Sonochemical synthesis of iron nitride nanoparticles

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A method for the preparation of nanoparticles of iron nitride powders is reported. Iron nitride particles have been synthesised by two methods. In the first, $Fe(CO)_5$ was sonicated in a decane solution under a gaseous mixture of NH_3 and H_2 (3.5 : 1 molar ratio) at *ca.* 0 °C. The second method was based on nitriding the sonochemically prepared amorphous iron at *ca.* 400 °C for 4 h under a mixed stream of NH_3–H_2 (3.5 : 1 molar ratio). Different products were obtained in the two cases. The product of the sonication of $Fe(CO)_5$ was amorphous $Fe_{2-3}N$ and a small quantity of iron oxide. The X-ray diffraction patterns in the second case showed Fe_4N as a main product. The magnetic properties of both products were measured. The coercive force H_C of the Fe_4N is 190 Oe, and the saturation magnetization σ_s is 170 emu g^{-1}.

The iron–nitrogen system has been the subject of study for many decades because of its remarkable mechanical and magnetic properties. Initial interest in the Fe–N system came from the nitriding of steels to improve their abrasive strength by surface hardening.[1,2] Recent interest has focused on the magnetic properties of iron nitrides, especially the high saturation magnetization and the high coercivity which are required for high-density magnetic recording. Among the published synthetic work, an almost equal number of papers describes the preparation of iron–nitride thin films[3–6] as the number devoted to the synthesis of fine particles.[7–10] In the synthesis of the thin films, methods such as thermal evaporation,[11,12] reactive sputtering,[13–15] and laser abalation[16] are employed. The iron nitride particles were synthesized by various chemical reactions, where the precursors varied from $Fe(CO)_5$ [10] to Fe_2O_3 [9] and Fe.[7,8]

The great interest in iron nitrides stems from their potential[17–21] use as magnetic recording heads and media. Iron and nitrogen, in bulk, form three metastable compounds which are stable at room temperature: Fe_8N, Fe_4N and Fe_2N.[4] Ferromagnetic iron nitride compounds (Fe_xN with $2<x<8$) have a high level of mechanical hardness, and their chemical stability is superior to that of the pure metal. In fact, their magnetic properties are what have attracted attention to these compounds. The saturation magnetization of γ'-Fe_4N, for example, is slightly lower than that of bulk iron but it is considerably higher than that of γ-Fe_2O_3. That led us to try to apply sonochemical methods for the preparation of iron nitrides.

Recently, Suslick *et al.*[22] have reported the preparation of nanostructured amorphous iron by a novel sonochemical method involving the irradiation of iron pentacarbonyl as a neat liquid or in a non-aqueous medium[23] by high-intensity ultrasound radiation. This method is based on the cavitation phenomenon, *viz.* the formation, growth, and implosive collapse of bubbles in a liquid medium.[24] The extremely high temperatures and very high cooling rates ($>10^7$ K s^{-1}) obtained during cavitation have been exploited in this method to dissociate metal carbonyl bonds to form nanophasic amorphous metals. Suslick *et al.* employed this new sonochemical method for the preparation of nanosized amorphous powders of Co and their alloys,[25,26] and metal carbide, Mo_2C.[27] Using polymeric ligands such as polyvinyl pyrrolidone (PVP) or oxide supports (alumina or silica), these nanosized clusters can be trapped as colloids or supported catalysts, respectively.[28] We have reported the preparation of amorphous Ni powder by sonochemical decomposition of nickel tetracarbonyl $Ni(CO)_4$ as a neat liquid or solution in decalin.[29] By varying the precursor $Fe(CO)_5$ concentration, we were able to control the particle size of amorphous Fe.[30] Nanosized amorphous powders of γ-Fe_2O_3 and Fe–Ni alloy were also prepared sonochemically.[31,32]

In this article we describe the synthesis of the nanocrystalline Fe_4N powder by nitriding sonochemically prepared, nanosized particles of amorphous iron powder under a mixed stream of NH_3–H_2 at 400 °C. We also show the formation of iron nitrides during sonication of $Fe(CO)_5$ decane solutions in the presence of NH_3–H_2.

