

Iron carbide nanoparticles produced by laser ablation in organic solvent

T. Matsue · Y. Yamada · Y. Kobayashi

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Abstract Laser ablation of iron in an organic solvent (pentane, hexane, or decane) was performed using an air-tight cell to produce iron carbide nanoparticles. Mössbauer spectra of the nanoparticles were obtained at room temperature. They revealed that the nanoparticles consisted of two paramagnetic components and magnetic components. The two paramagnetic components were a high-spin Fe(II) species and an amorphous iron carbide containing a large amount of carbon. Whereas the magnetic components measured at room temperature exhibited superparamagnetism, those measured at low temperature were fitted by a combination of four sextets, which were assigned to Fe_7C_3 . The Fe_7C_3 yield was higher in higher molecular weight solvents. Transmission electron microscopy (TEM) images of the samples showed that the nanoparticles were spherical with diameters in the range 10–100 nm.

Keywords Laser ablation in solvent · Iron carbide · Nanoparticles · Mössbauer spectroscopy · Transmission electron microscopy

1 Introduction

Iron carbides have been extensively investigated because of their various useful industrial applications. Whereas iron-based materials such as ferrite, austenite, martensite, and cementite (Fe_3C) are well understood, Hägg (Fe_5C_2) and Eckstrom–Adcock (Fe_7C_3) carbides, which are metastable iron carbides, are less well understood. Fe–C compounds have recently attracted renewed interest because Fe was

T. Matsue (✉) · Y. Yamada
Graduate School of Chemical Science and Technology,
Tokyo University of Science, Tokyo, Japan
e-mail: ta_matue@yahoo.co.jp

Y. Kobayashi
RIKEN, Tokyo, Japan

found to catalyze the synthesis of carbon nanotubes [1, 2]. Fe-C core-shell structured nanoparticles were also investigated [3, 4]. Fe_3C and Fe_7C_3 nanoparticles have been produced by CO_2 laser pyrolysis of a vapor mixture of $\text{Fe}(\text{CO})_5$ and C_2H_4 [5]. Iron carbides with high carbon contents were synthesized by mechanical alloying of iron and graphite powders; Mössbauer measurements revealed that Fe_3C and Fe_7C_3 were produced [6].

Nanoparticles produced by laser ablation of a solid metal in a liquid are expected to exhibit unique physical and chemical properties due to size effects. Noble metal nanoparticles such as gold nanoparticles have been extensively investigated [7, 8]. Laser ablation of Cu metal in water produced a mixture of amorphous and crystalline Cu_4O_3 nanoparticles [9]. The conventional method for producing metal or metal compound nanoparticles is laser ablation of a metal in a solvent. In this study, we produced iron carbide nanoparticles by laser ablation of Fe metal in organic solvents.

Most experiments involving laser ablation in solvents employ open-air conditions in which the target material is placed at the bottom of a vial filled with a solvent and the surface of the solvent is in contact with air. When laser light is irradiated through the surface of the solvent to the Fe metal sample at the bottom of the glass vial, bubbles produced by laser ablation disturb the surface, destabilizing the focal point and causing iron oxide to be produced because of dissolved air in the solvent. Therefore, we designed an air-tight cell to perform laser ablation under stationary conditions in inert gas atmosphere and to prevent the nanoparticles from being oxidized. A convex lens was directly attached to the side of the cell contacting the liquid and Ar gas was used to fill the space at the top of the cell.

2 Experiment

100 mL of an organic solvent (hexane, pentane, or decane), which had been degassed prior to use, was placed in the cell and a metal iron sample was placed in it. Ar gas was used to fill the space above the liquid surface to prevent oxidation. Laser ablation was performed for 18 h using a Nd:YAG laser (Continuum, Surelite I-10; wavelength: 532 nm; pulse repetition rate: 10 Hz; pulse energy: 190 mJ). The laser light was introduced through the convex lens attached to the cell. The produced nanoparticles were collected after removing the solvent and they were analyzed by Mössbauer spectroscopy. Transmission electron microscopy (TEM) images were obtained (Hitachi, H-9500 operated at 200 kV) from a sample prepared by placing a drop containing nanoparticles onto a 200-mesh copper grid coated with a collodion film.

