DESIGN OF SMC BASE ON FeSi AND MODIFIED RESIN

M. Strečková, M. Fáberová, R. Bureš, L. Kobera, J. Brus

Abstract

A design of soft magnetic material based on FeSi (core) and modified resin with silica (shell) was suggested. Hybride phenolic resisn was synthesized through modified sol-gel method. ^{13}C CP/MAS NMR and ^{29}Si CP/MAS NMR technique was performed for confirmation of the chemical structure of polymer matrix. The size and shape of silica nano-particles incorporated was shown by TEM. The hybride resin serves as a perfect insulating coating deposited on FeSi particles and the core-shell particles can be further compacted by standard powder metallurgy methods in order to prepare final samples for mechanical, electric and magnetic testing. The morphology and microstructure of the original particle, covered particle and fracture surface of final microcoposites was studied by SEM.

Keywords: SMC, core-shell powder, microcomposites, hybride resin, FeSi

INTRODUCTION

The insulating soft magnetic composites (SMCs) are traditionally designed from magnetic metal powders, which are covered ideally by a very thin insulating layer [1]. The dielectric materials used for the insulation can be selected from organic polymeric resins [2], or inorganic materials such as oxides, phosphates, or silicates [3,4]. As a core, Högänes Corporation has developed a high-purity FeSi powder which is quite superior with respect to the pure iron powder as it provides optimal ground for a further development of SMCs [5]. The main disadvantage of those materials usually lies in their low mechanical strength, because these materials are not sintered during their preparation. However, the mechanical and magnetic performance of SMCs can be basically tuned by selecting the appropriate base ferromagnetic material and applying a suitable insulating coating. To improve the mechanical hardness and flexural strength of the final SMCs, the organic polymers used for preparation of the insulating coatings are usually modified with some inorganic filler. Reinforced polymer composites are ordinarily prepared by an artificial incorporation of diverse inorganic additives (e.g. natural fibers, clays, silica, carbon nanorods or graphene) into the polymer matrix during their synthesis [6-8]. One should bear in mind that an incorporation of some inorganic fillers such as silica may cause incompatibility between hydrophilic particles and the hydrophobic polymer matrix. A coupling agent is a chemical substance which serves for creating a chemical bridge between the inorganic additive and organic polymer matrix at the relevant interface [9]. For the particular case of the silica filler, silane molecules with bifunctional groups may be used as the suitable coupling agent, providing a chemical bridge in between the inorganic additive and organic polymer matrix [10].

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In this work, the hybrid phenol-formaldehyde resin (PFR) modified by SiO_2 (PFRSi) nano-particles was synthesized as the insulating layer of the designed SMCs. The synthesis procedure and chemical identification of the modified resin was described in detail. The chemical modification of polymer matrix by silica was confirmed by NMR and FTIR analysis. The thermal degradation of hybride polymer was studied. TEM, SEM and EDX analysis was performed in order to provide a detailed characterization of silica nanoparticles intercalated in the polymer matrix.

EXPERIMENTAL

FeSi (3% of Si) spherical particles distributed by the Högänes Corporation was used as the base ferromagnetic material, which is available in granulometric fraction from 45 μm to 150 μm [5]. Phenol (Ph, 99%), formaldehyde (F, 37% aq.), ammonia (NH_3, 26% aq.), tetraethylorthosilicate (TEOS, 99%) and 3-glycidoxypropyltrimethoxysilane (GLYMO, 98%) were used for the synthesis of PFRSi. The tetrahydrofuran (THF, 99.9%) and absolute ethanol were used as the solvents.

The preparation of the hybride PFRSi polymer with the chemical incorporation of silica is depicted in Fig.1. The initial molar ratio for synthesis of PFRSi was $Ph/F/NH_3/GLYMO/TEOS$ 1.0/1.5/0.35/0.1/0.1. The predetermined amount of GLYMO was added to the prepared binary Phenol and Formaldehyde solution and mixed for 10 min. In the next step, TEOS was added to the ternary solution. NH_3 as a catalyst was added dropwise to the cooled mixture.

