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Detonation Synthesis of Carbon-Encapsulated Nickel Nanoparticles*

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Abstract: Carbon-encapsulated nickel nanoparticles (CENNPs) with core-shell structure were synthesized by detonation method using homemade composite explosives with negative oxygen balance. The detonation chemical reaction was initiated by a nonel tube detonator in a closed explosion vessel filled with nitrogen gas. X-ray diffraction (XRD), X-ray fluorescence (XRF), transmission electron microscopy (TEM) with selected area electron diffraction and Raman spectrum techniques were used to characterize the as-obtained detonation products. The XRD and XRF analysis showed that the detonation products mainly consisted of the well-crystallized face-centered cubic nickel nanocrystals, carbon and other microelement. TEM showed that most nanoparticles are made up of a nickel core with the size of 10～25 nm and a carbon shell with the thickness of 1～2 nm. The Raman spectrum analysis indicated that the coating carbon shell is mainly composed of graphite and amorphous carbon. Furthermore, the possible formation mechanism for CENNPs were also discussed.

Key words: carbon-encapsulated nickel nanoparticles; detonation synthesis; X-ray diffraction; formation mechanism

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1 Introduction

Carbon-encapsulated metal nanoparticles (CEMNPs) were discovered since the beginning of the end of last century, and the scientific community has payed a great deal of attention to the CEMNPs. In order to protect the metallic nanocrystals from air-oxidation and changing their natural properties, the best way was to handle and store metallic nanocrystalline with inert materials. Among inert materials[1-2], carbon is a relatively ideal material because it could form a carbon wall to enclose the metallic nanocrystalline, as reported by many researchers[3-4]. As an important nanomaterial, the carbon-encapsulated metal nanomaterials were recognized in a wide range of applications, such as magnetic recording[5], magnetic fluids[6], microelectronics[7], chemistry and medicine[8-9].

Up to the present, researchers have reported the synthesis processing of elementary nanoparticles of ferromagnetic metals, Fe, Co, Ni[10]. Bystrzejewski, *et al*.[11] used a modified arc discharge technique and succeeded in synthesizing controlled-size CENNPs that retained their intrinsic nanocrystalline pro-

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perites. Yu *et al*.[12] reported that the carbon-encapsulated cobalt/nickel nanoparticles with core/shell structure had been successfully synthesized with maize-derived starch as carbon source and metal nitrate as metal precursors in flowing hydrogen. High level energy consumption, low productive rate and intricate uses of various facilities have hindered the preparation of CEMNPs in high yield, hence, limiting their practical application.

It's well known that the detonation of explosives can generally produce powerful destructive shock waves by a fast chemical decomposition reaction and detonation transmission or violent combustion. During the exothermic reaction process, the shock waves also provide elemental building blocks and a unique high-pressure and high-temperature physical environment for the construction of various nanostructures. So the detonation method has been used as an effective tool for producing nano-diamond and graphite nanospheres in a short time[13-14] for tens of years. Recently, the detonation technique has also been utilized to prepare some common nanomaterials such as alumina[15], ferric oxide[16], zinc oxide[17], TiO_2[18], $LiMn_2O_4$[19], $SrAl_2O_4$[20], manganese ferrite[21], carbon encapsulated cobalt or iron nanoparticles[22-23]. However, there are few reports about the detonation synthesis of CENNPs by detonation method. In this present work, we present a fast, pollution-free and energy-saving method for the preparation of CENNPs by the detonation decomposition of homemade carbon- or nickel ion-containing explosives. Using X-ray diffraction (XRD), X-ray fluorescence (XRF), transmission electron microscopy (TEM) and Raman spectrum techniques, the obtained samples are characterized, and the possible growth mechanism of CENNPs is also discussed.

2 Experiment

2.1 Experimental Process

In our experiment, nickel nitrate, absolute ethyl ethanol, carbamide and pentaerythritol tetranitrate (PETN) were of analytical grade commercially available. The composite explosives prepared by a simple facility consisting of a thermostat and a container equipped with a stirrer. The nickel nitrate and carbamide with the mole ratio of about 1∶3 to 1∶4 were mixed and heated up to 75～80 ℃, and added to about 15 mL absolute ethyl alcohol, and then put PETN with the same weight of other agents into the mixture, which was then homogenized.