Experimental

Two approaches have been employed in this investigation for the preparation of iron nitrides. In the first, the starting material was a solution of $Fe(CO)_5$ in decane. The concentration of this solution was 2.0 M. It was sonicated using high intensity ultrasound radiation for 4 h by employing a direct immersion titanium horn (Sonics and Materials, VC-600, 20 kHz, 100 W cm^{-2}). The sonication was carried out under a stream of ammonia and hydrogen. The flow rate of this mixture was 130 cm^3 min^{-1}, and the ratio of the partial pressures of NH_3 : H_2 was 3.5 : 1 [H_2 (Gordon Gas, 99.995%) and NH_3 (BOC Gases, anhydrous, 99.995%)]. The sonication cell was kept immersed in a dry ice–acetone mixture, yielding a temperature of *ca.* 0 °C inside the sonication cell. At the end of the irradiation, the resulting solid product was washed thoroughly with dry pentane and centrifuged. This process was repeated four times. The product was then dried under vacuum and kept in a glove box (< 10 ppm O_2). In the second synthetic method, the starting material was amorphous iron nanoparticles, which were obtained following Suslick's method.[22,23] Amorphous iron (100 mg) was introduced into a furnace through which a mixture of NH_3 and H_2 was passed at a flow rate of 100 cm^3 min^{-1}. The amorphous iron was kept at 400 °C, and the molar ratio of ammonia : hydrogen was 3.5 : 1. The reaction took 4 h to reach completion under these conditions; Fe_4N was the only product in the latter case, while a mixed valency compound, $Fe_{2-3}N$ (small amounts of Fe_3O_4 were also detected), was obtained in the former preparation.

In the first case, the product ($Fe_{2-3}N$) was obtained in the amorphous form, while the second method yielded nanocrystalline Fe_4N as the final product as a consequence of the reaction temperature.

Iron pentacarbonyl (Aldrich) was filtered before use. Decane (Fluka) was dried with molecular sieves prior to its use.

Powder X-ray diffractograms were recorded on Rigaku X-ray diffractometer (Cu-Kα radiation, $\lambda = 0.154\,18$ nm). Scanning electron micrographs and energy dispersive X-ray analysis (EDX) were carried out on a JEOL-JSM-840 electron microscope. Transmission electron micrographs were obtained with a JEOL-JEM100SX electron microscope. Magnetization loops were measured at room temperature using an Oxford Instruments Vibrating Sample Magnetometer. Surface area (BET method) was measured on a Micromeritics-Gemini surface area analyzer, using nitrogen gas adsorption. Mössbauer spectra were measured by a standard constant acceleration spectrometer with a 25 mCi ^{57}Co(Rh) source.

Results

The identification of the products obtained *via* the two preparation methods was carried out by XRD measurements. In Fig. 1 and 2, the X-ray diffraction patterns of the products obtained by the two methods described above are presented. The first method, *i.e.*, the sonication of $Fe(CO)_5$ under a NH_3–H_2 gas mixture, yields an amorphous material, as shown by the XRD. This product was further heat-treated to convert it to the crystalline form. It was heated to 400 °C for 3 h under a flow of an NH_3–H_2 gas mixture ($NH_3 : H_2$ ratio was 3.5 : 1 and flow rate 100 cm^3 min^{-1}). Only diffraction peaks belonging to the $Fe_{2-3}N$ composition (*d*-spacing 2.33, 2.16, 2.05, 1.6 and 1.36 Å) and iron oxide (*d*-spacing 2.49 and 1.47 Å) can be detected in this figure. The X-ray pattern of the $Fe_{2-3}N$ compound is different from that of Fe_3N or of the Fe_2N patterns. This is a unique phase, which is frequently assigned as $Fe_{2-3}N$,[33] or ε-$Fe_{2.3}N$.[34] The iron oxide which is obtained as a minor impurity is assigned as fitting the Fe_3O_4 structure. It is worth noting that Fe_3O_4 as an impurity is also obtained when $Fe(CO)_5$ and ammonia undergo laser pyrolysis in an argon containing cell.[35] In this case the main products are γ′-Fe_4N and γ-Fe, and their ratio varies as a function of the reaction temperature. Fe_3O_4, on the other hand, is observed at all temperatures.[35]

