

Electromagnetic and microwave absorption properties of carbonyl iron and carbon fiber filled epoxy/silicone resin coatings

Y.C. Qing · W.C. Zhou · S. Jia · F. Luo · D.M. Zhu

Received: 3 December 2009 / Accepted: 22 April 2010 / Published online: 15 May 2010
© Springer-Verlag 2010

Abstract The microwave electromagnetic properties of carbonyl-iron particles as magnetic absorber and carbon fiber as conductive absorber filled insulating epoxy/silicone resin coatings were investigated. The complex permittivity of the coatings increased while the complex permeability remained almost constant in the frequency range of 2–18 GHz, when the carbon fiber content was increased and the carbonyl-iron content kept constant. The minimum reflection loss of the coatings shifted to the lower frequency region by increasing the carbon fiber content or coating thickness. When the content of carbonyl iron was 65 wt% and carbon fiber was 2 wt%, the reflection loss below –10 dB can obtain in the frequency range of 8–18 GHz with coating thickness being 1 mm.

1 Introduction

Microwave-absorbing materials have attracted much attention because of their ability to eliminate electromagnetic wave pollution, which mainly is caused by gigahertz electronic systems and telecommunications [1]. Recent developments in microwave absorber technology required a microwave absorber to have certain properties as follows [2, 3]:

- (1) strong microwave absorption properties over a wide frequency range;
- (2) thin and lightweight, especially for aircraft;
- (3) simple coating layer structure and less working time.

In general, the complex permittivity ($\epsilon' - j\epsilon''$) and complex permeability ($\mu' - j\mu''$) of the microwave absorber determined the absorption characteristic. Commonly, by incorporate the magnetic and/or dielectric fillers with the polymer matrices, the values of the complex permittivity and permeability of the composites can be altered effectively. In addition, the effects of the characteristic and content of the fillers, the configuration and internal fractal structure of the composites, and the frequency of electromagnetic waves on the microwave-absorbing properties were also widely investigated [4–18].

Carbon fiber (CF) is widely used as filler and absorber at the same time because of its low density, high modulus, high strength and wide availability. Therefore, the CF filled polymer matrix composites have been widely employed as microwave-absorbing materials in reducing backscattering from objects or radar targets, electromagnetic interfere suppressors and paints [6–10]. It is also well known that the carbonyl-iron (CI) particles filled composites have been widely investigated in past years because the CI particles possess high values of complex permeability in the frequency range of 2–18 GHz [11–18]. Zhang et al. investigated the microwave-absorbing properties for different shapes and aggregated states of carbonyl-iron particles dispersed in epoxy resin matrix at various volume concentrations (30–60%), of which the result indicates that the composites have excellent microwave attenuation properties [15]. However, there are no reported experimental results on the electromagnetic properties of the CI particles and CF as hybrid absorber filled epoxy/silicone resin composites. This work focuses on the combined dielectric loss of the CF and magnetic loss of the CI particles to develop single-layer microwave-absorbing coatings with both small thickness and broadband microwave absorption.

Y.C. Qing (✉) · W.C. Zhou · S. Jia · F. Luo · D.M. Zhu
State Key Laboratory of Solidification Processing, Northwestern
Polytechnical University, Xi'an Shaanxi 710072, China
e-mail: qtvbgyta@163.com
Fax: +86-29-88494574

The microwave-absorbing coatings in this work consist in an insulating polymer matrix (epoxy/silicone resin), CF as conductive absorber and CI as magnetic absorber. The microwave electromagnetic properties of these coatings with different CF content and a fixed CI particles content were characterized by the complex permittivity, complex permeability and reflection loss in the frequency range of 2–18 GHz.