In the process of preparation of composite explosive, nickel nitrate with six crystal water was incorporated with carbamide in water bath to form complex compound ($Ni[OC(NH_2)_2]_4(NO_3)_2$). And then the absolute ethyl ethanol and PETN were mixed with the complex compound to get a homogeneous solution, namely the composite explosive. The chemical formula of the composite explosive could be written as $C_{2.008}H_{6.094}O_{4.109}N_{1.36}Ni_{0.1}$, which is a negative-balance explosive.

The as-prepared composite explosive was packed in a thin plastic column bag about 300 g with a density of approximate 1.69 g/cm^3. The explosive charge was suspended in the explosion vessel, whose capacity is about 0.4 m^3, as shown in Fig. 1. The nitrogen gas was used in detonation process which provided an efficient cooling of detonation products and thus reduced the recombination of obtained nanoparticles. After the detonation, the detonation products were collected from the inner wall of the explosion vessel. The productive rate was about 10%～15%.

2.2 Characterization Methods

Crystalline phase was determined by X-ray Diffractometer (XRD) run at 40 kV and 30 mA, with a scan speed of 4.00° min^{-1} and a step of 0.02° using Cu K_α (0.145 06 nm). Transmission electron microscopy (TEM, Tecnai-20, resolution: 0.25 nm) operated at 200 kV was used to characterize the

structure and morphology of materials. X-ray fluorescence (XRF, Series-1800X) was applied to give us some basic components of detonation products concerning the elemental distributions based on the qualitative analysis. Raman spectrum (Renishaw Micro-Raman 2000, 632.8 nm He-Ne laser excitation), was utilized to investigate the components of carbon layers.

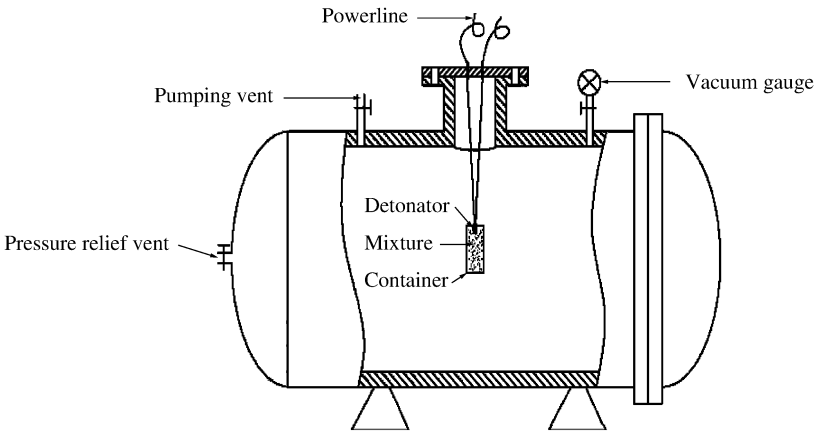


Fig. 1 Schematic diagram of explosion vessel

3 Results and Discussion

3.1 XRD Pattern and XRF Analysis

Fig. 2 shows the presence of sharp peaks of nickel crystal, corresponding to JCPDS No. 04-0850. The three broad peaks at $2\theta=44.30°$, 51.78° and 76.34° are assigned to the (111), (200) and (220) reflections, respectively, of nickel crystal with face-centered cubic structure. The XRD pattern of the detonation soots could be identified as graphite, amorphous carbon and hexagonal diamond (Lonsdaleite), and the diffraction peaks (26.4°, 28.5°, 21.7°, 37.9°, 43.1° and 62.6°) correspond to the three typical carbon. According to the data derived from the XRD pattern, the main components for the three kinds of carbon are 90.9%, 6.29% and 2.7% respectively. Using the Scherrer formula[24], the average grain size (D) can be describe as: $D=0.89\lambda/(\beta\cos\theta)$, where $\lambda=0.14506$ nm, θ is the Bragg angle of the peak, and β is the full width at half maximum. As can be seen from Fig. 2, $2\theta=44.30°$ and $\beta=0.5076$, so the calculated mean grain size of nickel nanoparticles is 15.73 nm.