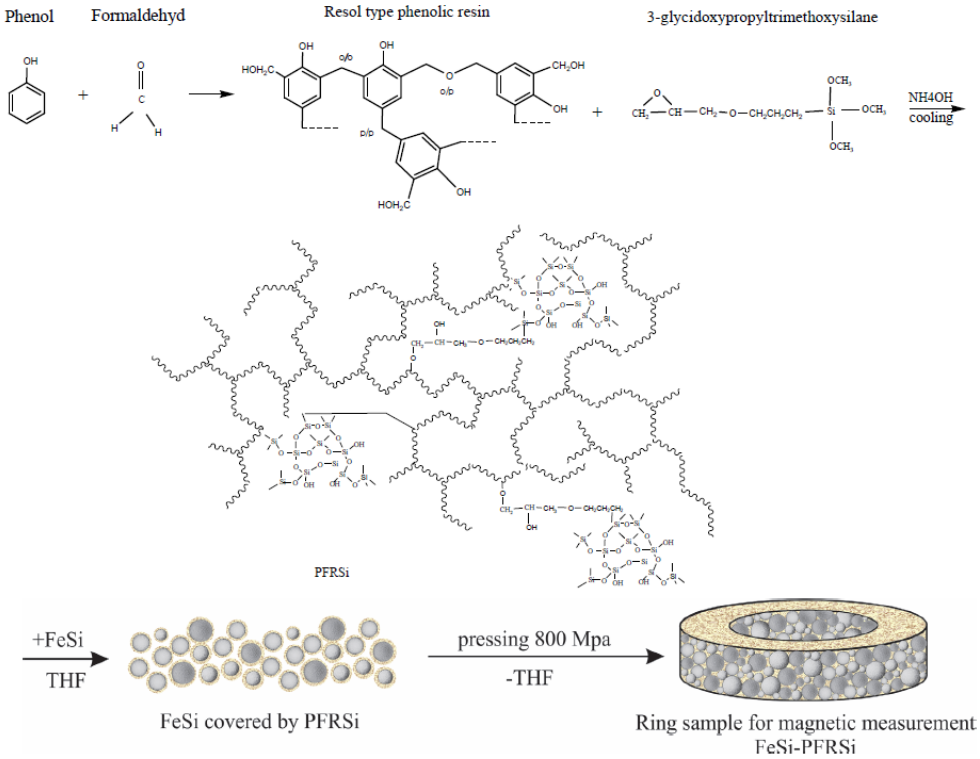

Fig.1 Synthesis of PFRSi, preparation of FeSi/PFRSi core-shell powder and final microcomposite ring for mangetic measurement.

RESULTS AND DISCUSSION

NMR

The NMR study was employed to confirm the structure and ordering of the prepared hybride organic-inorganic PFRSi resin. ^{13}C CP/MAS NMR technique was performed for the characterization of the resin (Fig.2). For a more detailed description of the prepared organic-inorganic polymeric system, the inorganic part was investigated by ^{29}Si CP/MAS NMR spectroscopy. Predominantly, the quantitative analysis of the recorded ^{29}Si CP/MAS NMR spectrum (Fig.3) allowed calculation of the polycondensation degree q_i:

$$q_i = (\sum_{n=1}^{3} nT^n * \tfrac{1}{3}) + (\sum_{n=1}^{4} nQ^n * \tfrac{1}{4}) \quad (1)$$

where T^n and Q^n are the mole fractions of each corresponding siloxane structure unit arising from from GLYMO and TEOS, respectively, and n denotes the total number of silicon atoms surrounding the central $–CH_2–SiO_3$ (from GLYMO) and SiO_4 (from TEOS) units. The mole fractions of siloxane units were obtained from the ^{29}Si CP/MAS NMR spectrum by deconvolution procedures. The obtained results thus suggest that T^3 units arising from GLYMO are dominant in the overall polymeric structure of $PFRSiO_2$ with a minor contribution of the other units (T^2, Q^3 and Q^4) arising from GLYMO and TEOS. Besides, the high polycondensation degree (q_i = 0.93) and the resulting spectrum also confirm an almost fully condensed polysiloxane network.

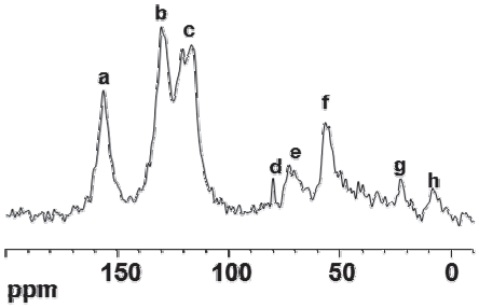

Fig.2. ^{13}C CP/MAS NMR spectrum of organic-inorganic $PFRSiO_2$ hybrid system.

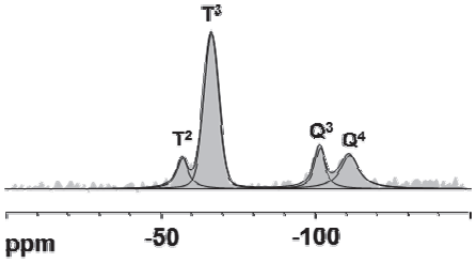

Fig.3. ^{29}Si CP/MAS NMR spectrum of PFRSi and the deconvolution on individual spectral components. The original spectrum is reflected by gray areas.

SEM and TEM

The original and covered FeSi particles by PFRSi resin were investigated by SEM (Figs.4,5). Ideal spherical morphology of the original commercial FeSi powder is shown in Fig.4. The FeSi surface covered with synthesized resin in bulk was observed on the fractured surface of FeSi/PFRSi (Fig.5). A more detailed SEM image on the microstructure of the fractured FeSi/PFRSi surface is depicted in Fig.6. It is quite apparent from this figure that the hybrid coating $PFRSiO_2$ has a tendency to cover the surface of FeSi microparticles completely and quite uniformly. The main confirmation as to sufficient coverage is the callosity of resin after falling out of one spherical FeSi particle. TEM provides insights into the morphology, substructure and size of SiO_2 nanoparticles synthesized in situ with the

PFR polymer matrix (Fig.7). SiO_2 particles have preferably nanorod shape in an average of 150 nm length and of 10 nm diameter.

