Mössbauer studies on the shape effect of $Fe_{84.94}Si_{9.68}Al_{5.38}$ particles on their microwave permeability*

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(Received 17 October 2012; revised manuscript received 4 January 2013)

Ball milling for long time (such as 10, 20, and 30 h) can transform $Fe_{84.94}Si_{9.68}Al_{5.38}$ alloy powders with irregular shapes into flakes. X-ray diffraction (XRD) and Mössbauer measurements have proven that the unmilled particles and the flakes obtained by milling for 10 h have the same $D0_3$-type superlattice structure. The flakes obtained by milling for 20 h and 30 h have the same disorder α-Fe(Si, Al) structure. There are more than 6 absorption peaks in the transmission Mössbauer spectra (TMSs) for the particles with $D0_3$-type superlattice structure, which can be fitted with 5 sextets representing 5 different Fe-site environments. However, only 6 TMS absorption peaks have been found for particles with a disorder α-Fe(Si, Al) structure, which can be fitted with the distributions of Mössbauer parameters (Bhf, isomer shift). The TMS results show that the flaky particles have a stronger tendency to possess the planar magnetic anisotropy. As the result, the flakes have larger microwave permeability values than particles with irregular shapes. The conversion electron Mössbauer spectra (CEMSs) also show the significantly different Fe-sites environments between the alloy surface and the inside.

Keywords: Mössbauer spectroscopy, magnetic permeability, superlattice

PACS: 33.45.+x, 07.55.–w, 68.65.Cd **DOI:** 10.1088/1674-1056/22/8/083303

1. Introduction

The "Sendust alloys" of $Fe_{(88-81)}Si_{(8-11)}Al_{(4-8)}$ (wt%) are ferromagnetic materials with extremely high initial permeability and large resistivity. The initial permeability of Fe–Si–Al alloy with 6.21 wt% Al, 9.66 wt% Si and Fe balance can be as high as 16130.[1] These soft ferromagnetic powders are widely used as magnetic cores due to their low magnetic losses at frequency far below 1 MHz. The permeability values of Fe–Si–Al at the higher frequencies, such as higher than 1 GHz, have been rarely investigated, especially by Mössbauer spectroscopy. Recently, academic interest in them was renewed due to their promising applications in suppressing the unwanted electromagnetic radiation from electronic devices working in the ultrahigh frequency (UHF) band.[2–4] Walser *et al.*,[5] Lu *et al.*,[6] and Han *et al.*[7] have theoretically proposed that the permeability of particles can be enhanced by transforming the spherical shape into flakes, thin films, oblate particles, nanotubes or microwires. In order to increase the bandwidth of electromagnetic wave absorption and reduce the absorber thickness, high permeability values are required, especially the high imaginary parts of permeability.[8] Composites with the flaky particles as fillers have been fabricated as electromagnetic wave absorbers, and have proven that magnetic particles with flaky shapes can effectively improve the absorption properties.[9,10] Currently, it is still necessary to understand the enhanced permeability on the atomic scale, which will be helpful for further increasing high frequency permeability. Mössbauer spectroscopy is a powerful tool to study the magnetic properties on the atomic scale with extremely high energy resolution.[11–17] Mössbauer spectroscopy has been employed to study the Fe–Si–Al alloys. However, it is found that the Mössbauer spectrum of Fe–Si–Al alloy is significantly dependent on the form of material (such as films, bulks, powder, ribbons), while the form of material depends on the fabrication method.[18–21] In this paper, Mössbauer experiments are carried out to uncover the possible changes of Fe atom environments in Fe–Si–Al particles, which were milled for different time lengths (0, 10, 20, and 30 h). We will present the Mössbauer spectra of Fe–Si–Al particles in irregular shapes and flakes. In order to show the distinct differences in Mössbauer spectrum and microwave permeability, we particularly compare the transmission Mössbauer spectra (TMSs) and conversion electron Mössbauer spectra (CEMSs) for two extreme cases: unmilled particles with irregular shapes and 30-h milling flaky particles.