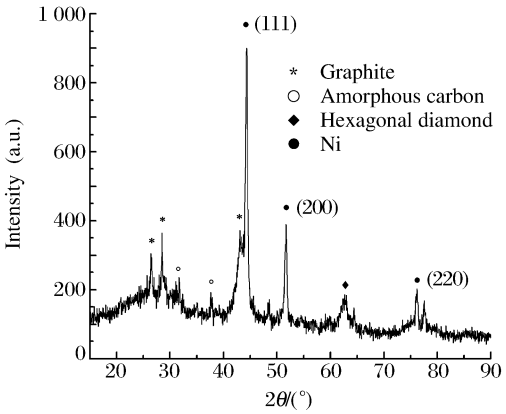


Fig. 2 XRD pattern of the detonation products

In order to further quantitatively investigate the detonation products, XRF examination is also employed. The results show the basic components of detonation products concerning the elemental contents, listed in Table 1. It can be seen from the Table 1, that the detonation soots are mainly composed of nickel and carbon amounting to 93.437% of the whole system. The other elements amounting to 6.570% which come from the chemical agents are relatively less than the primary composition (CENNPs). The detonation products mainly consist of graphite carbon and nickel crystal, which are the same as the XRD results.

Table 1 The XRF results of detonation products

Element	Line	Mass fraction /(%)	Element	Line	Mass fraction /(%)	Element	Line	Mass fraction /(%)
Ni	NiKa	60.673 4	Cl	ClLa	0.435 4	Na	NaKa	0.158 7
C	CKa	32.764 0	Cu	CuKa	0.250 4	Sb	SbLa	0.157 2
Si	SiKa	1.787 6	Mg	MgKa	0.223 1	Ti	TiKa	0.083 6
S	SKa	1.121 9	Co	CoKa	0.218 2	P	PKa	0.021 6
Ca	CaKa	0.943 0	Ra	RaLa	0.210 9	Cr	CrKa	0.080 6
K	KKa	0.544 7	Zn	ZnKa	0.186 3	Zr	ZrKa	0.000 5

3.2 TEM Images Analysis

The TEM images of the detonation products, as shown in Fig. 3(a), reveal that the as-synthesized nanoparticles have a core-shell structure, and the nickel nanocrystals are full of coverage of the carbon shell. In addition, most of the nickel nanocrystalline have a spherical or ellipsoidal shape, and are almost similar in size. More intuitionistic information of the detonation products morphology are obtained from Fig. 3(b). Obviously they have core-shell structure in which the thin shell are in the form of amorphous carbon and the bigger nickel cores are encapsulated with graphitic carbon. The nucleus diameter is about 10～25 nm, and the thickness of the carbon shell is about 1～2 nm.



Fig. 3 TEM photographs of detonation products

3.3 Raman Spectrum Analysis

Raman spectroscopy is a popular, nondestructive tool for structural characterization of carbons. Here, the G-band is associated with the E_{2g} mode (stretching vibrations) in the basal-plane of graphite, that is, the bond stretching of sp^2 pairs. And the origin of D-band has been explained as disorder-induced features due to the finite particle size effect, lattice distortion or amorphous carbon background signals[25]. Two wide peaks are observed at 1 363.61 cm^{-1} (D-band) and 1 579.43 cm^{-1} (G-band) in Fig. 4, which are indications of the heavy disorder relating to the graphite crystallite A_{1g} mode and the E_{2g} mode of graphite, respectively. The peak heights ratios, I_D/I_G, is about 0.86. The presented Raman data provide further evidence for the presence of both the ordered and disordered structures in the investigated materials. However, the carbon

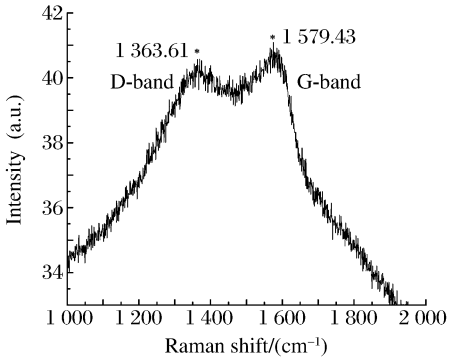


Fig. 4 Raman spectrum of CENNPs

in the detonation products exists in the form of graphite and amorphous carbon, and the graphite is a bit more than the amorphous carbon.

