MÖSSBAUER AND EXAFS STUDIES OF AMORPHOUS IRON PRODUCED BY THERMAL DECOMPOSITION OF CARBONYL IRON IN LIQUID PHASE

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Decomposition of iron carbonyl Fe(CO)$_5$ and Fe$_2$(CO)$_9$ in liquid phase gave amorphous and crystalline iron powders in the absence and presence of catalyst, respectively. The hyperfine fields were large in amorphous phases prepared from Fe(CO)$_5$ than from Fe$_2$(CO)$_9$. Crystalline iron, iron carbide and a trace amount of Fe$_3$O$_4$ were detected in the decomposition products of the amorphous phase prepared from Fe(CO)$_5$, and iron carbide was mainly included in the decomposition products of the amorphous phase prepared from Fe$_2$(CO)$_9$.

1. Introduction

The application of the chemical vapor deposition (CVD) method to deposit metals or metallic compounds on the surface of various substrates are limited more or less to the elements or compounds, which have gaseous organo-metallic compounds as their precursor. On the other hand, the chemical deposition in liquid phase (CDL) method does not need gaseous compounds to be decomposed. The technique can be applied to wide varieties of chemical compounds. An apparatus for CDL can be constructed far more easily. Iron is deposited on carbon fiber by heating Fe(CO)$_5$ and Fe$_2$(CO)$_9$ in diphenylmethane used as a solvent. Wonterghem et al. reported that decomposition of iron pentacarbonyl produced fine particles of metallic glass [1]. It was reported from X-ray diffraction patterns that crystalline iron was produced in the solvent containing Pd as catalyst, but that amorphous iron and poorly crystallized iron were produced in the solvent without Pd [2]. In the present paper, the thermal decomposition products in the absence and presence of Pd, and amorphous powders prepared from Fe(CO)$_5$ and Fe$_2$(CO)$_9$ were analyzed by the hyperfine distribution of Mössbauer spectra and by the radial distribution function.

2. Experimental details

2.1. SAMPLE PREPARATION

Fe(CO)$_5$ or Fe$_2$(CO)$_9$ were dissolved in diphenylmethane with and without PdCl$_2$ and thermally decomposed at 175°C under nitrogen atmosphere [2]. X-ray
diffraction patterns of these decomposition products without Pd did not show any clear peaks although weak peaks of iron appeared in the samples containing Pd. Thermogravimetry and differential thermal analysis of these samples gave an exothermic peak without the weight change at 300 to 330 °C. The annealing of the amorphous samples at lower and higher temperatures than the exothermic point for several hours in reduced pressure (1.33 Pa) transformed them to crystalline. Elemental analysis of total carbon showed that about 4 to 7 w% carbon was included in amorphous powders prepared.

2.2. Mössbauer Spectrometry and EXAFS

Mössbauer spectrometer (type S600) of Austin Science Associates Co. Ltd was used with 370 MBq $^{57}$Co(Rh) as γ ray source. Hyperfine field distributions were calculated following Hesse's method [3]. In order to confirm the amorphous phase of prepared samples, EXAFS measurements were carried out using synchrotron radiation (SR) at the BL-10B beam line of the Photon Factory in the National Laboratory of High Energy Physics in Japan. Iron foil was used as a standard material. EXAFS spectra of the K-absorption edge of iron were observed using Si semiconductor and data were processed by the computer program “EXAFS2” [4].

3. Results and discussion

X-ray absorption spectra for the Fe K-edge region of iron foil (10 μm thick), iron powder prepared from Fe(CO)$_5$ by CDL method, and annealed ones at 200 and 300 °C for 1 hour were measured. Comparison of these spectra with the spectra observed for crystalline iron foil revealed the difference in a small number of beat and weak intensity in the post-edge region of iron powder before annealing. The EXAFS intensity of annealed samples became a little higher than that of the iron powder before annealing. The result suggested that iron powder, decomposed from Fe(CO)$_5$, is amorphous and the Fe atoms have a small coordination number. The large peak was observed at about 0.25 nm in the radial distribution functions of all prepared samples. The peak at 0.48 nm, which was recognized in the distribution of α-Fe, could not be observed in both samples before and after annealing. The radial distribution function of iron powder before annealing was broad, compared to that of iron powders after annealing. Although the distance between iron and iron atoms in iron powders after annealing was almost the same as that in α-Fe, the maximum of radial distribution of iron powder before annealing comes in somewhat shorter regions than that of α-Fe.

