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A Mössbauer study of iron/polytetrafluoroethylene nanocomposites prepared by high-energy ball milling

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Abstract Iron/polytetrafluoroethylene (Fe/PTFE) nanocomposites were prepared by means of high-energy ball milling for different lengths of time. Three new components of FeF_2, FeF_3, and Fe_3C in the resultants were mainly investigated using the Mössbauer spectroscopy (MS). The components and average grain size of the nanocomposites were also measured using X-ray diffraction (XRD) and transmission electron microscopy (TEM), respectively.

Key words Nanocomposite, Polymer, High-energy ball milling, Mössbauer spectroscopy

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1 Introduction

High-energy ball milling has been widely used for the preparation of nanostructured materials, including a variety of materials having nanosized dimensions embedded in some ceramic or immerged matrices of metals. However, little attention has been paid to the preparation of metal–polymer nanocomposites by ball milling. Recently, iron fluorides have been investigated due to their simple chemical nature and various magnetic properties [1-3]. In this study, the high-energy ball milling technique was applied, which successfully synthesized nanocrystalline FeF_3 from a powder mixture of α-Fe and polytetrafluoroethylene (PTFE) in argon atmosphere. Products such as FeF_2 and Fe_3C (iron carbide) were also found at different ball-milling stages. The phase evolution and the microstructure of the samples were studied using Mössbauer spectroscopy (MS), X-ray diffraction (XRD), and transmission electron microscopy (TEM). The analyses suggest that the technique holds promise for the fabrication of various nanocomposites of alloys using polymers and metals. And it is also expected that the composite powder of metal–polymer systems may be suitable in various fields of applications such as plating solutions, polymer electrodes, and strengthened plastics [4].

2 Experimental

Mechanical alloying of α-Fe/PTFE mixture powder was carried out using a planetary ball-type milling machine with stainless steel vials and balls. The starting materials used in this study were α-Fe and PTFE powder with a size of several micrometers. The weight ratio of iron to PTFE was 20:1 and that of the balls to powder was about 15:1. The milling speed was $200\ r\cdot min^{-1}$. The vials were filled with argon to prevent the oxidation of iron. The milling is interrupted at different times to remove a small amount of sample for analysis in argon atmosphere. The samples were characterized by MS with a ^{57}Co (Pd) source of 420 MBq, XRD with Cu K_α radiation ($\lambda = 1.54050$ Å), and TEM. ^{57}Fe Mössbauer spectra were recorded at room and low temperature by cooling the sample in a cryostat.

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The isomer shifts were calibrated using a 25 μm α-Fe foil at room temperature.

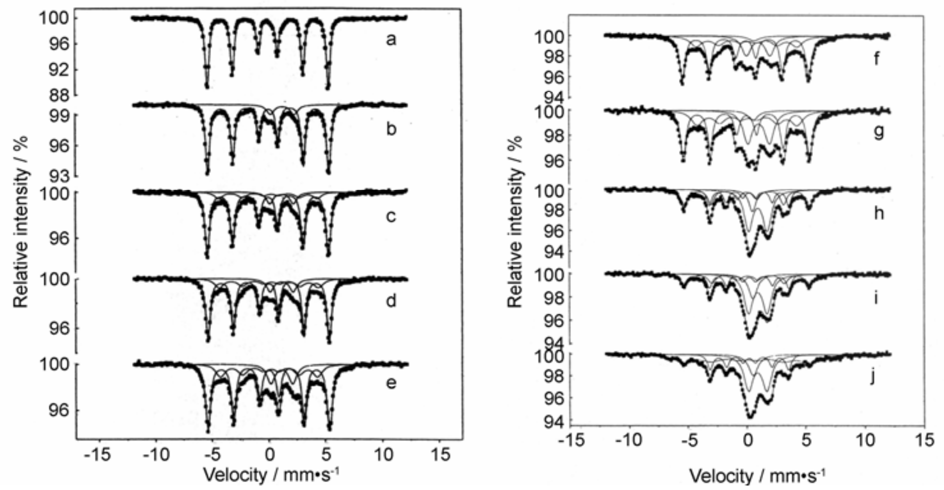
3 Results and discussions

Fig.1(a) shows Mössbauer spectra of α-Fe/PTFE at room temperature at different milling times ranging from 0 to 140 hours. Mössbauer spectra can be fitted into three components, that is, two sextets and one doublet, whose parameters and the relative area are shown in Table 1. It can be seen from Fig.1 and Table 1 that a sharp sextet 1 with the hyperfine magnetic field of 33 T corresponds to α-Fe. For the samples milled between 50 hours and 140 hours (samples b, c, d, e), a broad sextet 2 with the hyperfine magnetic field of about 26 T is attributed to the contribution from the interfacial component, as reported by Del Bianco *et al.* [5]. Mössbauer spectra include the doublet with large quadrupole splitting and isomer shift corresponding to Fe^{2+}. In order to prove that it could associate with the formation of FeF_2, Mössbauer spectra for Fe/PTFE mixture milled for 140 hours have been measured at both room and low temperatures, as shown in Fig.2. Because FeF_2 is an antiferromagnetic material with its Neel temperature at about 78 K, it has been observed that this doublet became the sextet with the hyperfine magnetic field 30.4 T at 15 K. This result is in good agreement with a previous study by Ramasamy [1]. To explain the formation of FeF_2, the mechanical-electron effect was introduced [6], and when Fe/PTFE was milled for a certain time, the following degrading reaction could occur