2. Experimental details

$Fe_{84.94}Si_{9.68}Al_{5.38}$ alloy was initially prepared by melting the starting materials (Al, Fe, and Si with high purities) in a hydrogen reduction furnace. The alloy ingot was then crashed and milled into particles with irregular shapes. These starting particles were milled into flakes by 10, 20,

*Project supported by the National Key Basic Research Program of China (Grant No. 2010CB334702), the China National Funds for Distinguished Young Scientists (Grant No. 51025208), the International Collaboration Project of Sichuan Province, China (Grant Nos. 2011HH0001 and 2012JQ0053), and the Program for New Century Excellent Talents in Universities, China (Grant No. NCET-11-0060).

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and 30 h respectively with a planetary miller. The rotation speed of miller is 150 r/min. The milling balls with a diameter of 15 mm are made of ZrO_2. The weight ratio of milling balls/Fe–Si–Al powders is 25 in each vessel of miller. Some ethanol was added into the vessels as the milling dispersant. The morphologies of particles were observed by a scanning electron microscopy (SEM). The X-ray diffraction (XRD) patterns were collected with Cu K_α radiation to identify the phase variations resulting from the attrition. The static magnetic properties were studied by taking the magnetic hysteresis loops. To measure the microwave permeability dispersion spectra, Fe–Si–Al powders were molded into the annular shape (the inner and out diameter are 3 and 7 respectively). For each sample, the weight ratio of the particles to the wax was kept at a constant of 4:1, and they have been mixed homogeneously. The complex relative permeability values were measured on a Network Analyzer (Agilent 8720 ET) in a frequency range of 0.5 GHz–10 GHz. Transmission Mössbauer spectroscopy with 25 mCi ^{57}Co γ-ray radiation source in rhodium (Rh) matrix was employed to study the shape effects of particles on the γ-ray absorption spectra. The velocity of radiation source was calibrated with a standard α-Fe foil. The Mössbauer spectra were least-squares fitted using the software called WinNormos-for-Igor. The conversion electron Mössbauer spectra were collected by using the detector (RIKON-5) with the mixing gas (He: 95 vol%, CH4: 5 vol%).

3. Results and discussion

The shapes of Fe–Si–Al starting particles are irregular as shown by the SEM images in Fig. 1(a). Ball attrition can effectively transform them into the flakes as shown in Fig. 1(b). It is well known that the "Sendust" alloys can have two kinds of crystal structures with ferromagnetic properties: the ordered structure $D0_3$ (superlattice) and the disordered α-Fe(Si, Al) structure. XRD patterns shown in Fig. 2(a) indicate that when the ball milling time is more than 20 h, the crystalline structure of Fe–Si–Al can be changed from the $D0_3$ phase into the α-Fe(Si, Al) phase. The diffraction peak around 31° in Fig. 2(b) is indicative of the formation of a $D0_3$ superlattice in the unmilled particles.[22,23] For the α-Fe(Si, Al) phase with a *bcc* lattice structure, Fe, Si, and Al atoms occupy the lattice sites in such a way that they form continuous substitutional solid solutions. However, for the $D0_3$ phase, Al and Si atoms dominantly occupy the body-centred site of its unit cell (superlattice), which is composed of eight *bcc* unit cells. These different site occupancies are important for decomposing the Mössbauer spectra later.

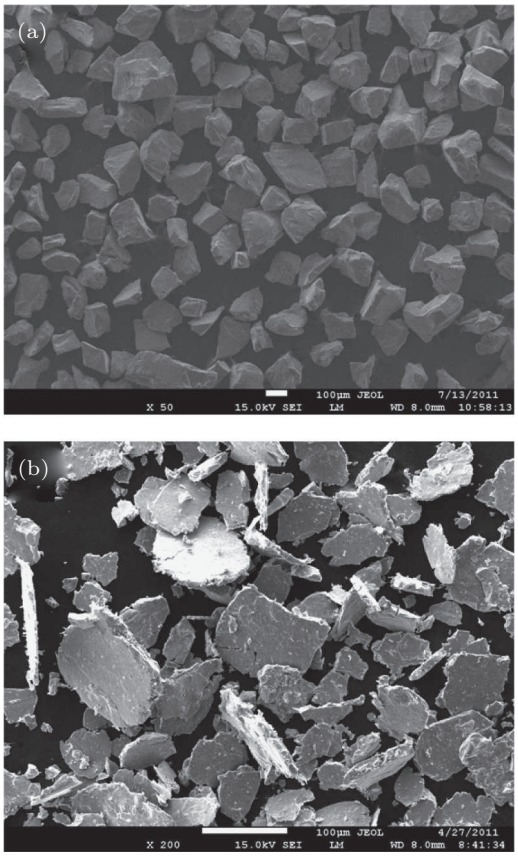


Fig. 1. SEM images of Fe–Si–Al alloy particles: (a) unmilled particles; (b) flaky particles by being milled for 30 h.

