Iron carbide films produced by laser deposition

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Abstract. Iron carbide films were produced by laser deposition of iron atoms onto aluminium substrates in an acetylene atmosphere. Gas-phase reaction of energetic Fe atoms with C₂H₂ yielded Fe/C particles as well as Fe and C atoms. The subsequent reaction on the Al substrate surface produced iron carbide films. The compositions of the films were measured using Mössbauer spectroscopy. The films produced in low-pressure C₂H₂ were mainly composed of Fe₇C₃ and Fe₃C, while the films produced in high-pressure C₂H₂ were composed of paramagnetic amorphous Fe-C. When the temperature of the Al substrate was increased, formation of crystalline Fe₇C₃ and Fe₃C was enhanced. The composition of iron carbide films was controlled both by the pressure of C₂H₂ and the temperature of the Al substrate. X-ray diffraction patterns and scanning electron micro spectroscopy was also applied to confirm the assignments.

1. Introduction
Iron carbides (Fe-C) have been extensively studied because of their various useful industrial applications. Iron-based materials such as ferrite, austenite, martensite, and cementite Fe₃C are well understood. Hägg (Fe₅C₂) and Eckstrom-Adcock (Fe₇C₃) carbides are known as metastable iron carbides. Recently, Fe-C compounds have attracted renewed attention because Fe was found to catalyze the synthesis of carbon nanotubes [1,2]. Nanocrystalline iron carbide particles, Fe₃C and Fe₇C₃, were produced by CO₂ laser pyrolysis of a vapor mixture of Fe(CO)₅ and C₂H₄ [3]. Iron carbide films have been formed by plasma-enhanced chemical vapor deposition introducing Fe(CO)₅ and H₂ [4]. Mechanical alloying of iron and graphite powders was found to yield iron carbides with high carbon content, and Mössbauer measurements show that Fe₃C and Fe₇C₃ were produced [5].

Laser deposition is a useful technique to produce films with controlled composition. We have previously reported the characteristics of iron films [6] and iron oxide films produced by laser deposition [7]. Laser ablation of Fe metal produces metal vapour consisting of Fe atoms having high translational energy and electronically excited states; the Fe atoms can react with any reactant gases that may be present. Unstable species or particles produced in a gas phase are deposited on a substrate and lose energy to the substrate to form films. Thus, the laser deposition technique associated with gas phase reaction can produce iron carbide species unobtainable under normal conditions. The formation of films containing metastable compounds is an attractive aspect of this technique. Here, we report the study of iron carbide films with various Fe/C composition ratios using laser deposition. Fe atoms were produced by laser ablation in a C₂H₂ atmosphere. The films were characterized using Mössbauer
spectroscopy and X-ray diffraction (XRD). The surface morphology was observed using scanning electron micro spectroscopy SEM.

2. Experimental
Laser light from a YAG laser (NewWave, TEMPEST 10, 532 nm, 100 mJ/pulse, 5 ns, 2 Hz) was focused by a convex lens onto the target $^{57}$Fe metal block in a C$_2$H$_2$ atmosphere. Laser-evaporated Fe atoms react with C$_2$H$_2$ in the gas-phase and form an iron carbide film by deposition onto an Al substrate. The temperature of the substrate was maintained at the desired temperature (300–600 K range) using a resistive heater. The amount of vaporized Fe atoms was estimated by weighing the samples before and after the laser deposition. One pulse of laser ablation produces $4 \times 10^9$ mol of Fe atoms, and the thickness of the laser-deposited films was controlled by varying the number of laser pulses. A film was produced by accumulating 14,400 laser pulses in order to obtain thick enough films to measure Mössbauer spectra. Mössbauer spectra of the Fe-C films on the Al substrates at room temperature were measured in a transmission geometry using a $^{57}$Co/Rh source. X-ray diffraction patterns of the films were obtained using RINT2500 (RIGAKU, Cu-K$_\alpha$). The surface morphology of the films was observed using a scanning electron microscope (S-500 HITACHI).

