Fe(CORE)/SiO_2(SHELL) COMPOSITE POWDER PREPARED BY THE SOL-GEL METHOD

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Abstract

Fe(core)/SiO_2(shell) composites were designed from alkoxide solutions by the hybrid sol-gel method. SiO_2 coatings prepared by pure inorganic sol-gel methods are usually brittle and easy to crack during curing because of the inflexibility of SiO_2 structure and the residual stress generated from volumetric shrinkage. Therefore, the hybrid organic-inorganic sols with addition of 3-glycidoxipropyltrimethoxysilane or phenol-formaldehyde resin were used to improve the quality and distribution of SiO_2 coating on Fe powder. The thermal degradation, both of the pure inorganic or of the hybride organic-inorganic silica sol, was studied. Optical visualization of Fe/SiO_2 powder confirmed the significant difference between internal shrinkage in the deposited silica coatings. SEM analysis established that coatings prepared from hybrid sols are more compact and smooth than those stemming from pure inorganic SiO_2 coatings. Preliminary study indicates high electrical resistivity, due to a sufficiently insulating character of the SiO_2 layer.

Keywords: core-shell powder, microcomposites, hybrid sol-gel method, SiO_2 coating, silane, phenol-formaldehyde resin

INTRODUCTION

Magnetic particles of metals such as Fe, Co and Ni coated by a thin layer of SiO_2 have been intensively studied because of several important benefits in comparison with base magnetic metals. Silica coating can provide a protective shell surrounding the magnetic core and enhance the resistance of core materials with respect to oxidation [1]. SiO_2-based coatings are widely used as thermal protection coatings for metals because of its high melting point, high emissivity and low thermal conductivity [2,3]. Nanomagnets encapsulated by inorganic materials, which could effectively protect them form oxidation and reduce the dipole interaction, are utilized in biomedicine for targeted drug delivery [4]. An easy control of the deposition process, controllable porosity and optical transparency, make silica an ideal, low-cost material to tailor surface properties by maintaining the physical integrity of the underling core [5].

Soft magnetic composites (SMCs) prepared by powder metallurgy methods result from pressing a ferromagnetic core (e.g. Fe powder) covered by a thin electroinsulating layer. For many years, researchers have been searching for fine soft magnetic materials with a high saturation magnetization, high permeability and low energy loss, which can be used in a wide frequency range and are especially useful at high frequencies [6]. Good insulation is generally required to minimize eddy current losses in SMC subjected from medium to high frequencies. To provide an as high as possible permeability, the amount of interparticle insulation should be minimized and the iron content maximized.

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Many methods may be employed in order to prepare SiO_2 coating, such as sol-gel, thermal oxidation and physical or chemical vapour deposition. The most promising technique, with a substantial diversity of possible additives and controllability during preparation of the coating, is sol-gel process. Many researchers have focused their attention on the preparation of SiO_2 coatings from aqueous or alcoholic environments [7,8]. The basic chemical reactions leading to the formation of a polymer solution from tetraethylortosilicate $Si(OC_2H_5)_4$ (TEOS) can be presented as follows:

hydrolysis

$$[\ (RO)_3 \equiv Si - OR\ ] + HOH \longrightarrow [\ (RO)_3 \equiv Si - OR\ ] + ROH$$

polymerization

$$[\ \equiv Si - OH\ ] + [\ RO - Si \equiv\ ] \longrightarrow [\ \equiv Si - O - Si \equiv\ ] + ROH$$