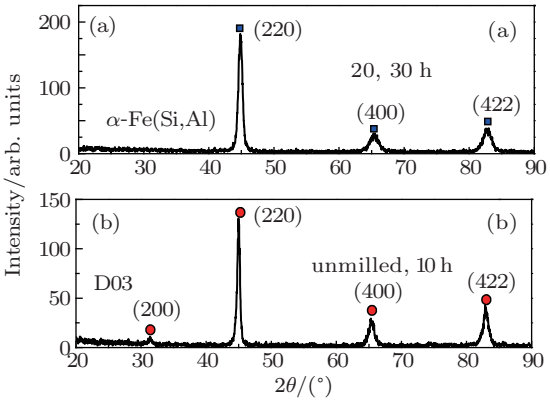


Fig. 2. (color online) XRD patterns of Fe–Si–Al particles.

The microwave permeability values of Fe–Si–Al particles are shown in Figs. 3(a) and 3(b). Obviously, the particles with a flaky shape exhibit significant enhancement in microwave permeability. With milling time increasing, both the real parts and imaginary parts of microwave permeability values increase, especially at the lower end of the frequency range. For instance, the real part of permeability of the Fe–Si–Al flake milled for 30 h is about 4.4 at 0.5 GHz. For the unmilled irregular shape particle, it is only about 1.3. Within 0.5 GHz–7 GHz, the μ' values of flaky particles milled for 30 h are obviously larger than those of unmilled particles.

As for the imaginary parts of permeability (μ'') values, the flaky particles of Fe–Si–Al have larger values in the whole measurement frequency range than those of unmilled particles (see Fig. 3(b)). There are some reasons for the increased permeability. Firstly, the eddy current effect can be greatly suppressed by transforming the irregular shape particles into flakes. Secondly, the shape-dependent Snoek's law given below indicates that higher permeability can be obtained in flaky particles: $(\mu_s - 1)f_r^2 = (\gamma/2\pi)^2 4\pi M_s[(H_k + 4\pi M_s D_z)]$, where D_z is the demagnetization factor along the direction normal to the particle plane. For sphere shape, D_z is about $4\pi/3$. For a thin flake, D_z is about 4π. Therefore, permeability can be enhanced by increasing D_z value as shown in our case. Similar results have already been found in magnetic thin films which can be thought of as "special flakes". Thin films have much larger permeability values than bulk materials due to their large D_z values and in-plane uniaxial anisotropies.[24] For bulk materials, the well-known Snoek law is given as $(\mu_s - 1)f_r = \frac{2}{3}\gamma 4\pi M_s$, in which no demagnetization factor is involved.

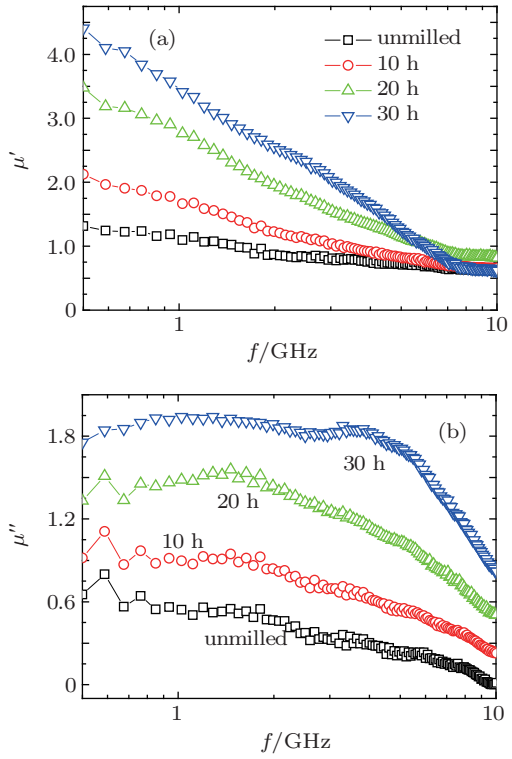


Fig. 3. (color online) Effects of particle shapes on the microwave permeability.

