Journal of Solid State Chemistry 231 (2015) 152–158

Contents lists available at ScienceDirect

Journal of Solid State Chemistry

journal homepage: www.elsevier.com/locate/jssc

Synthesis, microstructure and magnetic properties of $Fe_3Si_{0.7}Al_{0.3}@SiO_2$ core–shell particles and Fe_3Si/Al_2O_3 soft magnetic composite core

Jian Wang [a,b], Xi'an Fan [a,b,*], Zhaoyang Wu [a,b], Guangqiang Li [a,b]

[a] The State Key Laboratory of Refractories and Metallurgy, Wuhan University of Science and Technology, Wuhan, Hubei 430081, China
[b] Key Laboratory for Ferrous Metallurgy and Resources Utilization of Ministry of Education, Wuhan University of Science and Technology, Wuhan, Hubei 430081, China

ARTICLE INFO

Article history:
Received 10 June 2015
Received in revised form
3 August 2015
Accepted 12 August 2015
Available online 20 August 2015

Keywords:
$Fe_3Si_{0.7}Al_{0.3}@SiO_2$ core–shell particles
Fe_3Si/Al_2O_3 soft magnetic composite core
Magnetic properties
Electrical properties
Core loss

ABSTRACT

$Fe_3Si_{0.7}Al_{0.3}@SiO_2$ core–shell particles and Fe_3Si/Al_2O_3 soft magnetic composite core have been synthesized via a modified stöber method combined with following high temperature sintering process. Most of conductive $Fe_3Si_{0.7}Al_{0.3}$ particles could be uniformly coated by insulating SiO_2 using the modified stöber method. The $Fe_3Si_{0.7}Al_{0.3}@SiO_2$ core–shell particles exhibited good soft magnetic properties with low coercivity and high saturation magnetization. The reaction $4Al+3SiO_2=2\alpha\text{-}Al_2O_3+3Si$ took place during the sintering process. As a result the new Fe_3Si/Al_2O_3 composite was formed. The Fe_3Si/Al_2O_3 composite core displayed more excellent soft magnetic properties, better frequency stability at high frequencies, much higher electrical resistivity and lower core loss than the pure $Fe_3Si_{0.7}Al_{0.3}$ core. The method of introducing insulating layers surrounding magnetic particles provides a promising route to develop new and high compact soft magnetic materials with good magnetic and electric properties.

1. Introduction

Recently, soft magnetic composites (SMCs), which are widely used in electromagnetic applications, have drawn much attention because of their excellent properties such as high electrical resistivity, three-dimensional isotropic ferromagnetic behavior, very low eddy current loss and relatively low total core loss at medium and high frequencies [1–4]. Generally, SMCs are prepared by power metallurgy (PM) methods, in which ferromagnetic particles are separated by high resistivity or even insulating layers.

For ferromagnetic powders used for SMCs, Fe–Si–Al alloys with a composition of 9.6 wt% Si, 5.4 wt% Al and Fe balance, known as Sendust, have been extensive studied due to their high electrical resistivity, high saturation magnetization, low coercivity and matched permittivity [5]. As we all know, Fe–Si–Al core offers several advantages over the other soft magnetic cores. Compared with ferrite core, it has higher saturation magnetization, making it have promising applications in large current fields [1]. Compared with permalloy core, the raw materials are very cheap because those expensive materials such as Ni and Mo are not used. Compared with pure iron core, Fe–Si–Al core has a comparable permeability and lower core loss at high frequencies. Because of the above mentioned, Fe–Si–Al core is completely suitable for filtering inductors in switching power supply, line noise filters, power factor correction, fly-back transformer and pulse transformer application etc [6].

