

Effect of laser irradiation on iron carbide nanoparticles produced by laser ablation in ethanol

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Abstract Laser ablation in liquid is a useful mean of producing nanoparticles, based on both laser ablation (LA) and laser irradiation (LI) effects. In order to investigate the mechanism by which iron carbide nanoparticles are generated in ethanol, iron carbide nanoparticles were produced by LA of an iron block in a flowing ethanol solvent, which enabled separation and collection of the nanoparticles immediately following the process. These same particles were subsequently subjected to LI while suspended in stagnant ethanol. Both the LA and LA/LI nanoparticles were assessed using Mössbauer spectroscopy, X-ray diffraction and transmission electron microscopy. LA in flowing ethanol was found to produce nanoparticles composed of cementite (Fe₃C) and other metastable iron carbides with an average size of 16 nm, dispersed in amorphous carbon. LI of the LA nanoparticles suspended in ethanol increased the particle size to 38 nm and changed the composition to pure Fe₃C.

Keywords Iron carbide \cdot Nanoparticle \cdot Mössbauer spectroscopy \cdot Laser ablation in liquid \cdot Laser irradiation

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1 Introduction

Laser ablation in liquid (LAL) has been studied extensively as a technique for the synthesis of metal compound nanoparticles. Several groups have reported the formation of nanoparticles of iron carbide by LAL, employing an iron target in organic solvent, and have found that the most stable product is cementite (Fe₃C) [1–3]. The production of amorphous or metastable iron carbides by LAL is not yet well understood. However, because a high-density plasma vapor is rapidly quenched by the surrounding solvent in this method, metastable products might be preferentially obtained. Mössbauer spectroscopic analysis is a powerful tool for the investigation of the chemical states of iron carbide phases have been studied using this technique [4], even though the mechanism by which these compounds are obtained is not well understood.

LAL is typically performed in a stagnant solvent. However, if the particles remain suspended in the solvent, they can deteriorate as a result of prolonged laser irradiation, due to the effects of laser ablation (LA) and/or laser irradiation (LI). In a previous study, we carried out LAL syntheses using a cell with a circulating solvent to obtain particles produced solely by LA, and these products were compared with particles obtained using a stagnant solvent. It was found that the products of these two processes were different because of the LI of the particles suspended in the stagnant solvent [5].

In the present study, particles produced by LA and LA particles further modified by LI were analyzed separately in order to understand the LAL mechanism. The LA particles were prepared by LAL using a cell with flowing ethanol. Following the analysis of these particles, they were again dispersed in ethanol solvent and irradiated with laser light to obtain LA/LI particles.

2 Experimental

The procedure used to produce the iron carbide nanoparticles by LA in this study was almost the same as that described in our previous paper [5]. The cell used to generate nanoparticles was composed of an airtight vessel, a cellulose acetate filter (pore size: 0.45 μ m), a threenecked flask and a diaphragm pump. Prior to use, 200 mL of ethanol was degassed and transferred to the three-necked flask, after which an iron block (57Fe enriched) was placed in the solvent and the vessel headspace was replaced with argon to prevent oxidation. The interior of the vessel was maintained at atmospheric pressure using a balloon attached to the three-necked flask. LA was performed for 30 min with a Nd:YAG laser (Continum, Surelite I-10; $\lambda = 532$ nm; repetition rate: 10 Hz; pulse energy: 100 mJ; pulse width: 5 ns). The laser beam was introduced through a convex lens directly attached to the glass vessel and, during the LA, the solvent was kept in motion at a flow rate of 450 mL min⁻¹ using the diaphragm pump. The nascent LA particles, present as a black precipitate, were collected on the filter. The effects of LI on these iron carbide nanoparticles in a stagnant solvent were also investigated. The LA particles were again suspended in degassed ethanol and the solution was placed in the glass vial and irradiated with non-focused laser light for 3 h. The resultant LI particles were collected by centrifugation and filtration through a cellulose acetate filter. Both the LA and LI products were investigated using Mössbauer spectroscopy (Wissel, MDU1200, ⁵⁷Co/Rh source), X-ray diffraction (XRD; Rigaku, RINT2500, Cu-Kα, operated at 50 kV/300 mA) and transmission electron microscopy (TEM; JEOL, JEM-2100, operated at 200 kV).