As shown in Fig. 4, only the static magnetic properties of the unmilled particles (sample "A") and the flaky particles milled for 30 h (sample "B") are compared for the sake of page limitation. The saturation magnetization (M_s) values are 124.25 emu/g and 119.81 emu/g for samples "A" and "B" respectively. Their coercivity values are about 7.2×10^{-3} T and 1×10^{-2} T respectively. Clearly, the unmilled particles have slightly "soft" magnetic properties in terms of the coercivity values. Also, it can be seen from the hysteresis loops that sample "B" has a smaller saturation magnetic field than sample "A". As indicated from the shape-dependent Snoek's law mentioned previously, microwave permeability depends on D_z, M_s, f_r, and H_k, and the observed enhanced microwave permeability in this paper is the consequence of these factors. To understand the above differences in microwave permeability and static magnetic property, the following analyses of the Mössbauer spectra will be helpful.

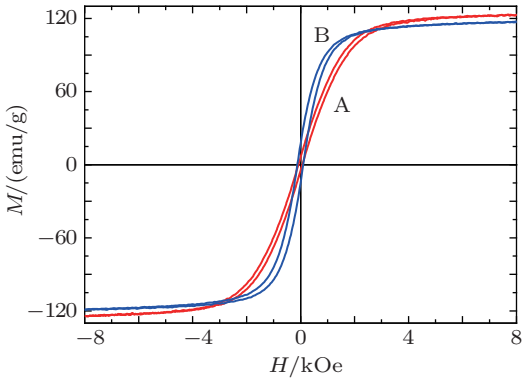


Fig. 4. (color online) Magnetic hysteresis loops of unmilled particles ("A") and flakes milled for 30 h ("B"). The unit 1 Oe=79.5775 A·m^{-1}.

The measured transmission Mössbauer spectra of Fe–Si–Al particles are shown in Fig. 5. The obvious solid state phase transition can be found from these Mössbauer spectra. The phase transition is believed to be due to the attrition process, in which the violent particle deformation and the heat due to the collision are critical for the phase transition. The particles with $D0_3$ superlattice structures are the unmilled particles and the particles being milled for 10 h. Their TMSs are shown in Figs. 5(a) and 5(b). It is obvious that each of them exhibits more than 6 absorption peaks in the TMS. However, there are only six absorption peaks found in the TMSs of flaky particles being milled for 20 h and 30 h, see Figs. 5(c) and 5(e). The measured Mössbauer spectra are fitted based on the fact that Fe atoms in the Fe–Si–Al system have different surrounding environments in these two crystal structures: disordered α-Fe(Si, Al) and ordered $D0_3$ structures.[25] For the unmilled particles with irregular shapes and flaky particles milled for 10 h, XRD results show that their crystalline structures are the ordered $D0_3$ superlattice, in which there are 7 possible different environments for iron atoms:[26] Fe-1: 8Fe0(Si, Al); Fe-2: 4Fe4(Al, Si) with poor Al; Fe-3: 4Fe4(Al, Si) with poor Si; Fe-4: 6Fe2(Si, Al); Fe-5: 8Fe0(Si, Al) with Si or Al as the next nearest neighbor; Fe-6: distorted 4Fe4(Si, Al); Fe-7: distorted 3Fe5(Si, Al). It should be noted that Fe surrounding environments depend on composition, fabrication method, etc.[18–21] The measured Mössbauer spectra of unmilled particles and particles being milled for 10 h can be decomposed