The sol-gel method consists of the application of a thin liquid layer of polymer solution on the substrate and subsequent gelation of this coating. A final heat treatment transforms the gel into glassy or ceramic form. The liquid film may be deposited in different ways. In the present work, the mechanical mixing sol-gel solution with Fe powder was used. The sol-gel process can be easily controlled to produce thin and lightweight coatings on large and complex areas, and the coatings can be repaired by sol-gel with low cost and working requirement [9]. Sol-gel method itself has a lot of advantages, such as a good homogeneity, high purity and low processing temperatures. The disadvantage of sol-gel prepared coating is that they are brittle and easy to crack during curing because of the inflexibility of SiO_2 structure and the residual stress generated from volumetric shrinkage [10]. Silane resin or silane-coupling agents are consequently added to improve filming ability of the traditional sol-gel methods [11]. The organic-inorganic hybrid network can avoid cracking of SiO_2 based coatings during the gel process [12]. This approach can reduce coatings' residual stress because volume change of silane resins is much lower during oxidation than that of traditional resins [13]. Magnetic properties of silica coated iron particles were also studied by Cheng et al. [14]. The core-shell SiO_2 magnetic microspheres (MMS) were prepared through the sol-gel method [15]. Here, the influence of silane-coupling agent on the preparation of SiO_2 MMS was studied and the results show that the selection of silane coupling agents and the coupling process itself are quite important for the preparation of SiO_2 MMS.

The main task of the present work is to compare different hybride organic-inorganic sols, which could be applied as suitable coating for Fe powder. The first water-based solution was constituted by the well know components such as TEOS, Ethanol, H_2O, HCl. Two additional solutions were modified by 3-glycidoxypropyl-trimetoxysilane (GLYMO) or phenolic resins. The thermal degradation of all the coatings prepared was studied. The quality of prepared layers was observed by optical microscopy. The morphology and macrostructure, thickness and distribution of prepared silica coating on Fe powder was studied by SEM.

EXPERIMENTAL

Materials and chemicals

The base ferromagnetic Fe powder (ASC 100.29, Höganäs AB) with a size fraction in the range from 45 to 212 μm was used. All chemicals used in the preparation of sols were in analytical grade without further purification. Tetraethoxysilane (TEOS, 99%

Merck), hydrochloric acid (HCl, 37% Aldrich), 3-glycidoxypropyl-trimetoxysilane (GLYMO, 98% Aldrich) and ethanol (Et–OH, absolute Aldrich) were used for the preparation of sols. Phenol (Ph, 99.0%, Aldrich), formaldehyde (F, 37% aq, Aldrich) and ammonia solution (NH_3, 26%, Aldrich) were used for chemical synthesis of the phenol-formaldehyde resin (PFR).

Preparation of sols

The molar ratios of each prepared sol are summarized in Table 1. The synthesis of PFR is described in our previous work - Strečková et al. [15] - in detail.

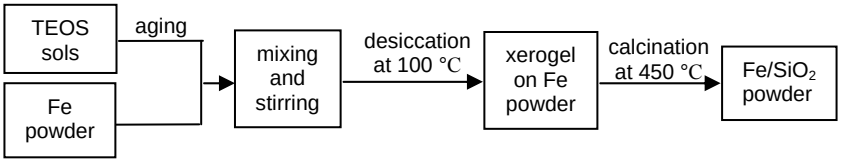
Tab.1. The molar ratio of prepared sols.

Sols	TEOS	H_2O	Et-OH	HCl	GLYMO	PFR
A [7]	1	4.5	17	0.01	-	-
B [14]*	1	4	4	0.10	-	-
C [14]*	1	4	4	0.01	4	-
D [9]*	1	4	4	0.01	4	200 mg

* Modified procedures of hybrid sol-gel methods according to the literature [14] or [9].

Preparation of Fe/SiO_2 powders

Fe-SiO_2 core-shell composite has been prepared according to the following schedule.



Characterization

The thermal degradation (TG) of prepared sols was studied by differential scanning calorimetry (DSC) (NETZSCH STA 449F1). The particle morphology and distribution of coating was characterized by scanning electron microscopy (SEM Jeol JSM-7000F) equipped with an energy dispersive X-ray spectroscopy EDX, after carbon coating. The distribution of each phase was observed by optical microscopy (OM LEICA DMIL LED). The electrical resistivity was determined on samples with a cylindrical shape 10 x 3 mm (d x h) by a Teraohmmeter-Picoampermeter Sefelec M1501P.