Fig. 1 a TEM image, b HR-TEM image, and c particle size distribution of nanoparticles produced by LA in flowing ethanol

3 Results and discussion

TEM and HR-TEM images of the LA particles are presented in Fig. 1a and b, respectively, showing that the particles had a spherical shape and were surrounded by amorphous carbon. A graphite shell was also observed at the interfaces between the particles and the amorphous carbon, with an interplanar distance, d, of 0.35 nm (as determined from the HR-TEM image). This amorphous carbon was generated by solvent decomposition during the LA. The particle size distribution is shown in Fig. 1c. The particle sizes ranged between 5 and 50 nm, with an average size of 16 nm.

The TEM image of the LI particles (Fig. 2a) demonstrates that the particles were spherical with a less homogeneous particle size distribution than the LA particles. The particle size distribution (Fig. 2b) became wider (ranging from 5 to 100 nm), and there were no LI particles smaller than the original LA particles. The average particle size also increased to 38 nm. It has been reported that laser fragmentation and laser melting occur during the LI of a colloidal solution, which would be expected to decrease and increase the particle size, respectively [6]. In the current work, it appears that laser melting occurred during LI because the LI particles were larger than the LA particles. During the laser melting process, fine particles are instantaneously heated by the pulsed laser light and adjacent particles consequently aggregate. In addition, because the temperature at the particle surfaces will vary depending on the energy density of the laser, it has been reported that the particle size can be adjusted [7, 8]. However, in these experiments, the particle size became inhomogeneous with a wider distribution. Because the starting material (the LA particles) was a mixture of iron carbide and amorphous carbon, aggregation would have been associated with chemical reactions between iron carbides and carbon atoms, such that the LI particles were not heated homogeneously.



Fig. 2 a TEM image and b particle size distribution of nanoparticles produced by LI of the LA particles suspended in ethanol



Fig. 3 XRD patterns obtained from a LA particles and b LI particles. Bars in the figure denote Fe₃C (PDF #00-035-0772)

XRD patterns of the LA particles (Fig. 3a) and LI particles (Fig. 3b) exhibit somewhat weak peaks corresponding to cementite (Fe₃C, PDF #00-035-0772). The LA particles were evidently too small to generate clear XRD peaks, whereas the larger LI particles produced a relatively clear XRD pattern.

Mössbauer spectra of the LA and LI particles were acquired to determine the compositions of the amorphous and minimally crystalline regions that were not observable in the XRD patterns. Mössbauer spectra of the LA particles obtained at 293 and 8 K are shown in Fig. 4, and the associated parameters are summarized in Table 1. The Mössbauer spectrum acquired at 293 K (Fig. 4a) was fitted to give a combination of a doublet, two sextets, and a component corresponding to a distributed hyperfine magnetic field (DHMF). One of the sextets, which had a small hyperfine magnetic field value, H, of 20.7 (1) T was assigned to Fe₃C, and the DHMF with a mode at H = 20 T was assigned to Fe₃C having lattice defects. This result was very similar to data for Fe₃C in a previous report [9]. Lattice defects would have resulted from rapid quenching during the LAL process. The paramagnetic doublet was assigned to small LA particles or to Fe atoms surrounded by a large number of lattice defects, having a blocking temperature below 293 K. The other sextet had a larger Hvalue of 26.4(1) T compared to that of Fe₃C. In our previous study, this spectral component was assigned to a so-called "Fe-C alloy" composed of a metallic iron lattice containing a



Fig. 4 Mössbauer spectra of LA particles acquired at **a** 293 and **b** 8 K. The distributions of hyperfine magnetic fields are indicated on the right side

Temperature	Component	$\delta \ { m mm~s^{-1}}$	$\Delta E q$ mm s ⁻¹	H T	Γ mm s ⁻¹	Yields %
293 K	Fe ₃ C	0.17(1)	0.09(3)	20.7(1)	0.76(3)	26
	Fe ₄ C	0.18(1)	-0.06(3)	26.4(1)	1.08(3)	34
	Fe ₃ C(DHMF)	0.17(1)	-0.07(2)	20 ^a		31
	Fe ₃ C(SPM)	0.26(2)	1.13(3)		0.88(6)	10
8 K	Fe ₃ C	0.34(2)	-0.00(4)	25.5(2)	0.79(8)	27
	Fe ₄ C	0.31(2)	0.03(4)	29.9(2)	0.89(8)	30
	Fe ₃ C(DHMF)	0.30(1)	0.02(2)	24 ^a		43

Table 1 Mössbauer parameters of the spectra shown in Fig. 4

^aHyperfine magnetic field at the mode of the distribution

small number of carbon atoms and having a lower H value than that of α -Fe [5]. However, it is also conceivable that this material was a metastable iron carbide phase.