into 5 sextet subspectra as shown in Figs. 5(a) and 5(b). Each sextet represents one kind of iron environment in these samples. For example, the "Fe-1" site denotes that an iron atom is surrounded by 8 iron atoms as the nearest neighbors. Due to the page limitation, only the fitting Mössbauer parameters of unmilled particles with $D0_3$ structure are presented in Table 1. Clearly, different sites have different values of hyperfine magnetic field (Bhf), isomer shift (IS), and quadrupole shift (QS). The occupancy probability of each site is represented by the relative area of each sextet. Nomura *et al.*[18] have shown that different fabrication processes of Fe–Si–Al alloys can result in different Fe-sites and therefore different Mössbauer spectra. Miyazaki *et al.*,[19] Stearns,[20] and Nomura *et al.*[21] have assigned the sites with different Bhf values (29.86, 21.33, 19.74, 24.09, and 27.36 T) to Fe-1, Fe-2, Fe-3, Fe-4, and Fe-5 respectively as shown in Table 1. Our extracted Mössbauer parameters are very close to their data. It can be inferred from the intensities of subspectra that the probability of Fe-3 site is the highest in these five possible iron environments. The average hyperfine magnetic field of sample A is calculated to be about 24.42 T. It is believed that in bulk Fe alloys, such as Y_xFe_{1-x} or Fe_3Si, the ratio of hyperfine magnetic field to Fe atomic magnetic moment (μ_{Fe}) is a constant: $Bhf/\langle m_{Fe}\rangle = 15\ T/\mu_B$, where μ_B is the Bohr magneton.[27,28] Therefore, we can calculate the average magnetic moment of sample A to be $\langle m_{Fe}\rangle = 24.42/15 \approx 1.63\ \mu_B$, which is smaller than that of bulk Fe ($2.2\ \mu_B$).

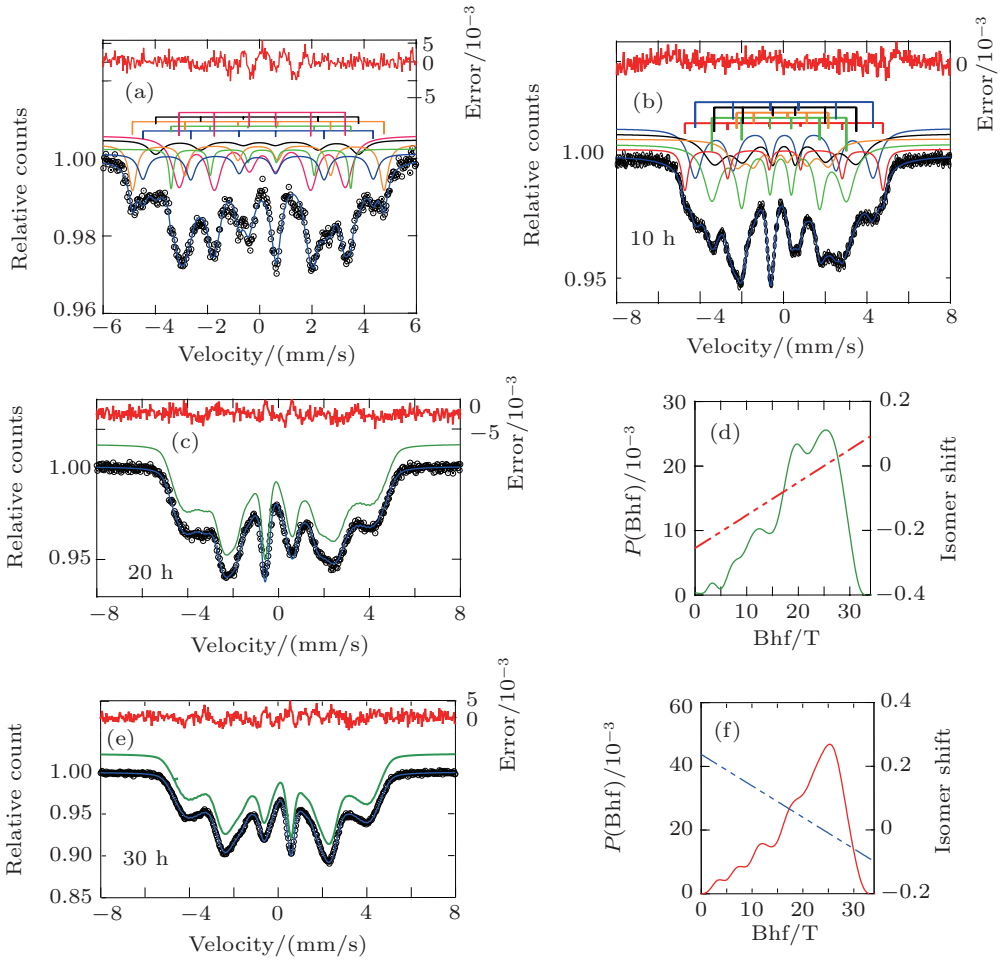


Fig. 5. (color online) Transmission Mössbauer spectra of Fe–Si–Al powder with different shapes and the distributions of Mössbauer parameters. Panel (a) is for unmilled particles with irregular shapes, panel (b) for flaky particles milled for 10 h, panels (c) and (d) for flaky particles milled for 20 h, panels (e) and (f) for flaky particles milled for 30 h.

