Formation mechanism and electromagnetic-microwave-absorbing properties of carbon-encapsulated permalloy nanoparticles prepared by detonation

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HIGHLIGHTS

- Carbon-encapsulated Fe–Ni alloy nano particles have been successful prepared by detonation.
- Most of the iron–nickel cores is composed of several to more than ten grains.
- Most of the inner carbon layer is derived from the precipitation of carbon in the alloy.
- The performance of wave absorption of the detonation product is excellent.

ARTICLE INFO

ABSTRACT

In this study, we used detonation to synthesise carbon-encapsulated Fe–Ni alloy nanoparticles using safety-composite explosive precursors doped with $Fe(NO_3)_3 \cdot 9H_2O$ and $Ni(NO_3)_2 \cdot 6H_2O$. We characterised the morphology, components and structure of the synthesised carbon-encapsulated alloy nanoparticles by X-ray diffraction, Raman spectroscopy and a transmission electron microscope equipped with an energy dispersive X-ray spectroscope (EDS). The results revealed the carbon-encapsulated Fe–Ni nanoparticles to have a core-shell structure. The grains ranged in size from 40 nm to 60 nm and were uniformly distributed. We determined the encapsulated metal core to be mainly composed of different proportions of Fe and Ni and the outer shell to be composed of graphite and amorphous carbon. In addition, we observed onion carbon formed by the graphitisation of diamond clusters in the vicinity of the nanoparticles. We determined the electromagnetic characteristics of the Fe–Ni alloy nanoparticle composites using an Agilent microwave network analyser in a band range of 2–18 GHz. The experimental results for a coating thickness of 2 mm are as follows: In nanoparticles in which the atomic ratio of iron and nickel is 1: 4, the reflection loss R(dB) of the absorption layer has a double absorption peak, with peak values of −14.6 dB (9.7 GHz) and −7.7 dB (14.3 GHz) and the absorption band of −10 dB ranges from 8.5 GHz to 11.8 GHz. In nanoparticles in which the atomic ratio of iron and nickel is 1: 1, the reflection loss R(dB) reaches 30 dB at 12.88 GHz and the absorption band of −10 dB ranges from 9.7 to 14.4 GHz, which indicates a wide absorption band and an excellent absorbing property.

1. Introduction

One of the most important components in modern weapon systems is stealth technology whereby stealth fighters are difficult to detect or track during actual combat, which plays a huge role in operational effectiveness in modern warfare [1,2]. However, the shape of stealth fighters is often limited by the aerodynamics and the radar-absorbing area can be significantly reduced by the absorbing and transmitting wave-material coatings [3–6]. Therefore, nonmetallic composite materials that can absorb electromagnetic waves are a necessary component of stealth aircrafts. In areas where metal materials must be used,

an electromagnetic-wave-absorbing coating is applied as an effective stealth material. While the traditional absorbing material is strongly absorbent, new absorbing materials are also required to be 'thin, light, wide and strong'. Permalloy (Fe–Ni alloy)—a high performance soft magnetic material commonly used in electromagnetic devices [7]—is characterised by high permeability, high saturation strength [8], low coercive force and a high Curie temperature [9]. However, because of its low resistivity, bulk permalloy materials are unsuitable for use in high-frequency and microwave applications in which a powder or thin strip is required [10]. In magnetic absorbing materials, the nano-effect causes electromagnetic waves to be much better absorbed, especially
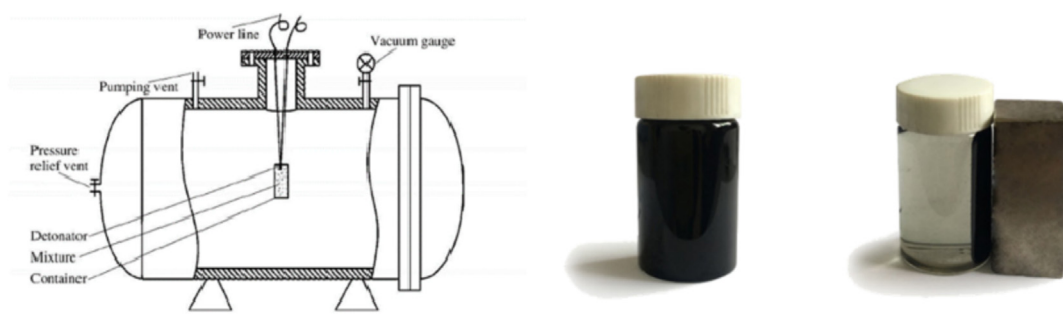

Fig. 1. (a) Schematic diagram of pressure vessel used in detonation synthesis Fig. 1(b) Behaviour of detonation products in response to a magnetic field.

high-frequency electromagnetic waves [11]. The surface, small volume and quantum size of nanoparticles can yield many physical and chemical effects that differ from those of bulk materials [12–14]. However, due to the high surface energy and strong interaction between the particles, metal nanoparticles are easily oxidised and agglomerated, so it is usually necessary to use metal nanoparticles in an isolated oxygen environment or to directly prepare them with an anti-oxidation and agglomerated surface, such as a coating of carbon or silicon dioxide on the surface of the nanometal [15,16].