2 Experimental

CI particles and CF filled epoxy/silicone resin were used to fabricate microwave-absorbing coatings. The CI particles are thin flakes of 2–5 μm in diameter and of below 1 μm in thickness. The upright CF has a length of 10–20 μm and diameter about 7 μm . The specimens of CF2, CF3, CF4, CF5, and CF6 contained a fixed concentration of 65 wt% CI particles, and 2, 3, 4, 5, and 6 wt% CF, respectively. These specimens allowed us to investigate the variation of electromagnetic and microwave-absorbing properties which resulting from the different CF content. The CF and CI particles were individually dispersed in the ethanol solution by an ultrasonic bath at room temperature for 1 h. Subsequently, the solution of CF and CI particles were mixed together and the mixtures were stirred for 10 min at 2000 rpm. After the epoxy/silicone resin and hardener had been added into the mixtures, the mixtures were uniformly mixed by stirring at 2000 rpm for 30 min and kept under low vacuum by a mechanical rotary pump to remove the air. Finally, the mixtures were preured at 90°C for 30 min and postcured at 120°C for 2 h. The coatings were cut into toroidal shape with a dimension of an outer diameter of 7.0 mm and inner diameter of 3.03 mm. The complex permittivity and permeability of the coatings were measured using the toroidal samples in the frequency range of 2–18 GHz, by a network analyzer (Agilent technologies E8362B:10 MHz–20 GHz). The morphology of the coating was observed using a scanning electron microscopy (SEM; Model JSM-6360, JEOL, Tokyo, Japan).

3 Results and discussion

3.1 Morphology of the microwave-absorbing coatings

Figure 1 represents the microstructures of the CF2 and CF6 coatings. The backscatter electron images show that the CI particles and upright CF were uniformly separated in the epoxy/silicon resin matrix. The microwave-absorbing coatings can be successfully fabricated through the uniform dispersion of two different fillers. Furthermore, with the concentration of CF increased, some pristine CF might be cracked into shorter fiber due to a strong mixing shear force during the mixing process, as shown in Fig. 1(b).

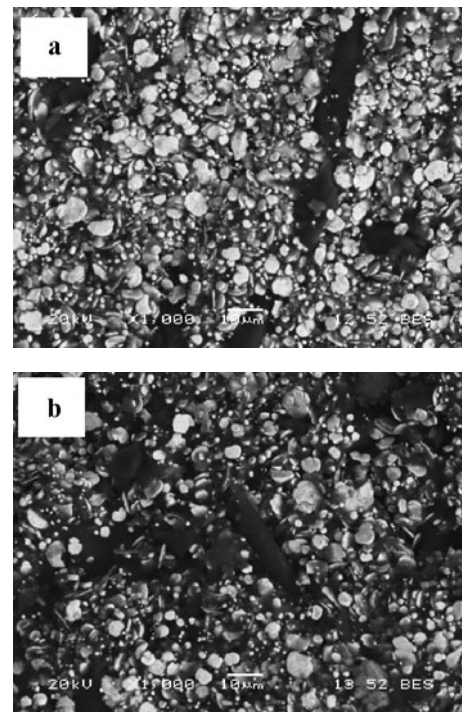


Fig. 1 SEM images of the (a) CF2 and (b) CF6 coatings

3.2 Electromagnetic properties of the microwave-absorbing coatings

In order to investigate the intrinsic reasons for microwave absorption of the coatings, the complex permittivity and permeability of the coatings were measured using the T/R coaxial line method. The complex permittivity of the coatings in microwave frequency band is simply expressed by $\varepsilon^* = \varepsilon' - j\varepsilon''$, where ε' is dielectric constant and ε'' is the lossy term [19]. Figure 2 shows the complex permittivity of the coatings with different CF content. With increasing the CF content, both real and imaginary part of the permittivity increased in the frequency range of 2–18 GHz. In general, concerning the dielectric relaxation in the frequency domain, the complex permittivity also can be fitted empirically by power laws: $\varepsilon' - \varepsilon'_\infty \propto F^{-b'}$ and $\varepsilon'' \propto F^{-b''}$, where ε'_∞ denoted high frequency permittivity [20, 21]. The results of the fitted b' and b'' varied from 0.31 to 0.45. Furthermore, the values of the complex permittivity of the coatings decreased with increasing frequency, which exhibited a visible frequency-dependent dielectric response.

Figure 3 represents the complex permittivity and loss tangent of the coatings with different CF content at 2 GHz. It is visible that the real and imaginary part of the complex permittivity increased sharply when the CF content was larger than 3 wt%. In general, the dielectric constant of composites depends on the configuration and internal fractal structure, which is proportional to the quantity of charge stored on the surface when the composites are under an applied