RESULTS AND DISCUSSION

Thermal analysis

Thermogravimetric curves of silica xerogels samples achieved from sols A, C, D after drying and grinding in air are depicted in Fig.1a,b. The highest heat resistance in the region from 25°C to 300°C was observed in the sample D, which was modified by PFR. On the other hand, the highest weight loss up to 300°C was detected in pure silica sol (sample A). The weight loss in this region is connected with desorption of physisorbed water. The loss of chemically bonded water usually took place at higher temperatures, around 600°C. The gel containing only TEOS as Si precursor behaves as a common silica xerogel, which was described by many researchers. A greater weight loss is evident in the sample D above 300°C, due to a release of volatile monomers during crosslinking of the resin with an

inorganic component. In the TG trace of the sample A, the plateau is observed above 350°C, which implies a stable inorganic silica phase. According to [17], the gradual heating up to 200°C is related to the elimination of adsorbed water and the further heating up to 450°C corresponds to the dehydroxylation of the surface through a condensation reaction. The very interesting sharp mass loss was observed in the sample C around 150°C (depictured as a red circle in Fig.1a), which can be attributed to a significant combustion of the organic part of the sol. It is well known that pure inorganic SiO_2 coatings has much better heat resistance above 300°C than those coming from modified silica sols. However, it turns out that the heat resistance of silica sols can be substantially improved up to 300°C by the addition of PFR, because Si-OH groups from the surface of SiO_2 particles may chemically react with a phenolic resin. The strong Si-O-C chemical bonding consequently leads to the formation of more stable coatings, which manifest itself in a higher thermal stability as well [18]. Accordingly, the destruction of stronger chemical bonds is displayed in different exothermal effects by the sample D at higher temperatures (see Fig.1b).

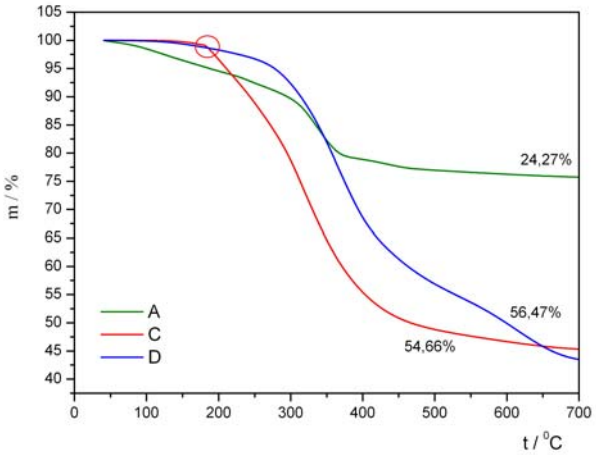


Fig.1a. TG traces of the samples A, C, D.

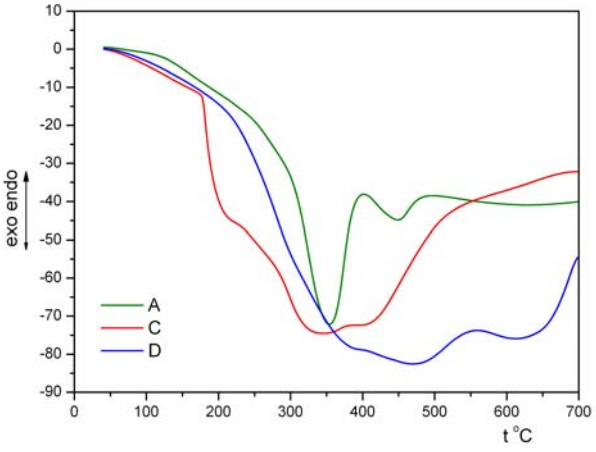


Fig.1b. DSC traces of the samples A, C, D.

Optical microscopy characterization

The significant difference between prepared silica coatings deposited on a microscope glass substrate and dried at 100°C is shown in Fig.2a,b,c. The incorporation of organic molecules into the essentially inorganic matrix using the sol-gel method has a significant effect on the adhesive strength and mechanical strength of the prepared coating. When the organic groups were integrated into the glass matrix, the shrinkage is decreased rapidly, because the bulky organic components fill the pores between the inorganic oxide chains, and they will generally improve the properties of the final layer [14]. It is clearly seen that the coating acquired from sol A has considerable internal stress in comparison with coatings obtained from sol C or D. A disruption and large gap was observed in the coating A. Evident decrease of contraction in the coating of sample C and the totally different way of internal stress creation in sample D (in the form of fish scales) can be attributed to the incorporation of bulky organic molecules to the inorganic matrix and changed initial viscosity, toughness and adhesion of the prepared substrate. It should be noted that the adhesive strength and other physical properties can be influenced by using a different substrate.