$$-CF_2-CF_2-CF_3 + e \begin{cases} \longrightarrow -CF_2-{\cdot}CF-CF_3 + F \\ \longrightarrow -CF_2-CF_2-{\cdot}CF_2 + F \end{cases} \qquad (1)$$

where “e” corresponds to the high-energy fast electron, which can inject in the carbonaceous polymer, and result in the free F atoms that have high reactivity and oxidation. Then, the F atoms strongly interact with Fe to form a new compound, FeF_2.

Fig.1(b) shows Mössbauer spectra at room temperature of Fe/PTFE mixture milled for 200 – 400 hours. For the two samples that were milled for 200 hours and 250 hours (samples f and g), excepting the two sextets and one doublet, Mössbauer spectra show the appearance of a broad singlet having an isomer shift of 0.58 and 0.49 $mm{\cdot}s^{-1}$. This singlet can be associated with the formation of ferric fluoride FeF_3, as described by Grenech [3]. The formation of FeF_3 can be explained to be the result of the mechanical-electron effect further induced by the milling. As expected, the production of both FeF_2 and FeF_3 increases with the increasing of milling time, and is accompanied with a decreasing of α-Fe as shown in Fig.3. The sextet for FeF_3 at a low temperature also shows the magnetic field $H = 52.2$ T and an isomer shift IS = 0.49 $mm{\cdot}s^{-1}$[7].



(a) (b)

Fig.1 Mössbauer spectra at room temperature of the samples Fe/PTFE mixture milled for a) 0 h, b) 50 h, c) 70 h, d) 100 h, e) 140 h, f) 200 h, g) 250 h, h) 300 h, i) 350 h, j) 400 h.

Table 1 Mössbauer hyperfine parameters

Sample	Milling time / h	S	H (T)	IS / mm·s^{-1}	QS / mm·s^{-1}	Γ / mm·s^{-1}	Area / %
a	0	Sextet 1	33.0	0.00	0.00	0.23	100
b	50	Doublet		1.24	2.13	0.40	9.6
		Sextet 1	33.0	0.01	0.00	0.21	81.9
		Sextet 2	26.6	0.21	0.46	0.36	8.4
c	70	Doublet		1.17	2.11	0.37	9.6
		Sextet 1	33.0	0.04	0.00	0.24	76.0
		Sextet 2	26.8	0.10	0.25	0.43	14.4
d	100	Doublet		1.17	2.01	0.31	16.5
		Sextet 1	33.1	0.01	0.01	0.24	68.9
		Sextet 2	27.0	0.14	0.20	0.47	20.4
e	140	Doublet		1.14	1.95	0.42	13.6
		Sextet 1	33.2	0.02	0.02	0.26	63
		Sextet 2	26.5	0.12	0.15	0.50	23.4
f	200	Singlet		0.47		0.56	2.7
		Doublet		1.02	1.98	0.45	17.0
		Sextet 1	33.3	-0.03	0.02	0.28	53.4
		Sextet 2	26.5	0.10	0.10	0.61	26.9
g	250	Singlet		0.58		0.52	3.9
		Doublet		1.05	1.82	0.47	22.3
		Sextet 1	33.1	0.03	0.02	0.28	45.1
		Sextet 2	26.3	0.14	0.12	0.61	28.7
h	300	Singlet		0.49		0.49	11.0
		Doublet		0.99	1.53	0.43	37.3
		Sextet 1	32.9	0.05	0.05	0.32	30.7
		Sextet 2	20.8	0.22	0.00	0.25	21.0
i	350	Singlet		0.52		0.59	16.9
		Doublet		0.97	1.53	0.44	39.0
		Sextet 1	33.1	0.06	0.01	0.36	23.4
		Sextet 2	20.8	0.22	0.01	0.29	20.8

Note: S: Subspectra; H: Hyperfine magnetic field; IS: Isomer shift; QS: Quadrupole splitting; Γ: line width;
Area: Relative subspectral area.