3. Result and Discussion
Laser deposition of Fe onto Al substrates at 600 K was carried out by varying the pressure of the C$_2$H$_2$ atmosphere to produce iron carbide films. The Mössbauer spectra of the films are shown in figure 1. The composition of the films varied depending on the C$_2$H$_2$ pressure. The film formed at the lowest pressure of 1.0 Pa (figure 1a) had several components, fitted into the combination of five sets of sextets and one doublet. Sextet absorption of $\alpha$-Fe ($H = 330$ kOe) and cementite Fe$_3$C ($H = 210$ kOe) were easily assigned. The other three sets of sextets were assigned to Fe$_7$C$_3$ based on Mössbauer parameters reported previously [3]. A hexagonal [8] form of Fe$_7$C$_3$ containing three inequivalent Fe sites has been reported. However, orthorhombic [9] and pseudo-hexagonal [10] Fe$_7$C$_3$ structures were also reported. With increasing pressure of C$_2$H$_2$ gas (figure 1b, c and d), the intensity of the doublet increased, while absorption of Fe$_7$C and Fe-C$_3$ decreased. Generally, Fe$_7$C$_3$ is formed in bulk only under very high temperatures and pressures, but thin films of Fe$_7$C$_3$ could be prepared at 600 K and low pressures by laser deposition. The yields of Fe$_7$C and Fe-C$_3$ changed depending on the pressure. Similar results were obtained using plasma-enhanced chemical vapor deposition [4].

The film produced at 13 Pa of C$_2$H$_2$ (figure 1e) did not contain Fe$_7$C and Fe-C$_3$, and the spectrum was fitted by a combination of a singlet, a doublet and $\alpha$-Fe. The singlet and doublet were assigned to $\gamma$-Fe containing C atoms, and the intensity of the doublet is large because of the excess amount of C atoms. At the highest C$_2$H$_2$ pressure of 130 Pa (figure 1f), doublet absorption ($\delta = 0.18$ mm/s and $\Delta Eq = 1.19$ mm/s) was observed, which was assigned to paramagnetic iron carbide species. The determination of this species is not simple because some other assignments are possible; the doublet may be due to the superparamagnetic nature of small Fe$_7$C particles, or small oxide particles produced by handling in air after production in the vessel. We measured the Mössbauer spectrum of this sample at 14 K, and the spectrum did not show a magnetic sextet or superparamagnetic broadening. Therefore, the doublet is not iron oxide particles, and was assigned to amorphous Fe-C containing a large amount of carbon atoms. Similar Mössbauer parameters were reported in literature [1, 5]. The Mössbauer parameters obtained in this experiment are summarized in table 1. The singlet corresponding to $\gamma$-Fe was produced only at the pressure of 13 Pa of C$_2$H$_2$ (figure 1e), while the doublets observed at pressures below 13 Pa of C$_2$H$_2$ (figure 1a-d) yielded Mössbauer parameters between $\delta = 0.0 \sim 0.2$ mm/s and $\Delta Eq = 0.6 \sim 1.0$ mm/s. These doublets might result partly because of C atoms in $\gamma$-Fe, but the C atom site is not well defined because of the large defects of $\gamma$-Fe in the films. The doublet obtained at a very high pressure of 130 Pa (figure 1f; $\delta = 0.18$ mm/s and $\Delta Eq = 1.19$ mm/s) obviously corresponds to a different C-rich amorphous phase.

It is presumed that laser-evaporated iron atoms collide with C$_2$H$_2$ molecules in the gas phase to form C atoms and Fe$_x$C$_y$ clusters. The Fe$_x$C$_y$ clusters as well as Fe and C atoms are deposited onto the
Al substrate, and migrate to form a stable solid structure by releasing energy to the substrate. The pressure of C\textsubscript{2}H\textsubscript{2} controls the concentration of C atoms in the films. Similar results were also reported for a study of ball-milling of Fe/C [5]; Fe\textsubscript{3}C and Fe\textsubscript{7}C\textsubscript{3} were produced at low concentrations of C, and the paramagnetic component appeared at a very high C concentration, assigned to fine particles of high carbon iron carbides.