3 Results and discussion

Iron carbide nanoparticles were produced by laser ablation of a Fe metal block in an organic solvent (pentane, hexane, or decane) and their Mössbauer spectra were measured (Fig. 1). The Mössbauer spectrum of the nanoparticles produced in pentane measured at 293 K (Fig. 1a) had a paramagnetic doublet as the dominant absorption. The spectrum was fitted by two doublets and a broad absorption. One of the paramagnetic doublets ($D1$: $\delta = 0.35$ mm/s and $\Delta E_Q = 0.96$ mm/s) was assigned to

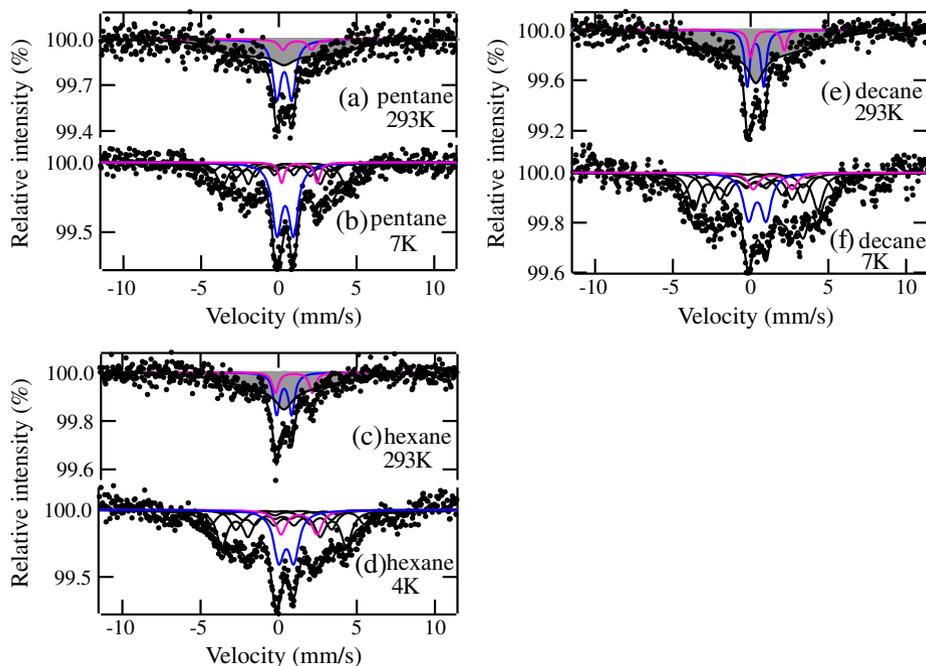


Fig. 1 Mossbauer spectra of nanoparticles produced (a) in pentane measured at 293 K, (b) in pentane measured at 7 K, (c) in hexane measured at 293 K, (d) in hexane measured at 4 K, (e) in decane measured at 293 K, and (f) in decane measured at 7 K