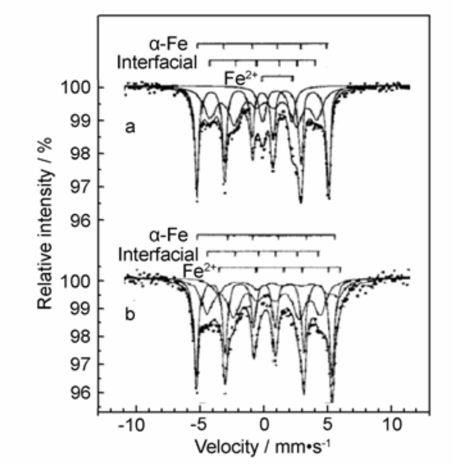


Fig.2 Mössbauer spectra of the samples Fe/PTFE mixture milled for 140h. (a) Room temperature, (b) 15K.

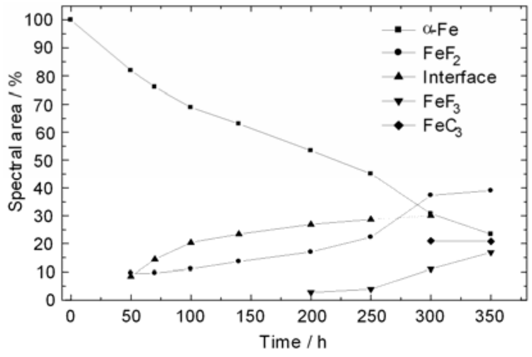


Fig.3 Spectral areas as functions of milling time for various fractions of α-Fe/PTFE mixture.

After 300 hours of milling, the second sextet corresponding to the interfacial component shows a sudden decrease of the hyperfine magnetic field (from 26.3 T for the sample milled for 250 hours to 20.8 T for the sample milled for 350 hours) as well as a decrease in the line width of the second sextet (from 0.61 to 0.29 mm·s^{-1}). All these features indicate the appearance of a new-order phase in the interfacial region. The hyperfine parameters of this component (isomer shift 0.22 mm·s^{-1} and average magnetic hyperfine field 20.8 T) are similar to those for iron carbide Fe_3C [8]. The formation of iron carbide Fe_3C can be understood on the basis of high surficial activity of the iron nanoparticles [9]. The carbon atoms could result from the broken C-C and C-F bonds in PTFE due to further degradation by ball milling.

The XRD patterns of the samples milled for 0 hour and 350 hours are shown in Fig.4. From the XRD results, it can be found that the line width of Fe peaks is increased with increasing of milling time. The average grain size of the sample milled for 350 hours calculated using the Scherrer equation is about 5 nm. It can also be seen that the extra diffraction peaks indicate the presence of FeF_2, FeF_3 [10, 11], and Fe_3C [8] beside α-Fe. It is in good agreement with the Mössbauer measurement results.

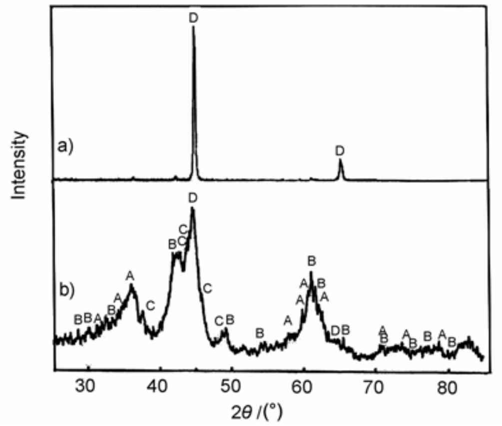


Fig.4 X-ray diffraction pattern for α-Fe /PTFE mixture milled for a) 0 h and b) 350 h (A: FeF_2; B: FeF_3; C: Fe_3C; D: α–Fe).

Fig.5 shows the micrograph of transmission electron microscopy of the α-Fe/PTFE mixture milled for 350 hours. The average grain size obtained is about 5 nm. The micrograph also shows the presence of several phases for the α-Fe/PTFE nanocomposites corresponding to several regions with different brightness in one grain.

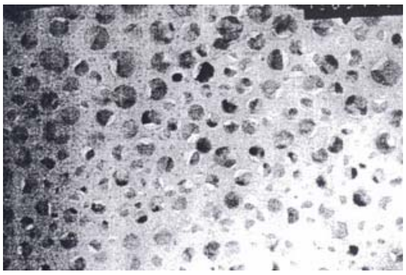


Fig.5 TEM photograph for the α-Fe /PTFE mixture milled for 350h.

4 Conclusions

Iron/PTFE nanocomposites were successfully prepared by high-energy ball milling under argon atmosphere. New components FeF_2, FeF_3, and Fe_3C were formed in the different stages of ball milling and proved by MS and XRD. According to the result of TEM, the average grain size milled for 350 hours is about 5 nm.

The characterization of these materials has shown that organometallic interactions occur primarily during ball milling process and that the technique has been established as a new and reproducible processing for the synthesis of new polymer /metal nanocomposites.

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