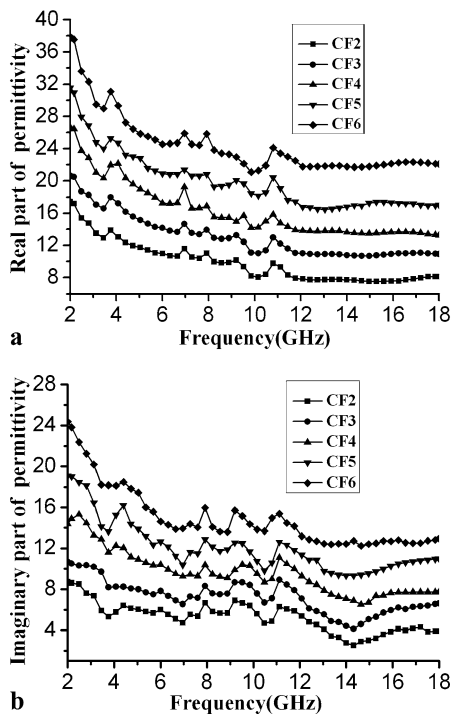


Fig. 2 The (a) real and (b) imaginary part of permittivity of the CF2, CF3, CF4, CF5 and CF6 coatings as a function of frequency

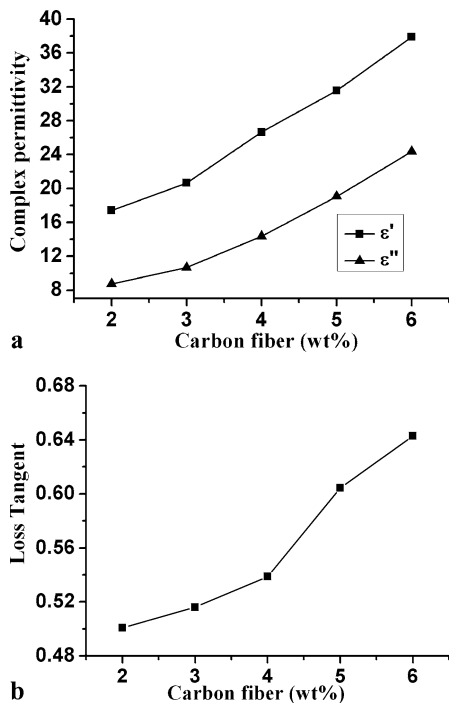


Fig. 3 Effect of CF content on the (a) complex permittivity and (b) dissipation factor of the coatings at 2 GHz

electric field. As the CF content increased, the CF/resin/CI interfaces increased, as shown in Fig. 1. Thus, a great deal of charge forms due to the polarization of the CF/resin/CI inter-

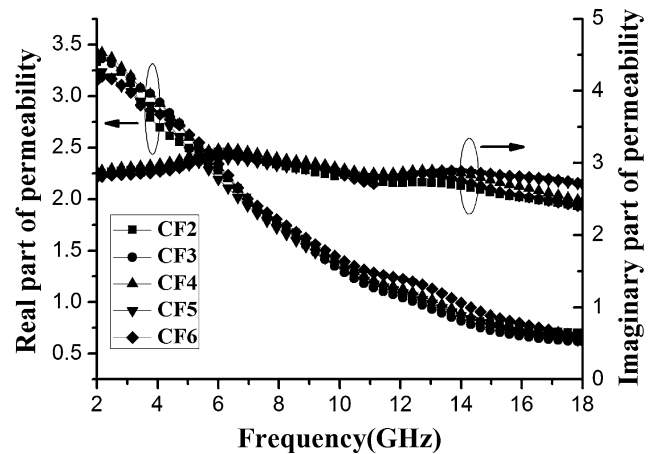


Fig. 4 Frequency dependence of the real and imaginary part of the permeability of CF2, CF3, CF4, CF5 and CF6 coatings

faces. From this point of view, the higher dielectric constant can obtain in the coatings with the higher CF content. The imaginary part of the complex permittivity (ϵ'') accounts for the energy loss dissipative mechanisms in the materials. When the coating is subjected to an electric field, the dependence of ϵ'' with frequency was usually described by a sum of two terms: $\sigma_0/2\pi f$ accounting for the conductive effects and ϵ''_R accounting for the relaxation effects. Much research showed that the conductivity of composites increased with increasing the CF content [22–24]. When the conductive filler content got below the percolation threshold, the main term affecting the ϵ'' is the interfacial polarization and its associated relaxation, while the conductivity term plays a secondary role. This phenomenon can also be explained by Maxwell–Wagner–Sillars theory, which accounts for the dielectric loss due to the interfacial polarization [25–27]. Thus, it is reasonable that the values of ϵ'' increased with increasing CF content. It is obvious that there is a certain relation between the complex permittivity and the microstructure as well as filler content of the filler-polymer composites. The dissipation factor (loss tangent) was calculated, and it increased with increasing CF content. In the microwave range of frequency, the loss tangent of the conductive fillers filling the polymer, determined by the loss tangent of the matrix and filling materials, shows reorientation of the permanent dipoles and the interface polarization [28, 29]. So the loss tangent of the coatings increased with increasing CF content and the CF/resin/CI interfaces.