Fig.4. The original FeSi particles.

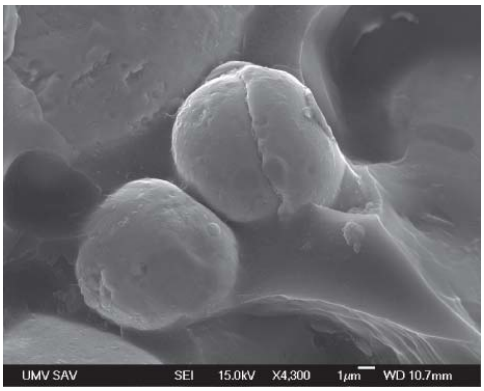

Fig.5. The covered FeSi particles by PFRSi resin inside bulk material.

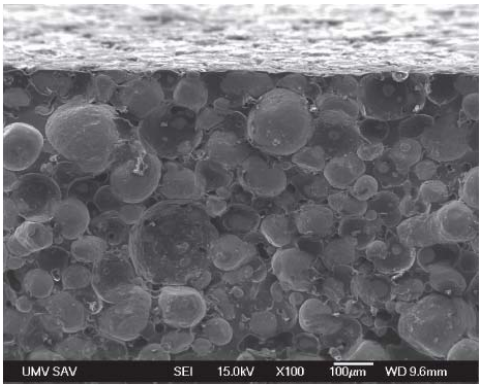

Fig.6. SEM image of the fractured surface.

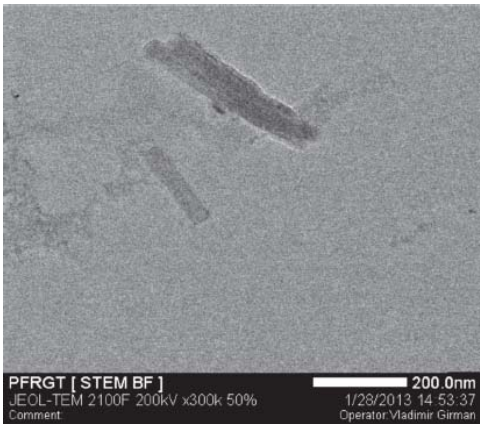

Fig.7 TEM image of the hybrid polymer PFRSi.

CONCLUSION

The novel SMC, which is composed of spherical FeSi powder linked together through the phenolic resin chemically modified silica nano-particles, has been prepared and investigated in detail. A modified sol-gel method was used for the synthesis of hybride resin PFRSi. The structure of polymer and chemical bonding of the silica nano-particles was confirmed by NMR. The incorporation of silica nano-rods to the polymer matrix was visualized by TEM. SEM images give evidence of negligible porosity, uniform distribution of the hybrid resin around FeSi particles, as well as dimensional shape stability of the final samples after thermal treatment. It has been shown that the prepared hybrid resin offers a

reliable option for being used as an electroinsulating layer, which perfectly covers the surface of magnetic particles and avoids the inter-particle contacts.

Acknowledgements

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REFERENCES

[1] Bas, JA., Calero, JA., Dougan, MJ.: J. Magn. Magn. Mater., vol. 254-255, 2003, p. 391
[2] Strečková, M., Sopčák, T., Medvecký, Ľ., Bureš, R., Fáberová, M., Batko, I., Briančin, J.: Chem. Eng. J., vol. 180, 2012, p. 343
[3] Bruncková, H., Kabátová, M., Dudrová, E.: Surf. Interface Anal., vol. 42, 2010, p. 13
[4] Kabátová, M., Dudrová, E., Bruncková, H.: Surf. Interface Anal., vol. 45, 2013, p. 1166
[5] Hoganes datasheet, www.haganas.com
[6] Hernandez-Padron, G., Rojas, F., Garcia-Gardun, M., Canseco, MA., Castano, VM.: Mater. Sci. Eng. A, vol. 355, 2003, p. 338
[7] Hasegawa, I., Fukuda, Y., Kajiwara, M.: J. Eur. Ceram. Soc., vol. 17, 1997, p. 1467
[8] Zhang, X., Shen, L., Xia, X., Wang, H., Du, Q.: Mater. Chem. Phys., vol. 111, 2008, p. 368
[9] Xie, Y., Hill, CAS., Xiao, Z., Militz, H., Mai, C.: Composites: Part A, vol. 41, 2010, p. 806
[10] Strečková, M., Medvecký, Ľ., Füzer, J., Kollár, P., Bureš, R., Fáberová, M.: Materials Letters, vol. 101, 2013, p. 37