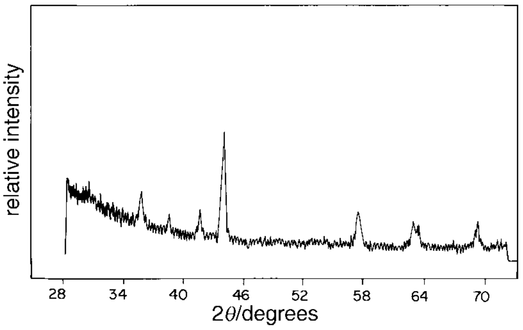

Fig. 1 X-Ray diffraction pattern of the product ($Fe_{2-3}N$), prepared by sonication of a 2.0 M solution $Fe(CO)_5$ in decane under an NH_3–H_2 mixture ($NH_3 : H_2$ ratio 3.5 : 1, flow rate 100 cm^3 min^{-1}) for 4 h, then heated under the same gas mixture at 400 °C for 3 h

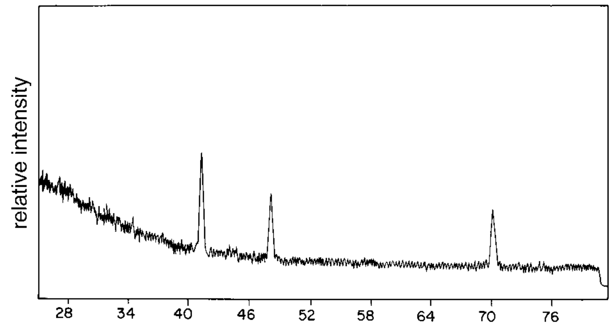

Fig. 2 X-Ray diffraction patterns of the product (Fe_4N), prepared by heating of the amorphous iron powder at 400 °C for 4 h under a mixed stream of NH_3 and H_2 ($NH_3 : H_2$ ratio 3.5 : 1, flow rate 100 cm^3 min^{-1})

Unlike the first method, which yielded a mixed valency iron nitride, $Fe_{2-3}N$, and an impurity of an iron oxide, the application of the second method led to only one product, γ-Fe_4N, (*d*-spacing 2.19, 1.90 and 1.34 Å) with no evidence from XRD for the existence of other iron nitrides, Fe_2O_3, or Fe (Fig. 2). In fact, this is not surprising, since this observation is similar to that reported by Tagawa and coworkers.[8] The only difference is that, owing to the small particle size and the amorphous state of the iron, a faster reaction will be observed using our method.

The TEM picture of Fe_4N is presented in Fig. 3 and shows the composites of small particles (30–50 nm) which are agglomerated due to the magnetic forces acting between the particles. The crystalline nature of the particles is clearly observed. The surface area of this powder is 40.6 m^2 g^{-1} (by BET). The size of the amorphous iron particles which serve as the precursor to the synthesis of Fe_4N is about 10–20 nm.[22,30]

In comparison to the results presented in ref. 22 and 30, the TEM results show that the reaction that takes place at an elevated temperature causes further agglomeration. This is also demonstrated by the surface area value. The product of the sonication process is always an amorphous material, and we have detected a drop of 2–3 in the surface area in the conversion of the amorphous material to the crystalline state.

Fig. 4 shows the room temperature magnetization loop of the Fe_4N powder. The coercive force H_C of the Fe_4N is 190 Oe and the saturation magnetization $\sigma_s = 170$ emu g^{-1}. Various values can be found in the literature for the saturation magnetization and the coercive force. Previous investigations report σ_s values of 58.6 emu g^{-1} ($H_C = 500$ Oe),[35] 120 emu g^{-1} ($H_C = 670$ Oe),[36] 160 emu g^{-1} ($H_C = 1000$ Oe),[9] 180 emu g^{-1} ($H_C = 600$ Oe)[7] and 193 emu g^{-1} ($H_C = 640$ Oe).[8] As is evident from Fig. 4, the magnetization is not saturated even at 15 kG. This is due to the small size of the particles. Although the TEM picture reveals typical sizes of 30–50 nm, it is believed that the individual particles might be smaller and only because of the

