.*, 2003, **249**, 413.
- [8] Kang XU and Chunji XUE: *Prog. in Chem.*, 1997, **9**, 201. (in Chinese)
- [9] V.Yu.Dolmatov: *Rus. Chem. Rev.*, 2001, **70**, 607.
- [10] Shourong YUN, Fenglei HUANG, Feng MA, Yi TONG, Pengwan CHEN, Gang ZHOU, Quan CHEN and Sheng ZHAO: *Study and Development World Sci. Technol.*, 2000, **22**(1), 39. (in Chinese)
- [11] Yongwei ZHU, Baichun WANG, Lifang CHEN, Xiangyang XU and Xiangqian SHEN: *Mater. Rev.*, 2002, **16**(12), 27. (in Chinese)
- [12] Zengshou JIN and Kang XU: *Energetic Mater.*, 1999, **7**(1), 38. (in Chinese)
- [13] Pengwan CHEN: *Ph.D. Thesis*, Beijing Polytechnique University, Beijing, 1999. (in Chinese)
- [14] Xiangyang XU, Yongwei ZHU, Baichun WANG and Xiangqian SHEN: *Trans. Nonferrous Met. Soc. China*, 2003, **13**(6), 1415.
- [15] V.L.Kuznetsov, M.N.Aleksandrov, I.V.Zagoruiko, A.L.Chivilin, E.M.Moroz, V.N.Kolomichuk, V.A.Likholobov, P.M.Brylyakov and G.V.Sakovitch: *Carbon*, 1991, **29**, 665.
- [16] E.Mironov, A.Koretz and E.Petrov: *Diamond Relat. Mater.*, 2002, **11**, 872.
- [17] G.A.Chiganova, V.A.Boonger and A.S.Chiganov: *Colloid J.*, 1993, **55**, 774.
- [18] L.V.Agibalova, A.P.Voznyakovskii, V.V.Klyubin and S.Yu.Lebedev: *Superhard Mater.*, 1998, (4), 79.
- [19] A.P.Voznyakovskii, V.Yu.Dolmatov, V.V.Klyubin and L.V.Agibalova: *Superhard Mater.*, 2000, (2), 58.
- [20] A.P.Voznyakovskii, T.Gujimura and V.Yu.Dolmatov: *Superhard Mater.*, 2002, (6), 22.
- [21] G.P.Bogatyreva, M.N.Voloshin and V.S.Shamraeva: *J. Superhard Mater.*, 2002, **138**, 55.