The Mössbauer spectrum of the LA particles at 8 K (Fig. 4b) was fitted to give a combination of two sextets and a DHMF component. One of the sextets (H = 25.5(2) T) and the DHMF (mode at H = 24 T) were assigned to pure Fe₃C and Fe₃C having lattice defects, respectively. At low temperature, these values were almost identical to those of Fe₃C in a previous report [9]. Although the paramagnetic doublet disappeared at 8 K, the sum of the area intensities of the doublet and DHMF at 293 K (41%) was almost the same as the proportional area of the DHMF at 8 K (43%). The smaller particles (or Fe atoms surrounded by lattice defects) that generated a doublet at 293 K evidently became part of the DHMF at 8 K because of a blocking temperature above 8 K. The second sextet had a larger H value of



Fig. 5 Mössbauer spectra of LI particles acquired at a 293 and b 3 K. The distributions of hyperfine magnetic fields are indicated on the right side

29.9(2) T compared to that of Fe₃C. Recently, the Mössbauer parameters of metastable iron carbides were predicted on the basis of density functional theory calculations [10], and the parameters determined for Fe₄C were almost the same as for the sextet in the present work. Fe₄C has a structure in which carbon atoms are situated in an fcc austenite γ -iron structure that is stable at high temperatures [11, 12]. It is believed that Fe₄C was not observed in the XRD patterns obtained in this work because the particle sizes were too small.

The Mössbauer spectra of the LI particles obtained at 293 and 3 K are shown in Fig. 5, and the associated Mössbauer parameters are summarized in Table 2. The Mössbauer spectrum at 293 K (Fig. 5a) was fitted to give a combination of a sextet (H = 20.7(6) T) attributed to Fe₃C and a DHMF (mode at H = 19 T) ascribed to Fe₃C having lattice defects. The paramagnetic doublet is not present in this spectrum because of the aggregation and crystal growth induced by LI. The Fe₄C also disappeared as the reaction between Fe₄C and the amorphous carbon covering the particles was induced by LI to produce stable Fe₃C. The spectrum at 3 K (Fig. 5b) also shows the presence of Fe₃C (H = 25.7(2) T) and a DHMF (mode at H = 19 T), although the DHMF distribution is narrower than that of the LA particles.

It has been reported that applying pulsed laser irradiation to a colloidal solution causes the particles to degrade due to localized heating. In the case of laser melting, in particular, the particle size can be tuned by varying the pulse energy to give instantaneous temperatures on the order of several thousand K [8]. In this study, the iron carbide nanoparticles were found to melt and agglomerate and the associated instantaneous heating also induced reactions that formed stable Fe_3C . The data demonstrate that LI enhanced both the aggregation and the chemical reactions so as to stabilize the LA particles. In the conventional LAL method using a stagnant solvent, the particles are exposed to the effects of both LA

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Temperature	Component	$\delta \ { m mm} \ { m s}^{-1}$	$\Delta E q$ mm s ⁻¹	H T	Γ mm s ⁻¹	Yields %
(a) 293 K	Fe ₃ C	0.18(1)	0.02(2)	20.7(6)	0.66(1)	59
	Fe ₃ C(DHMF)	0.19(1)	0.03(3)	19 ^a		41
(b) 3 K	Fe ₃ C Fe ₃ C(DHMF)	0.31(3) 0.28(1)	0.11(6) -0.02(2)	25.7(2) 25 ^a	1.04(3)	55 45
	2 ()	- ()	- ()			

 Table 2
 Mössbauer parameters of the spectra shown in Fig. 5

^aHyperfine magnetic field at the mode of the distribution

and LI. Thus, in order to obtain metastable LA particles, it is important to eliminate the effects of LI.

4 Conclusion

The effects of LA and LI during the production of iron carbide particles in ethanol were studied. The LA particles generated in flowing ethanol were found to be spherical with a 16 nm average diameter, and were covered in graphite. These particles were composed of both pure Fe_3C and metastable Fe_4C , with some portion of the Fe_3C having a large number of lattice defects. The LI particles were obtained by LI of LA particles suspended in stagnant ethanol, and consisted of stable Fe_3C nanoparticles with a larger average diameter of 38 nm. LI was found to induce particle aggregation as a result of laser melting and also reaction of the metastable Fe_4C to form stable Fe_3C . The results of this study demonstrate that it is important to suppress the effects of LI in order to obtain metastable species by LA.

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