Carbon-coated iron–nickel alloy nanoparticles are ideal absorbing materials because of their electromagnetic-wave-absorption frequency bandwidth and strong electromagnetic absorption ability. To date, the main methods used to synthesise carbon-coated nanometal particles are the arc discharge method and chemical vapour deposition. These methods involve complicated equipment, high energy consumption, high cost, difficulty in controlling the process parameters and small synthetic yield, thus making it difficult to achieve industry-level synthesis [17–20]. The detonation method has the advantages of a fast reaction rate, high yield, low cost and good repeatability, which solves the difficulties of the existing complex and expensive manufacturing process of wave-absorbing coating materials [21–24]. The detonation can be controlled by adjusting the composition of the precursor and the safety of the explosive can be improved by adjusting the nature of precursor components [25].

1.1. Synthesis of carbon-encapsulated permalloy nanoparticles by detonation

The first step in the synthesis of carbon-coated Fe–Ni alloy by the detonation method is to prepare a negative oxygen explosive containing iron–nickel metal atoms. The encapsulated metal core is mainly composed of different proportions of Fe and Ni and the carbon coating is formed by the residual carbon from the negative oxygen detonation. To prevent any segregation of the metal elements in the detonation products, the iron and nickel atoms must be evenly mixed on a microscopic scale in the detonation precursor. The simplest and most practical way to do so is to use an iron-salt and nickel-salt solution as the raw material. Iron nitrate and nickel nitrate are ideal choices because they have high solubility, are inexpensive and they decompose into non-polluting products after detonation. However, ferric ions and divalent nickel ions have a strong oxidising effect and promote the combustion of the catalyst. If untreated metal nitrate is mixed with a high explosive, the safety of the explosives cannot be guaranteed [26]. For this reason, we used urea as the complexing agent, and we encapsulated the metal ions within urea molecules to reduce the oxidation of the ferric and divalent nickel ions. The coordination bonds between the oxygen atoms in the urea carbonyl groups are formed by Fe^{3+} and Ni^{2+} ions, which result in metal cations wrapped in urea molecules to form the complexes ([Fe$(H_2NCONH_2)_6](NO_3)_3$ and Ni$(H_2NCONH_2)_4](NO_3)_2$) [27]. Our examination of [Fe$(H_2NCONH_2)_6](NO_3)_3$ by IR spectroscopy reveals there to be a strong absorption of NO_3^- at the characteristic absorption peak

of 1383 cm^{-1}, which indicates the presence of NO_3^- on the exterior of the complexes. Therefore, the complexation of urea effectively blocks the oxidation of Fe3+ and Ni2+, which ensures the safety of the explosives [28].

In the experiments, we used $C_{10}H_8$ as the carbon source of the precursor. We melted the preformed complex in a water bath at 353 K. We then maintained the complex in the water bath and added specific amounts of RDX and naphthalene to form a light-green solid composite explosive after cooling.

Then, we suspended the explosives in closed pressure vessels designed specifically for detonation experiments [29,30]. We used a pump to yield a vacuum pressure of −0.09 MPa. We then filled the vessels with argon as a shielding gas until reaching standard atmospheric pressure. We used a detonator to set off the charges. After detonation, we left the products to stand for 5 min, then collected them with absorbent cotton and washed and dried them with ethanol to obtain dark-grey powder solids. We synthesised approximately 30% detonation products in the experiments.

Next, we dispersed a small amount of the detonation products in ethanol, which formed a black liquid. We poured this liquid into a glass bottle, sealed it, and placed a magnet on one side of the bottle to observe the resulting magnetic absorption, as shown in Fig. 1(b).

1.2. Characterisation and discussion of carbon-encapsulated permalloy nanoparticles by detonation

We analysed the crystal structure of the detonation products by X-ray diffraction (XRD, Rigaku, D/Max 2400, Japan), as shown in Fig. 2. Table 2 shows the crystal structure and related parameters of the detonation products, in which we observed (111)(200)(220) characteristic diffraction peaks corresponding to a face-centred cubic (fcc) structure of the Fe–Ni alloy crystal and the (002) diffraction peaks of graphite. The main (111) diffraction peaks in the two samples deviated in the XRD spectra. The deviation of the main peak indicated that the compositions and crystal structures of the alloy nanoparticles differed in the detonation products, as revealed by the crystal spacing results, and which is also illustrated by the calculated interplanar spacing (d in Table 2). The lattice spacing of the d(111) plane of the 1# sample (d = 0.207 nm, lattice constant a = 0.359 nm) with a low nickel content is greater than the lattice spacing of the d(111) plane of the 2# sample (d = 0.205 nm, lattice constant a = 0.355 nm) with a high nickel content. These results are consistent with the fact that the radius of the iron atom (0.127 nm) is greater than that of the nickel atom (0.124 nm). The average atomic radii of the 1# and 2# samples are 0.1255 nm (= 0.5 × 0.127 + 0.5 × 0.124) and 0.1246 nm (= 0.2 × 0.127 + 0.8 × 0.124), respectively, which we calculated by the atomic contents of iron and nickel, respectively, which differ by 0.722%, and which is close to the d value difference of the two samples (0.976%) (See Fig. 3, Table 1).

To obtain these results, we used the Scherrer formula, with D= $k/\cos θ$ and k is 0.89, where $λ$ is the wavelength of the Cu target