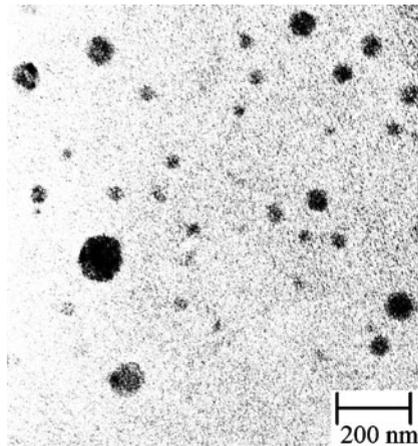
amorphous iron carbides containing a large amount of carbon. Species with similar Mössbauer parameters were also found in previous studies of laser deposition of iron carbides [10] and ball milling [6]. The other doublet (D2: $\delta = 1.19$ mm/s and $\Delta E_Q = 1.84$ mm/s) was a high-spin Fe(II) species and has not been reported in other studies. This species has not been assigned yet; it may be an organometallic compound containing Fe^{II}-C chemical bonds. The broad absorption was attributed to a magnetic component exhibiting superparamagnetism, which was fitted by assuming it has a single relaxation time using Wickman's formula [11]. The same sample was measured at a low temperature of 7 K (Fig. 1b); the two paramagnetic doublets were almost the same in the spectra obtained at 7 and 293 K, whereas the magnetic components became sharper at the lower temperature. The absorption of the magnetic component was fitted assuming a distribution of hyperfine magnetic fields in the range of 100 to 310 kOe, and the distribution coincided with the combination of four sets of sextets of Fe₇C₃ [5]. Therefore, the absorption of the magnetic component was fitted by the combination of four sets of sextets, in which absorption peaks had relatively large half width because of the defects in Fe₇C₃. Iron oxides were not produced in the present study as we employed an air-tight cell. Similar experiments were performed using organic solvents of hexane (Figs. 1c and d) and decane (Figs. 1e and f). The obtained particles were almost independent of the solvent used. However, the yields of the species varied slightly with the solvent.

Table 1 Mössbauer parameters of nanoparticles produced in organic Solvents

Solvents		Measured at 293 K				Measured at low temperature (7 K, 4 K)		
		δ (mm/s)	ΔE_q (mm/s)	τ (ns)	Yields (%)	δ (mm/s)	ΔE_q (mm/s)	Yields (%)
Pentane	D1	0.35(2)	0.96(3)		34	0.41(2)	1.06(3)	34
	D2	1.19(9)	1.84(18)		6	1.33(3)	2.29(7)	6
	Fe_7C_3^*			7.8	60			60
Hexane	D1	0.34(4)	0.95(8)		22	0.41(2)	1.14(4)	22
	D2	0.98(23)	2.30(43)		11	1.16(5)	2.12(9)	11
	Fe_7C_3^*			4.2	67			67
Decane	D1	0.31(1)	1.06(2)		19	0.43(5)	1.13(8)	19
	D2	1.09(2)	2.15(5)		7	1.42(9)	2.50(20)	7
	Fe_7C_3^*			5.0	74			74

* Mössbauer parameters of Fe_3C_3 are fixed according to the literature [5]. site I: $\delta = 0.56$ mm/s, $\Delta E_q = 0.05$ mm/s, $H = 303$ kOe; site II: $\delta = 0.27$ mm/s, $\Delta E_q = -0.05$ mm/s, $H = 212$ kOe; site III: $\delta = 0.29$ mm/s, $\Delta E_q = 0.08$ mm/s, $H = 190$ kOe; site IV: $\delta = 0.35$ mm/s, $\Delta E_q = 0.00$ mm/s, $H = 247$ kOe

Fig. 2 TEM image of nanoparticles produced by laser ablation of Fe in decane



Nanoparticles produced in larger molecular weight solvents had higher Fe_7C_3 yields (Table 1). TEM images of the nanoparticles produced in the organic solvents were obtained. Figure 2 shows a TEM image of the nanoparticles produced in decane. Spherical nanoparticles were produced with diameters in the range 10–100 nm.

4 Conclusions

Iron carbide nanoparticles were produced by laser ablation in organic solvents in stationary condition in inert gas atmosphere using a newly designed cell. The products were assigned to amorphous iron carbides containing a large amount of

carbon: the high-spin Fe(II) species and metastable Fe₇C₃. Iron oxide was not found in the nanoparticles. The nanoparticles exhibited superparamagnetism at room temperature due to their small size (10–100 nm). A high-spin Fe(II) species was found that had not been reported in previous studies.

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