Table 1. Transmission Mössbauer parameters of Fe–Si–Al particles with irregular shapes.

Sites	Bhf/T	IS/(mm/s)	QS/(mm/s)	Intensity/%
Fe-1	29.86	–0.062	0.0175	13.48
Fe-2	21.33	0.073	–0.0500	3.25
Fe-3	19.74	0.104	–0.0098	55.91
Fe-4	24.09	–0.053	–0.0888	13.36
Fe-5	27.36	–0.073	0.0263	13.99

According to the previous XRD results, we can learn that the flaky Fe–Si–Al particles milled for 20 h and 30 h are of α-Fe(Si,Al) phase with the disordered *bcc* structure, in which Fe, Si, and Al atoms randomly occupy the atom sites of *bcc* crystal structure. Therefore Fe atoms can have a plenty of different iron environments, which means that the Mössbauer spectra should be fitted with a distribution of Mössbauer pa-

rameters (Bhf, IS or QS). Our fitting results accord very well with the measured data as shown in Figs. 5(d)–5(f). For the flaky particles with disordered *bcc* structure, only six absorption peaks are found in the TMSs of flakes milled for 20 h and 30 h. Their similar TMS spectra also indicate that they have the same crystalline structures. Besides, it can be seen from Figs. 5(d) and 5(f) that there are wide distributions of magnetic hyperfine magnetic field (Bhf) and the isomer shift values in the flaky particles with disordered α-Fe(Si,Al) structure. As for the particles milled for 30 h, its average $\langle$Bhf$\rangle$ is found to be 20.54 T. The average magnetic moment $\langle m_{\mathrm{Fe}}\rangle$ of this sample is calculated to be about 1.37 μ_{B}, which is smaller than that of unmilled particles. Since the average hyperfine magnetic field is, to some extent, proportional to the value of saturation magnetization (M_{s}). The observed decrease of M_{s} value (sample B) obtained by the VSM measurements can be justified by the calculated values of $\langle$Bhf$\rangle$ for both samples.[29]

Moreover, according to the well-established theory on the relationship between the peak intensity of a sextet and the direction of magnetic moment:[27,30]

$$I_{2,5}/I_{3,4} = \frac{4\sin^2\theta}{1+\cos^2\theta}, \tag{1}$$

where θ is the angle between magnetic moment and incoming γ-ray, and I is the intensity of an absorption peak. If the orientations of magnetic moments are random, the ratio of $I_{2,5}/I_{3,4}$ should be 2. Clearly, as shown in Figs. 5(c) and 5(d), the intensity ratio of $I_{2,5}/I_{3,4}$ is obviously different from 2. For unmilled particles, the angle θ is about 47.53° for Fe-3 site with the highest probability. For flakes milled for 30 h, the average angle $\langle\theta\rangle$ is about 56.5°. In other words, Mössbauer spectra in Fig. 5(c) indicate that the flaky particles have a stronger tendency to possessing a planar anisotropy, which is beneficial to the increase of the magnetic permeability.

Table 2. CEMS Mössbauer parameters of Fe–Si–Al particles with irregular shapes.

Fe-sites	Bhf/T	IS/(mm/s)	QS/(mm/s)	Intensity/%
Fe-1	29.256	–0.041571	0.01887	7.08
Fe-2	20.359	0.10159	–0.052387	15.21
Fe-3	18.289	0.12324	–0.067849	10.84
Fe-4	23.802	0.006916	–0.04283	57.66
Fe-5	27.115	–0.026507	0.07555	9.21

Since the Fe–Si–Al flakes are obtained by ball attrition, it is interesting for us to know whether the attrition could change the Fe-site on the particle surface. Are there any differences in the Mössbauer spectrum between the surface and the bulk? CEMS measurements can provide information about a surface with a depth of about 200 nm. Therefore, CEMS measurements are carried out. As shown in Fig. 6, the CEMSs of unmilled particles in Fig. 6 each can be decomposed into 5 sextets. The obtained Mössbauer parameters are listed in Table 2. In the bulk of unmilled particles, most of Fe sites are Fe-3 site with a proportion of 55.91% (please see Table 1). However, on the surfaces of unmilled particles, 57.66% Fe sites are Fe-4 site (see Table 2).