Figure 4 shows the real and imaginary part complex permeability of the coatings as a function of frequency. The real part of the complex permeability of the coatings decreased from 3.4 to 0.7 with frequency increasing from 2 to 18 GHz. The imaginary part of the complex permeability exhibits a peak in a broad frequency range of 2–18 GHz and the resonance frequency is about 6 GHz.

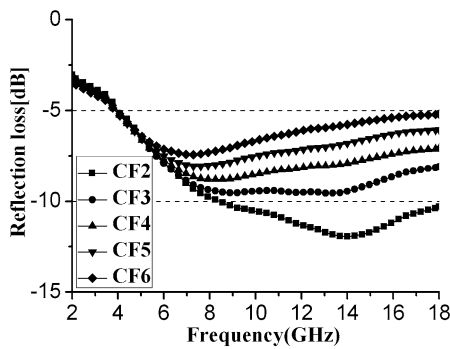


Fig. 5 Microwave absorption characteristics of the coatings with CI particles and different carbon fiber content for a single layer of 1 mm thickness

Compared to our previous work [14], the real part of the permittivity of the CI filled epoxy/silicone resin is almost constant, and the imaginary part of permittivity is fairly low in the frequency range of 2–18 GHz. When CF is added into the coatings, both the real and imaginary part of the permittivity sharply increased in the lower frequency range and the values of the complex permittivity of the coatings decreased with increasing frequency in the frequency range of 2–18 GHz. It is interesting to note that the dielectric properties of the coatings mainly are determined by the CF, which act as the conductive filler in the coatings. By comparing with the much increased of the complex permittivity, the complex permeability of the coatings remains nearly constant although the CF content increased, indicating no magnetic loss contribution from the CF.

3.3 Microwave-absorbing properties of the microwave-absorbing coatings

Figure 5 shows the relationship between reflection loss of the coatings and frequency for the coatings with different CF content. When the thickness of the coating is 1 mm, reflection loss values less than -5 dB can obtain in the frequency range of 4–18 GHz for all coatings. The strong microwave absorption (>10 dB, for over 90% microwave absorption) can get in the frequency range of 8–18 GHz for the CF2 coating. The frequency bands of reflection loss below -10 dB of the coatings were broader than those previously reported for flake-shaped CI powder filled epoxy resin composites [15], CF filled composites [16], CI/La_{0.6}Sr_{0.4}MnO₃ composites [17] and carbon nanofibers and NiFe particles filled composites [18].

The reflection loss of the CF2 coating with different coating thickness was shown in Fig. 6. The minimum reflection loss shifted to the lower frequency region from 14 to 3.5 GHz as the coating thickness increased from 1 to 3 mm. It is worth noting that the microwave absorption peak of the coating can be tuned easily by simply change the coating thickness. In addition, reflection loss values below -10 dB

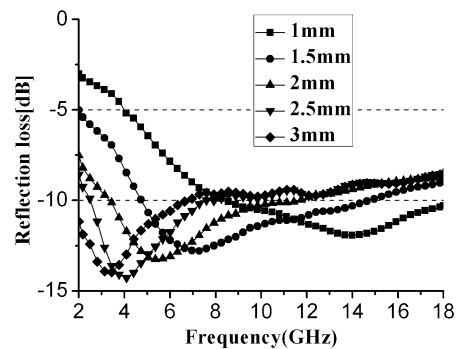


Fig. 6 Reflection loss of the CF2 coating with different thickness versus frequency

can be obtained in the frequency range of 8–18, 5–15, 3.4–11.7, 2.5–8 and 2–6.8 GHz, when the coating thickness is 1, 1.5, 2, 2.5 and 3 mm, respectively. It is clear that the reflection loss in the high frequency range, i.e., 8–18 GHz, is almost constant with the coating thickness increasing from 2.5 to 3 mm. When the coating thickness is larger than 2.5 mm, the reflection loss of the CF2 coating shows strong microwave absorption in the S-band (2–4 GHz) and C-band (4–8 GHz). The above results imply that we can get higher microwave absorption over a broad frequency range by varying the thickness and content of the CF in the coatings to meet different demands.