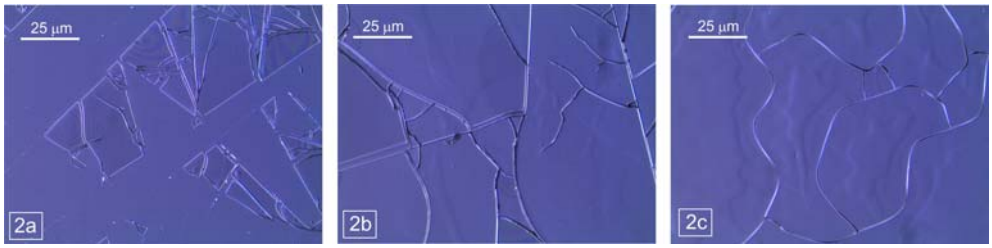


Fig.2. OM image of silica coating on a glass substrate prepared from sol: (a) A, (b) C, (c) D.

SEM Characterization

The microstructure and morphology of Fe/SiO_2 particles prepared from different sol-gel solutions were examined by scanning electron microscopy (SEM) supplemented by EDX analysis and/or mapping analysis of individual elements. The comparison of surface morphology of pure Fe particles and Fe particles coated by SiO_2 prepared from the sol marked as A in Table 1 after drying at 100 °C for 1h is illustrated in Fig.3a,b. It is quite clear from this figure that the SiO_2 coating forms a regular, but cracked, continuous shell with a thickness around 4 μm. EDX analysis (from site marked as X) has confirmed that the areas with a higher content of SiO_2 have a glassy character, which causes a predisposition to exfoliation from the particle surface. The cross-section of Fe/SiO_2 particles coated from sol A, complemented by mapping EDX analysis of Si and O, is shown in Fig.4a,b,c. The brittleness and cracks of silica coating prepared from the sol A become much more pronounced on those Fe particles which were milled before the coating process (Fig.4a). Different silica distribution after drying was observed in the samples prepared from the solution marked as C in Table 1 (Fig.5a). GLYMO caused a higher surface tension in the sol and affected the wetting of Fe powder. A very thin layer of silica coating was indeed confirmed by the mapping analysis of Si and Fe elements, as shown in Fig.5b and 5c. However, the higher content of SiO_2 in both sols C and D is responsible for the creation of clusters, which consist of several aggregated Fe particles surrounded by silica. Moreover, some discrete SiO_2 parts can be detected in Fig.5a by mapping of Si. A continuous net around Fe particles was observed in the sample Fe/SiO_2 acquired from the sol D

(Fig.6a,b,c), where phenolic resin was added to the sol C. The coating created from the hybride organic-inorganic sol very effectively covers the surface of Fe powder without any visible exfoliation. Fe/SiO_2 powder prepared from sol A was compressed at 800 MPa to a cylindrical sample shape for an electrical resistivity test. This composition of sol represents around 8 wt.% of SiO_2 coating in the prepared green compact. Note that the higher content of silica does not allow compression of the microcomposite powder to the required final shape. The measured value of electrical resistivity was 7.4322 x 10^{12} μΩ·m. The preparation of sols with a lower content of silica and its application as a suitable coating on Fe powder without creation of such clusters will be therefore subject of our future work.