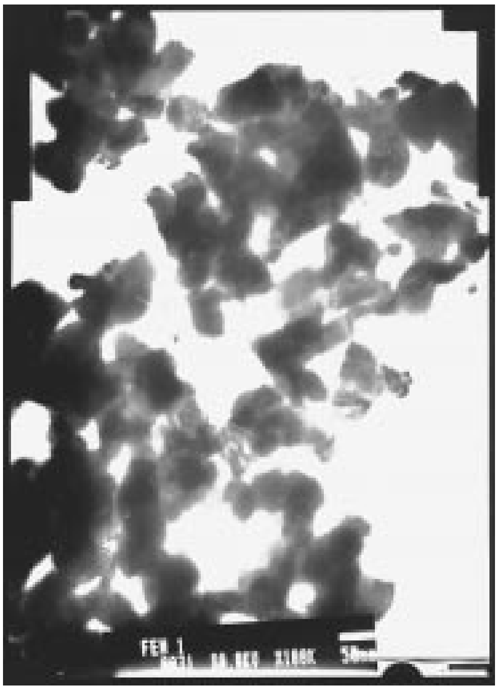

Fig. 3 TEM picture of Fe_4N, prepared by heating of the amorphous iron powder

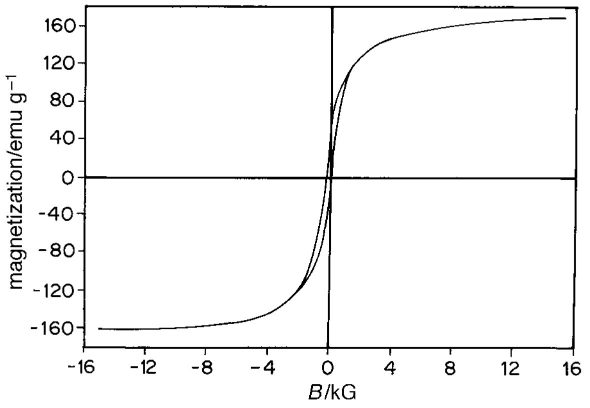

Fig. 4 Room-temperature magnetization loop of the Fe_4N powder, prepared by heating amorphous iron

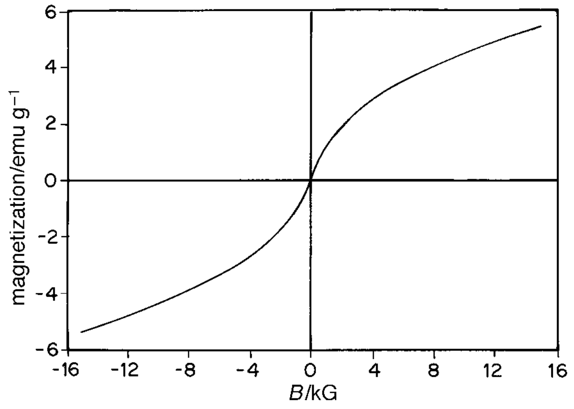

Fig. 5 Room-temperature magnetization loop of the amorphous material obtained by sonication of the $Fe(CO)_5$ solution in decane under a mixed stream of NH_3 and H_2

agglomeration do they appear in these sizes. In this situation thermal fluctuations randomize a magnetic moment of each particle, leading to a paramagnetic like response at higher fields. This might be the reason why the saturation magnetization is somewhat smaller than in ref. 7 and 8. In Fig. 5 and 6, we present the room-temperature magnetization loops of the amorphous product of the $Fe(CO)_5$ sonication, and the crystalline $Fe_{2-3}N$ obtained after its heating, respectively. The magnetization of the amorphous form does not show hysteresis and does not saturate. This is behavior typical for a superparamagnetic material. The explanation for this behavior is attributed to the small particle size of the as-prepared amorphous product, unlike the crystalline Fe_4N, which is a result of an elevated temperature reaction between amorphous iron and ammonia. The conversion of the amorphous material to the crystalline phase causes a drastic change in the magnetic properties, where the magnetization at 15 kG is raised from 5.5 to 80 emu g^{-1}. This change is also reflected in the detection of hysteresis.