According to the transmission theory, for a single-layer absorber backed by a perfect conductor, the input impedance of the absorber Z_{in} of a metal-backed microwave-absorbing coating is given by

$$Z_{in} = Z_0 \sqrt{\frac{\mu_r}{\epsilon_r}} \tanh \left[j \frac{2\pi}{c} \sqrt{\mu_r \epsilon_r} f d \right], \quad (1)$$

where $Z_0 = \sqrt{\mu_0/\epsilon_0}$ is the impedance of the free space; μ_r and ϵ_r are the relative permeability and permittivity of the absorber; f is the frequency of the electromagnetic wave; d is the thickness of the absorber; c is the velocity of light in free space.

The reflection loss (RL) is given by following relation:

$$RL \text{ (dB)} = 20 \log |(Z_{in} - Z_0)/(Z_{in} + Z_0)|. \quad (2)$$

As we know, the design of EM waves absorbing materials with low reflection requires two important conditions. The first is “impedance matching characteristic” in which the intrinsic impedance of material is made equal to the impedance of free space. The second is “attenuation characteristic” in which the incident EM waves must enter and get attenuated rapidly through the material layer, thus reducing the emerging wave to an acceptable low magnitude [30–32]. It can be noticed from relation (1) and (2) that the combinations of six parameters (ϵ' , ϵ'' , μ' , μ'' , f and d) determine the microwave absorption of the composites. The minimizing reflection of incident plane wave can occur when Z_{in}

is close to the constant Z_0 . As shown in Fig. 5, the CF2 coating shows a high microwave absorption in the high frequency range (8–18 GHz) compared to the other coatings, which indicates that the Z_{in} of CF2 coating should match Z_0 most when the thickness of the coating is 1 mm and at the frequency range of 8–18 GHz. The lower reflection loss of the CF3–CF6 coatings can probably be attributed to the coatings with too large a complex permittivity, which can cause additional reflective wave on the coatings surface. Therefore, when the CF content increased, more reflection can be caused on the coatings surface and decrease the microwave absorption. We also calculated the reflection loss of the CI particles (65 wt%) filled coating with coating thickness being 1 mm, and the result shows that the reflection below -5 dB and -10 dB can be obtained in the frequency range of 6.7–18 GHz and 0 GHz, respectively. The results indicated that although the Z_{in} of the coating without carbon fiber should match Z_0 most compared to the CF and CI particles filled coatings, the imaginary part of the complex permittivity of the CI particles filled coatings is low in the frequency range of 2–18 GHz, which resulted in a poor absorption in the high frequency range. Thus, the control of the complex permittivity is significant for the use of the CF and CI particles to design a single-layer microwave-absorbing coating, when the complex permeability and the thickness of the coatings is kept constant. Furthermore, considering the high dielectric and magnetic loss of the CF2–CF6 coatings, broadband absorption coatings could be achieved using a multilayered absorbing structure with more optimization of the impedance matching characteristic and attenuation characteristic. We believe that the CF and CI filled coatings shall have great potential for broad bandwidth microwave-absorbing materials.

4 Conclusions

CI particles and CF as hybrid fillers were used to fabricate microwave-absorbing coatings through conventional technology. The electromagnetic and microwave-absorbing properties of the coatings as function of CF content are investigated. The results showed that it is useful to control the complex permittivity of the filled coatings by changing the CF content. When the coatings thickness reached 1 mm, reflection loss values below -5 dB can be obtained in the frequency range of 4–18 GHz, independent of the CF content (2–6 wt%). Furthermore, the reflection loss values below -10 dB can get in the frequency range of 2–18 GHz over a CF2 coating thickness of 1–3 mm. The high performance microwave coatings with wide band microwave absorption can be developed by the above magnetic-type and dielectric-type hybrid absorbers.

Acknowledgements This research was supported by the fund of the State Key Laboratory of Solidification Processing in NWPU, NO, KP200901.