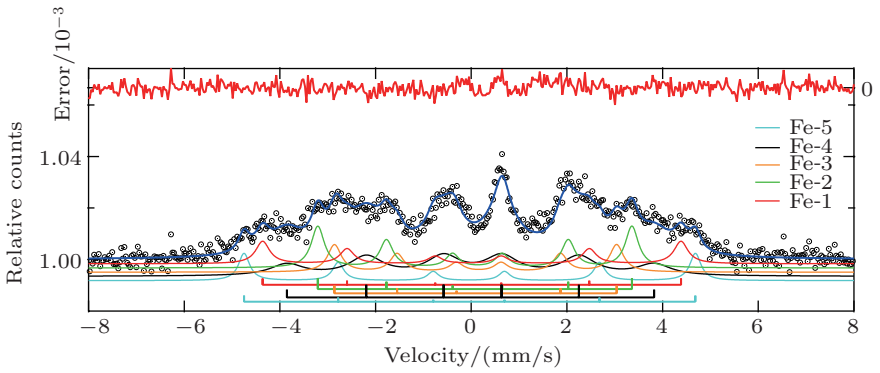


Fig. 6. (color online) CEMSs of Fe–Si–Al unmilled particles.

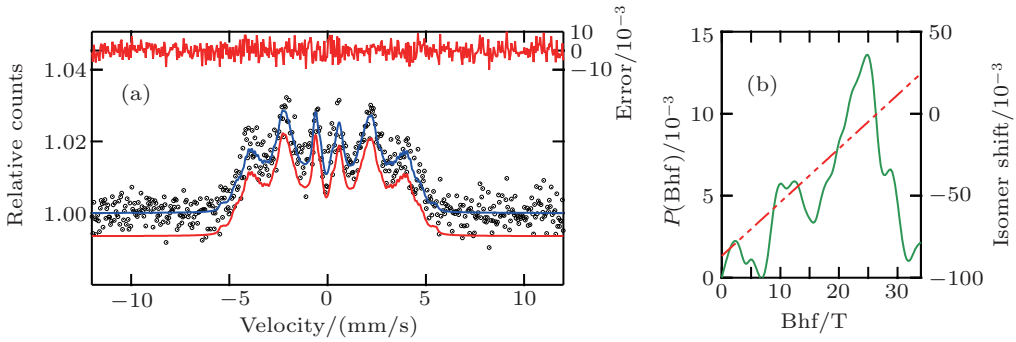


Fig. 7. (color online) CEMSs of Fe–Si–Al flaky particles obtained by 30-h attrition.

For the flakes obtained by 30-h attrition, their CEMSs are shown in Fig. 7(a), which can also be fitted with the distribution of hyperfine magnetic field. The fitting results are shown in Fig. 7(b). The distribution of hyperfine magnetic field (Bhf) has three strong peaks in the curve of P(Bhf) versus Bhf, which are different from those shown in Fig. 5(f). Besides, it is found that the dependence of isomer shift value on Bhf is also different from that shown in Fig. 5(f).

These CEMS measurements indicate different electronic and magnetic environments for Fe atoms between the surface and the bulk.

4. Conclusions

The unmilled Fe–Si–Al particles with irregular shapes are of the ordered $D0_3$-type superlattice structure. After ball milling for 30 h, they are transformed into the flaky shape and the disordered α-Fe(Si, Al) crystal structures. The microwave permeability values of Fe–Si–Al flaky particles are found to be significantly increased. Mössbauer spectra are found to be greatly changed by ball milling and show that there are more than 5 different Fe-site environments in the unmilled particles with 5 different magnetic moments. For the flaky particles, Mössbauer spectra reveal that the hyperfine magnetic field and isomer shift are widely distributed and the average magnetic moment to be about 1.63 μ_B.

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