XRD patterns of the film sample were also measured (figure 2). The most intense peak corresponds to the Al substrate, and Fe\textsubscript{3}C is observed in the film produced at 1.0 Pa C\textsubscript{2}H\textsubscript{2} (figure 2a). Fe\textsubscript{7}C\textsubscript{3} is observed in films produced at 2.7 and 5.3 Pa of C\textsubscript{2}H\textsubscript{2} (figure 2b). The intensity ratio of the XRD patterns did not correspond to the yield estimated by Mössbauer spectra because XRD is only sensitive to crystalline structures and is insensitive to very short range arrangements or amorphous structures. The film produced at a high pressure of C\textsubscript{2}H\textsubscript{2} did not show any diffraction corresponding to iron carbides, and thus paramagnetic iron carbide may be amorphous, which was not observed by XRD. SEM micrographs of the films produced at 13 and 2.7 Pa are shown in figure 3. The film produced at 13 Pa (figure 3a) has a rugged surface because the atoms or the small particles produced in a gas phase deposited onto the substrate with insufficient energy for migration on the surface. The film produced at 2.7 Pa (figure 3b) has a smooth surface because of the formation of crystalline iron carbides.

We also carried out similar experiments by changing the substrate temperature to gauge the effects of reactions on the substrates. The migration of Fe and C atoms on the film surface and crystal...
Table 1. Mössbauer parameters of the species produced by laser deposition of Fe in a C₂H₂ atmosphere.

| Component | δ (mm/s) | ΔE_q (mm/s) | H (kOe) |
|-----------|----------|-------------|---------|
| Fe₂C₃     | 0.28     | -0.32       | 229     |
| Fe₃C     | 0.15     | 0.27        | 162     |
| Fe₃C     | 0.16     | 0.14        | 210     |
| α-Fe      | 0        | 0           | 330     |
| γ-Fe      | 0.1      | 0           |         |
| Paramagnetic amorphous | 0.18 | 1.19 | |

formation were restricted to substrates at low temperatures. Mössbauer spectra were obtained for the films formed by laser-deposition of Fe in a C₂H₂ atmosphere ranging from 1 to 130 Pa, while the temperature of the Al substrates was maintained at 300 K during the deposition. The major components of the films were paramagnetic Fe/C compounds showing doublets independent of the C₂H₂ pressure. Fe₃C was not found even in the film produced in a low-pressure C₂H₂ atmosphere (1.0 Pa), and broad absorption with magnetic distributions was observed. The broad absorption was fitted assuming hyperfine magnetic distributions; the distribution had a maximum at H = 130 kOe showing the formation of iron carbides with large defects. The energy of the deposited Fe/C atoms on the substrates at 300 K was not sufficient to crystallize Fe₃C. Generally, laser evaporated Fe atoms have high energy (several hundreds of eV) but they are cooled by collisions with C₂H₂ molecules. XRD patterns showing very a small peak corresponding to Fe₃C were obtained.

4. Conclusions

Iron carbide films with various compositions were produced by laser deposition of Fe in a C₂H₂ atmosphere. Films containing Fe₃C and Fe₇C₃ were produced by laser deposition of Fe onto an Al substrate at 600 K in a low-pressure C₂H₂ atmosphere. When the films were produced at a high C₂H₂ pressure, paramagnetic amorphous Fe-C was obtained. The XRD patterns of the films and SEM observations were in agreement with this result. The films produced in low-pressure C₂H₂ had a smooth surface, while those produced in high-pressure C₂H₂ had a rugged surface. Both gas-phase and surface reactions govern the composition of the iron carbide films, and the surface reaction was enhanced by increasing the substrate temperature.

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