References

1. W. Hayt, J. Buck, *Engineering Electromagnetics* (McGraw-Hill, New York, 2001)
2. K.J. Vinoy, R.M. Jha, *Radar Absorbing Materials from Theory to Design and Characterization* (Kluwer Academic, Boston, 1996)
3. D.R.J. White, *A Handbook on Shielding Design Methodology and Procedures: Interference Control Technologies* (Gainesville: A, 1986)
4. J.H. Oh, K.S. Oh, C.G. Kim, C.S. Hong, *Compos., Part B Eng.* **35**, 49 (2004)
5. D.A. Makeiff, T. Huber, *Synth. Met.* **156**, 497 (2006)
6. J.H. Du, C. Sun, S. Bai, G. Su, Z. Ying, H.M. Cheng, *J. Mater. Res. Soc.* **17**, 1232 (2002)
7. N.C. Das, D. Khastgir, T.K. Chaki, A. Chakraborty, *Compos., Part A* **31**, 1069 (2000)
8. Z.M. Dang, Y. Shen, L.Z. Fan, N. Cai, C.W. Nan, S.J. Zhao, *J. Appl. Phys.* **93**, 5543 (2003)
9. K. Akif, P. Andan, Y. Ulku, *Mater. Res. Bull.* **31**, 1195 (1996)
10. R.A. Tellakula, V.K. Varadan, T.C. Shami, G.N. Mathur, *Smart. Mater. Struct.* **13**, 1040 (2004)
11. M.A. Abshinova, A.V. Lopatin, N.E. Kazantseva, J. Vilckova, P. Saha, *Compos. Part A* **38**, 2471 (2007)
12. S. Kimura, T. Kato, T. Hyodo, Y. Shimizu, M. Egashira, *J. Magn. Magn. Mater.* **312**, 181 (2007)
13. I. Kim, S. Bae, J. Kim, *Mater. Lett.* **62**, 3043 (2008)
14. Y.C. Qing, W.C. Zhou, F. Luo, D.M. Zhu, *J. Magn. Magn. Mater.* **321**, 25 (2009)
15. B. Zhang, Y. Feng, J. Xiong, Y. Yang, H. Lu, *IEEE Trans. Magn.* **42**, 1778 (2006)
16. G. Shen, M. Xu, Z. Xu, *Mater. Chem. Phys.* **105**, 268 (2007)
17. Y.L. Cheng, J.M. Dai, D.J. Wu, Y.P. Sun, *J. Magn. Magn. Mater.* **322**, 97 (2010)
18. K.Y. Park, J.H. Han, S.B. Lee, J.B. Kim, J.W. Yi, S.K. Lee, *Compos. Sci. Technol.* **69**, 1271 (2009)
19. R. Che, L.M. Peng, X. Duan, Q. Chen, X. Liang, *Adv. Mater.* **16**, 401 (2004)
20. M. Malhi, M. Achour, F. Lahjomri, Y. Bensalah, *J. Mater. Sci. Lett.* **18**, 613 (1999)
21. C.W. Nan, *Prog. Mater. Sci.* **37**, 1 (1993)
22. J. Torrents, T. Mason, A. Peled, S. Shah, E. Garboczi, *J. Mater. Sci.* **36**, 4003 (2001)
23. Y. Sha, K.A. Jose, C.P. Neo, V.K. Varadan, *Microw. Opt. Technol. Lett.* **32**, 245 (2002)
24. J.F. Nascimewo, T.A. Ezquefwa, F.J. Balta-Calleja, J.C. Seferis, *Polym. Compos.* **16**, 109 (1995)
25. J.H. Wu, D.D.L. Chung, *Carbon* **40**, 445 (2002)
26. D.D.L. Chung, *Carbon Fiber Composites* (Butterworth-Heinemann, Boston, 1994)
27. D.D.L. Chung, *J. Mater. Sci.* **39**, 2645 (2004)
28. L.M. Ang, T.S.A. Hor, G.Q. Xu, C.H. Tung, S.P. Zhao, J.L.S. Wang, *Carbon* **38**, 363 (2000)
29. J.R. Liu, M. Itoh, T. Horikawa, E. Taguchi, H. Mori, K. Machida, *Appl. Phys. A* **82**, 509 (2006)
30. J.Y. Shin, J.H. Oh, *IEEE Trans. Magn.* **29**, 3437 (1993)
31. S. Yoshida, M. Sato, E. Sugawara, Y. Shimada, *J. Appl. Phys.* **85**, 4636 (1999)
32. P. Singh, V.K. Babbar, A. Razdan, S.L. Srivastava, T.C. Goel, *Mater. Sci. Eng. B* **78**, 70 (2000)