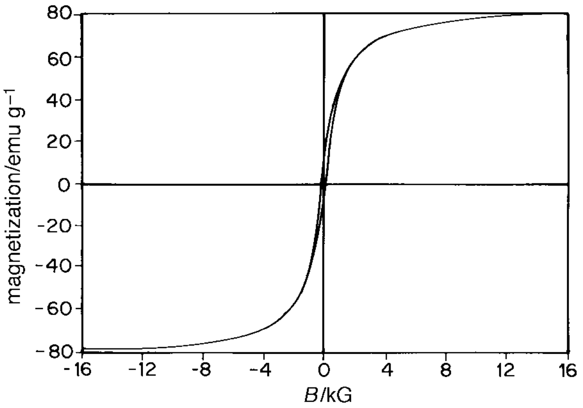

Fig. 6 Room-temperature magnetization loop of the crystalline $Fe_{2-3}N$ powder, prepared by heating the amorphous product of the sonication of the $Fe(CO)_5$ solution in decane

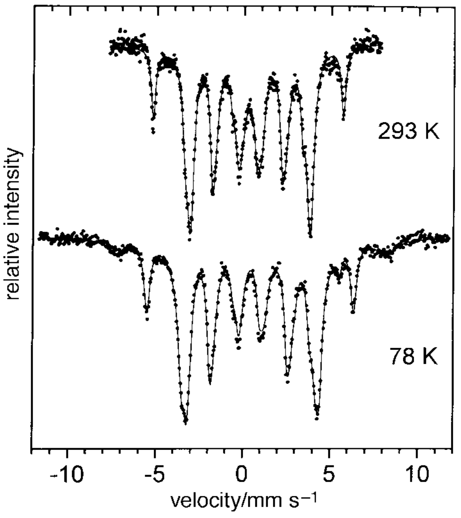

Fig. 7 Mössbauer spectra of the Fe_4N powder, prepared by heating the amorphous iron powder

The XRD pattern of the product obtained by the second method (Fig. 2) shows only one phase, γ-Fe_4N (d-spacing 2.19, 1.90 and 1.34 Å), with no evidence for the existence of other iron nitrides, Fe_2O_3 or Fe. The Mössbauer spectra, however, revealed a small amount of other phases, too. The Mössbauer spectra of the product, obtained by the second method, are shown in Fig. 7. Mössbauer parameters measured at 78 and 293 K are summarized in Table 1. According to these parameters, Fe_4N can be identified as the main product, containing about 83% of the iron atoms. The broad sextet, with a 47.7 T hyperfine field at 78 K, is amorphous Fe_2O_3, which is super-

Table 1 Mössbauer parameters of the product obtained by the second method

temperature/K	hyperfine field/T	isomer shift/mm s^{-1}	quadrupole splitting/mm s^{-1}	linewidth/mm s^{-1}	relative amount (%)	phase
78	36.8	0.38	0.03	0.37	18	Fe_4N
	23.9	0.41	−0.17	0.55	43	
	23.8	0.45	0.27	0.35	22	
	47.7	0.59	−0.20	1.18	13	amorphous Fe_2O_3
293	31.8	0.35	0.10	0.41	4	$Fe_{1-x}N_x$
	33.9	0.22	0.01	0.31	18	Fe_4N
	21.9	0.29	−0.18	0.51	39	
	21.6	0.31	0.19	0.36	31	
	0	0.35	0.94	0.87	12	amorphous Fe_2O_3

paramagnetic at room temperature. The Mössbauer parameters agree well with those measured on pure amorphous Fe_2O_3 prepared by the sonochemical method.[30,31] The Mössbauer spectra at 78 K reveal a third component, most probably an iron nitride, but the amount (*ca.* 4%) is too small to be identified.

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