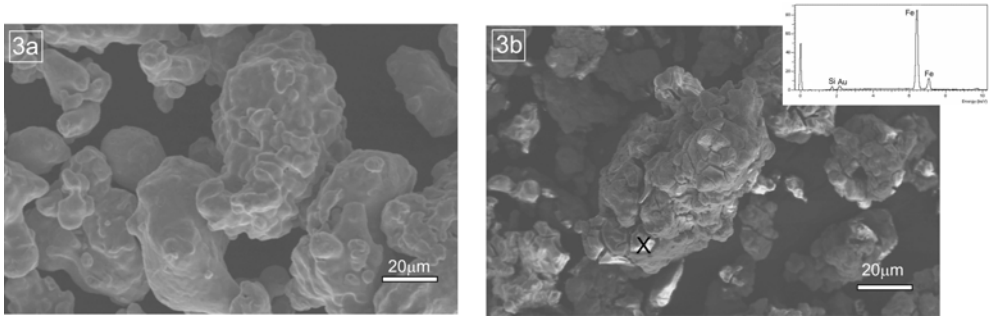


Fig.3.Comparison of SEM images of pure Fe powder and Fe/SiO_2 coated powder prepared from the sol A with EDX analysis from site X.

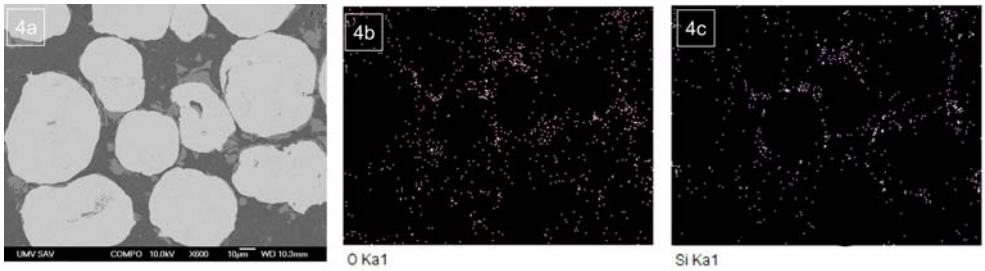


Fig.4. SEM image of Fe/SiO_2 powder prepared from the sol A: (a) cross-section; (b) Si map; (c) O map.

Fig.5. SEM image of Fe/SiO_2 powder prepared from the sol C: (a) cross-section; (b) Si map; (c) Fe map.

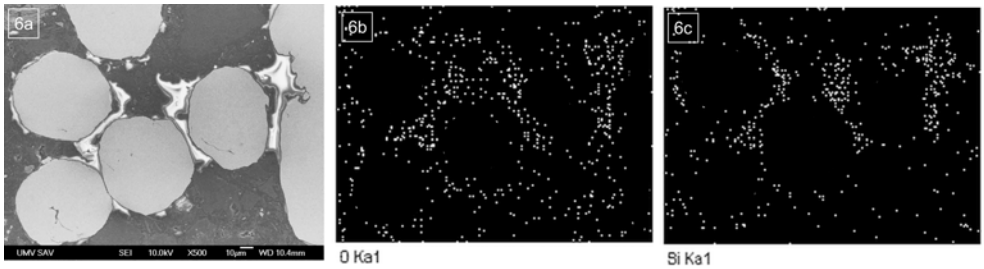


Fig.6. SEM image of Fe/SiO_2 powder prepared from the sol D: (a) cross-section; (b) Si map; (c) O map.

CONCLUSION

Three different solutions have been used for the design of suitable coatings on Fe powder particles. TG analysis has confirmed a slower thermal degradation of the coatings with addition of silane or phenolic resins in the region from 0 to 200°C. It has been shown that the highly porous silica networks are considerably influenced by introducing organic chains into the basic silica skeleton. The addition of GLYMO or PFR leads to an increase of the elasticity and the coating shrinkage and consequently the hybride coatings are less sensitive to cracking during drying than the purely inorganic sol-gel coatings. The higher toughness and better adhesion was found in the samples prepared from the sols containing the phenolic resin. It also turns out that Fe/SiO_2 composites prepared from sols C and D contain clusters with a higher content of silica. Due to this, Fe particles are sticking to each other by the hard silica, which does not allow compression of the microcomposite powder into the required final shape. This disadvantage could be eliminated by a variation of starting molar ratio aimed at a decrease of SiO_2 content in the prepared sols. The more detailed study of electrical resistivity and magnetic properties of microcomposite samples prepared in this way will be subject of our further investigation.

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