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Influence of Al on synthesis and properties of carbon-encapsulated iron nanoparticles

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ABSTRACT

Each method of encapsulation of Fe nanoparticles in carbon coatings results in formation of thermodynamically unstable austenite phase. The presence of austenite is highly unwanted because it drastically worsens the magnetic performance of carbon-encapsulated iron nanoparticles. This paper verifies whether the inclusion of Al, which is known as efficient ferrite stabilizing element, may eliminate this unwanted paramagnetic phase in carbon-encapsulated iron nanoparticles synthesized via carbon arc discharge route. The influence of Al on the synthesis yield, morphology, phase composition and magnetic properties of carbon-encapsulated iron nanoparticles was studied. The inclusion of Al surprisingly yielded an anomalous increase of austenite content. It was also found that the austenite content monotonically increases with the Al concentration in the anode. The inclusion of Al also diminished the structural ordering of carbon coatings and substantially narrowed the diameter distribution of encapsulated iron nanoparticles.

1. Introduction

Magnetic nanoparticles have size-dependent properties [1]. The most fascinating feature is switching between the ferromagnetic and superparamagnetic state, when the diameter of a magnetic nanoparticle is below the single domain size. The occurrence of superparamagnetism in nanoparticles is reflected in their applications, e.g. data storage [2], mobile catalyst platforms [3], sensors [4], mobile sorbents [5,6] and various biomedical purposes (drug delivery, hyperthermia, targeted molecular imaging) [7–9]. The nanoparticles made of pure metallic phases (e.g. transition metals) have substantially better magnetic performance in comparison to their oxide counterparts. It can be lucidly expressed in their saturation magnetization, which is 220 emu/g and 80–90 emu/g for metallic iron and iron oxide, respectively [10]. Nevertheless, the magnetic nanoparticles made of pure metallic phases are pronounced to spontaneous undesirable processes: (i) surface oxidation, (ii) agglomeration, and (iii) corrosion. The encapsulation of metallic magnetic nanoparticles in thin protective coatings is a way to improve their chemical stability and to preserve their inherent physical properties. The literature review shows that several encapsulation materials were proposed, e.g. silica, polymers, boron nitride, gold and carbon [11]. Many of them have significant drawbacks. As for example, polymer-coated nanoparticles have limited stability at elevated temperature, because the polymeric coating may become permeable. Silica coatings frequently have a porous structure and can be easily dissolved in alkaline solutions. Gold is an inert material, however, is expensive and has high density. Boron-nitride and carbon are considered as optimal encapsulating agents, because they are free from these drawbacks. They are resistant to acids, bases, greases, oils and remain stable at high temperature (up to 350–400 °C under oxygen atmosphere) [12].

Carbon-encapsulated iron nanoparticles (CEINs) are frequently studied among other carbon-encapsulated magnetic nanoparticles (e.g. Co, Ni, Fe–Nd–B). CEINs can be fabricated using a variety of synthesis routes: (i) carbon arc [13,14], thermal plasma [15], combustion synthesis [16], flame synthesis [17] and chemical vapor deposition [18]. None of these routes results is the CEIN product with a superior magnetic performance. The saturation magnetization is always lower from the theoretical value predicted from the chemical composition (i.e. the content of Fe and C). Namely, two reasons lead to the reduced magnetic performance of carbon-encapsulated iron nanoparticles. The first one is related to the presence of hollow carbon onion-like particles, which are a by-product formed after various purification processes (e.g. acid treatment). The purification is a necessary step in the synthesis protocol, because it eliminates the non-encapsulated and partially

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encapsulated magnetic nanoparticles. The second reason results directly from the phase composition of CEINs. The encapsulation of iron in carbon **always leads** to formation of three types of crystalline nanoparticles: bcc-Fe, Fe_3C and fcc-Fe [19–21]. The bcc Fe (the so-called alpha Fe) is the most common phase, because it is thermodynamically stable at room temperature and has high saturation magnetization (220 emu/g at RT). The presence of iron carbide (Fe_3C) is also acceptable, because this phase is ferromagnetic with the saturation magnetization of ca. 165 emu/g. The fcc-Fe (the so-called gamma iron) and its alloys with C (austenite) are totally undesirable constituents, because they are paramagnetic and their presence causes a substantial reduction of the inducible magnetic moment. The gamma iron and austenite are thermodynamically unstable at room temperature, however, they are frequently observed in carbon-encapsulated iron nanoparticles fabricated by various synthesis approaches [20,21]. This work aims to verify if it is possible to minimalize the content of unwanted paramagnetic phases, which are formed in CEINs fabricated via carbon arc discharge route. To realize this task it has been decided to incorporate a ferrite stabilizing agent (aluminum) in the synthesis process. The role of Al in the metallurgy of steel is known since many years. Its presence, even at low contents (above 1.5 wt.%, see Fig. S1 in Supplementary Data), hampers the formation of fcc-Fe and stabilizes the bcc-Fe related phases.