3.4 Detonation Synthesis Mechanism

It's well known that the detonation process of explosive is extremely rapid and complex[26], accompanying with the production of violent shock wave, high temperature and high pressure. In general, the detonation temperature can reach up to several thousands degree centigrade, and the detonation pressure can amount to dozens of GPa. The decomposition of negative-oxygen balance explosives could generate high temperature and high pressure through a transformation of embodied chemical energy to thermal energy, and then react with each other to form small species, such as ionic and molecular radicals.

During the detonation process, the metal nickel ions and surplus carbon ions were in gas state or in gas-like state under the high pressure and high temperature conditions, as shown in Fig. 5(a), due to the solidification point of metal nickel (about 3 003 K) and graphite carbon (about 3 743 K). With the sharp decreasing of detonation reaction temperature, the cooling rate of gas-state atom cluster was accelerated, and the diffusion range of gas-state atom cluster was restrained in the nitrogen gas. Because the solidification point of graphite carbon is higher than that of nickel, the carbon ions were agglomerated firstly, and in the meanwhile the nickel was in the gas state till the temperature dropped to the solidification point of nickel. The free carbon atom or cluster of carbons were captured and adsorbed on to the surface of the liquid micro nickel particles, as seen in Fig. 5(b). As the solid solubility of carbon in nickel was decreased and saturated, the small atoms were rearranged and agglomerated into the solid products while being cooled. In order to prevent the further agglomeration of nickel microliquid drops, the carbon aions will be deposited layer by layer during the instant time (several microsecond), as presented in Fig. 5(c). Finally, with temperature further decreasing, the nickel and carbon microliquid drops were transformed into solid state, namely the CENNPs with the core-shell structure was formed, as shown in Fig. 5(d).

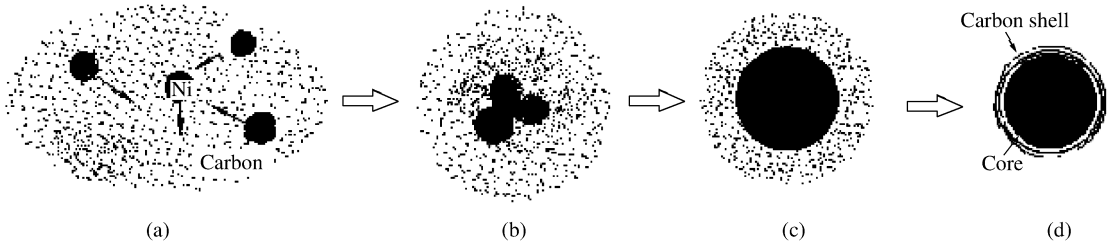


Fig. 5　Schematic of the CENNPs formation process

4 Conclusions

Using the composite explosives designed specially, the CENNPs have been successfully synthesized. The experimental results showed that the procedure is greatly simplified, and the yields are also increased obviously. The as-prepared spherical and ellipsoidal nanoparticles were composed of a big nickel core inside with an average diameter of 15.73 nm and thin carbon outer layer of 1～2 nm thick. The productive rate of CENNPs was about 10%～15%. The proposed method may provide a potential way for practical application in the days to come.

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爆轰法合成碳包覆镍纳米颗粒的研究

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摘要:采用自制的负氧平衡复合炸药前驱体,在密闭容器中充氮气保护下爆轰合成了碳包覆镍纳米颗粒。利用 X 射线衍射、X 射线荧光、透射电镜和拉曼光谱等技术,对爆炸产物的组成成分、结构形貌等进行了观测。结果表明,爆轰产物主要由具有面心立方结构的镍晶核和碳元素构成,此外还含有其它微量元素;合成的纳米颗粒呈球形或椭球形状,颗粒尺寸主要分布在 10～25 nm 范围,包覆的碳壳厚度约 1～2 nm,核壳结构完备。结合观测结果,对爆轰法合成碳包覆纳米颗粒的形成机制进行了简单的讨论。

关键词:碳包覆镍纳米颗粒;爆轰合成;X 射线衍射;合成机制

中图分类号:O389;O521.9　　**文献标识码**:A