Mössbauer spectra and hyperfine field distributions of iron powder produced from Fe(CO)$_5$ by the CDL method and the annealed samples were shown in figs. 1 and 2, respectively. The powders before and after annealing at 250 °C for 1
hour gave the broad peaks representative to the amorphous phase. On the other hand, the annealed sample at 300 °C for 1 hour showed clear peaks, which consisted of α-Fe, Fe₃C, and Fe₃O₄. The trace amount of Fe₃O₄ is considered to be produced by the partial oxidation of iron species by the oxygen impurities present in the gaseous atmosphere or by the direct decomposition of iron carbonyl. Peaks due to second nearest neighboring atoms were not clearly observed in the radial distribution of the annealed sample at 300 °C because of mixed compounds detected in the Mössbauer spectrum.

The Mössbauer spectra of a sample produced in the presence of 1.0 mol% PdCl₂ at 175 °C for 6 hours was shown in fig. 3. The magnetic sextet of α-Fe and a doublet were observed at room temperature and 80 K. This doublet (I.S. = 0.35 mm/s and Q.S. = 0.71 mm/s at room temperature) was probably assigned to iron carbide in high dispersed form (< 6 nm) because the parameters were similar to I.S. = 0.36 mm/s, Q.S. = 0.76 mm/s of ε carbide extracted from Fe-C-Si
Fig. 2. Magnetic hyperfine distributions of Mössbauer spectra (fig. 1).

Fig. 3. Mössbauer spectra of iron powder produced in the liquid phase from Fe(CO)$_5$ in the presence of Pd as catalyst. a) room temp., b) 80 K.
tempered at 300 °C for 1 hour [5] and the decomposition products from Fe(CO)₅ in the presence of Pd contained 4.69 wt% carbon.

The difference in mechanism between annealing with and without PdCl₂ is considered as follows. Stable and amorphous iron compounds are produced because carbonyl may be mainly decomposed into CO₂ and C, and because carbon is incorporated into the iron matrix. On the other hand, as the release of CO from Fe(CO)₅ in the presence of Pd was about 3 times faster than in the absence of Pd [2], a part of the iron can be grown easily as crystalline. Small amounts of fine particles of iron oxides may be included since iron powders was
sometime fired when powders were taken out from a reaction vessel in a case of solvent of ether or cedar.

The decomposition of \( \text{Fe}_2(\text{CO})_9 \) in the liquid phase also gave amorphous powders. The Mössbauer spectra and hyperfine field distributions of the decomposition product and the sample annealed at 300°C for 1 hour were shown in figs. 4 and 5, respectively. The magnetic hyperfine field of the sample prepared from \( \text{Fe}_2(\text{CO})_9 \) was small and the center of the Mössbauer spectrum was a little shifted, compared with those of the amorphous sample from \( \text{Fe}(\text{CO})_5 \). Much amounts of iron carbides were produced in the annealed sample as shown in fig. 4b). The interatomic distance between Fe atoms was about 0.23 nm, shorter than 0.25 nm of \( \alpha\)-Fe and decomposition products of \( \text{Fe}(\text{CO})_5 \). This amorphous phase is considered to mainly consist of poor crystalline carbides rather than iron.

### 4. Conclusion

When iron carbonyls were decomposed in liquid phase, carbons included in the raw iron powders were found to play an important role in the formation of the amorphous phase. Decomposition products of iron carbonyl were composed of the amorphous phase of iron, iron carbide, and magnetite although crystalline metal iron and fine particles of iron carbide were produced in the presence of the \( \text{PdCl}_2 \) catalyst. The samples prepared from \( \text{Fe}_2(\text{CO})_9 \) were considered to be mainly composed of amorphous phase of iron carbide rather than iron because they contained more carbons than samples prepared from \( \text{Fe}(\text{CO})_5 \). Amorphous iron products have bright prospects for soft magnetic films.

### References