2. Experimental

Carbon-encapsulated iron nanoparticles were synthesized via carbon arc discharge route. The detailed description of the reactor is presented elsewhere [22]. The graphite rods with the diameter of 8 mm were used as cathodes. The anodes were prepared from graphite rods (8 mm in diameter). The rod was drilled (6 mm in diameter, 40 mm in length) and filled with a mixture of graphite, iron and aluminum fine powders. Five anodes with various Al content were prepared (Table 1). The carbon content was always at the same level (77.5 at.%), whilst the total content of Fe and Al was 22.5 at.%. The anodes differed with the atomic ratio between Al and Fe (the relative Al content varied between 0% and 25%). The carbon arc discharge was performed under Ar–H_2 (1:1) atmosphere at 60 kPa. The arc current was kept at 70 A. The typical arcing time was between 5 and 10 min. The erosion rate was between 4.3 and 5.5 mg s^{-1} (no correlation between Al content and erosion rate was found). The raw products were collected from the lid and inner walls of the reactor chamber. The product formation rate, which shows how much of the product is formed in a unit time, diminishes monotonically with an increase of Al content (Table 1). The raw products were subjected to the purification procedure (5 h boiling in 3 M HNO_3 with subsequent washing in water and ethanol) in order to remove the non-encapsulated metal nanoparticles. The purification yield (which visualizes the amount of the material recovered after acid treatment) was between 24% and 31% (Table 1). Similarly to the erosion rate, no correlation between Al content and purification yield was found.

The morphology was analyzed by transmission electron microscopy (TEM). The phase composition was studied by powder X-ray diffraction (Cu K-alpha radiation with a step of 0.02 °.) and Mössbauer spectroscopy. The ^{57}Fe Mössbauer measurements were performed in a transmission geometry at room temperature. A constant acceleration spectrometer with a ^{57}Co-in-Rh source of activity about 25 mCi was used. The Mössbauer spectra were fitted using the NORMOS program. A relative fraction of each spectral component was calculated as a ratio of the area of the relevant subspectrum to the total spectral area, assuming similar Debye–Waller factors for each phase. The isomer shifts were given relatively to the α-Fe standard at room temperature. Raman spectra were acquired using a 515 nm excitation laser with a resolution of 2 cm^{-1}. Thermogravimetry was performed under N_2–O_2 (4:6) atmosphere at the heating rate of 10 °C min^{-1}. Magnetic measurements were carried out using a vibrating magnetometer at room temperature. Electron energy loss spectra were acquired using a built-in Omega filter in Zeiss Libra TEM microscope.

3. Results and discussion

Fig. 1 shows the selected TEM images for the raw and purified carbon-encapsulated iron nanoparticles obtained from anodes without (#1) and with Al (#5) (Table 1). The raw products are composed of nearly uniform spherical nanoparticles (Fig. 1a and b). In the case of the sample obtained from anode #1 most of the nanoparticles have the diameter in the range 20–70 nm. The product synthesized from the anode #5 has similar morphology (Fig. 1b), however, a fraction of the particles with lower diameter is substantially higher. The representative TEM image of the purified product exhibit similar morphological features to those of the raw samples (Fig. 1c). The carbon-encapsulated iron nanoparticles are present. The metallic nanoparticles are tightly covered by carbon coatings, which have a thickness of 5–10 nm. In other words, one can say that the carbon coatings perfectly isolate the encapsulated nanoparticles and they could not be dissolved during nitric acid treatment. This observation proves that the encapsulation was successful and it qualitatively agrees with the data from Table 1 (purification yield). Additionally the purified sample contains also some amount of hollow carbon onion-like particles (Fig. 1c). The presence of this type of nanostructures authenticates that a fraction of pristinely metallic nanoparticles was encapsulated in defected carbon coatings. Importantly, each of the studied purified CEIN samples (obtained from anodes #1–#5) contain these hollow particles.

The rough analysis of the TEM images points to the fact, that the inclusion of Al influences the diameter distribution of carbon-encapsulated iron nanoparticles. Therefore, the histograms of diameter distribution (Fig. 2) for the purified CEINs were obtained (at least 300 objects on microscopic images were analyzed, the mean diameter was evaluated from the log-normal fit). The purified CEINs obtained without Al have broad diameter distribution and the largest mean diameter. Evidently, the mean diameter for CEINs synthesized with the addition of Al is ca. 2 times lower (30–33 nm). Recent studies showed that the diameter of CEINs fabricated via carbon arc discharge route is a function of Fe content in anode [23]. As a matter of fact, the Fe content in anodes #1–#5 varies between 16.9 at.% and 22.5 at.%. According to reference [23], this range of Fe content corresponds to the mean diameter between 58 and 70 nm. Hence, the observed reduction of the mean diameter in CEINs formed from anodes #2–#4 cannot be exclusively related to the changes of Fe content in the anode. Therefore, this effect is likely caused by the inclusion of Al. Indeed, the presence of Al in carbon steels results in a substantial reduction of the grain size [24,25] Obviously, the direct analogy between carbon steel and carbon-encapsulated iron nanoparticles can be far from the ideal, however, we do believe that aluminum may play the same role and may dictate the diameter distribution.

The phase composition was evaluated from powder X-ray diffractograms. Figs. 3 and 4 show the diffractograms in the 2Θ range between 35° and 55° (this range is typical for investigation of Fe-related phases, because of the presence of the strongest reflections). In general, the diffractograms look very similar for the raw and purified products obtained from the same electrode. The

Table 1
Anode composition, product formation rate and purification yield.

Anode	Carbon content (at.%)	Iron content (at.%)	Aluminum content (at.%)	Relative aluminum content (%)	Product formation rate (mg s^{-1})	Purification yield (%)
#1	77.5	22.5	0	0	1.80	24
#2	77.5	21.4	1.1	5	1.78	31
#3	77.5	20.2	2.3	10	1.66	27
#4	77.5	19.1	3.4	15	1.68	31
#5	77.5	16.9	5.6	25	1.10	24