Generally, Fe–Si–Al core is used mainly at high frequencies. However, it must be pointed out that as operating frequency (f) increases, the eddy current loss ($W_e \propto f^2$) increases rapidly much more than hysteresis loss ($W_h \propto f$) so that the total core loss is dominated by W_e at about $f>100$ kHz [7,8]. Eddy current loss not only worsens the overall magnetic properties but also can produce lots of heat due to Joule effect [9]. In order to relieve energy loss caused by eddy current loss, it is critical to increase resistivity of Fe–Si–Al core. Coating high resistivity or even insulating layers on the surface of Fe–Si–Al powders can effectively increase the resistivity of core.

In general, insulating coatings can be separated into two categories, organic and inorganic coatings. Because of low thermal stability for organic coatings, the heat treatment temperature selected for core is often very low (< 700 °C) to avoid decomposition of organic coatings. Because of the relative low heat treatment temperature, the density and compactness are also very low for the cores with organic coatings, which cause a serious decline in their mechanical and magnetic properties. Thus inorganic coatings are favored due to their high thermal stability. Recently, inorganic

* Corresponding author at: 185#, School of Materials and Metallurgy, Wuhan University of Science and Technology, 947 Heping Road, Qingshan District, Wuhan 430081, China. Fax: +86 2768862529.
E-mail addresses: snove418562@163.com (J. Wang), groupfxa@163.com (X. Fan), wustwuzhaoyang@163.com (Z. Wu).

http://dx.doi.org/10.1016/j.jssc.2015.08.016
0022-4596/

coatings such as phosphate, Al_2O_3 and AlN have been investigated in SMCs. Taghvaei et al. [10,11] obtained iron-phosphate-based soft magnetic composites with high electrical resistivity and high density. Zhong et al. [12] investigated the structure and properties of FeSiAl-based soft magnetic composites with Al_2O_3 and AlN insulating layer prepared by selective nitridation and oxidation. The results confirmed that Al_2O_3 and AlN insulating layers can increase obviously electrical resistivity, decrease loss factor, improve frequency stability and quality factor, especially in high-frequency range. Yaghtin et al. [13] prepared iron-based soft magnetic composites with Al_2O_3 insulation coating by sol–gel method. Besides, silica coating techniques have been also used to prepared soft magnetic composites [14–16]. SiO_2 is commonly used as surfaced shell of magnetic core–shell nanoparticles because of its good chemical inertness, high suspension stability and non-toxicity [16–24]. In recent years, silica-coated iron particles have also been investigated as a novel kind of SMCs by many researchers [9,14,15], while few studies have been carried out for the FeSiAl-based soft magnetic materials.

In the present work, $Fe_3Si_{0.7}Al_{0.3}@SiO_2$ core–shell particles were synthesized by a modified stöber method [25] with a silane-coupling agent as modification additive [18]. And then high temperature sintering (at 1100 °C) was used to obtain the high-density composite cores. Their microstructure, electrical and magnetic properties have been investigated systemically.

2. Experimental

2.1. Materials and reagents

All chemicals used were of analytical grade and were used as received without further purification. The commercial water atomized $Fe_3Si_{0.7}Al_{0.3}$ alloy powders with a composition of 9.6 wt% Si, 5.4 wt% Al and Fe balance were purchased from Hunan Ruihua Hitech Material CO., LTD. Tetraethyl orthosilicate (TEOS), 3-triethoxysilypropylamine (APTES), aqueous ammonia (25 wt%) and ethanol absolute were purchased from Tianli Chemical Reagent Company, Tianjin, China. Distilled water (H_2O) was prepared by Automatic Double Pure Water Distillatory (SZ-93A, China) in laboratory.

2.2. Preparation of $Fe_3Si_{0.7}Al_{0.3}@SiO_2$ core–shell particles

In a typical synthetic procedure, 50 g $Fe_3Si_{0.7}Al_{0.3}$ powders were dispersed in 500 ml ethanol absolute by mechanical stirring for 10 min, and then 3.0 g APTES and 10 ml deionized water were added to the mixture under mechanical stirring for 1 h at 50 °C. And then, 20 ml TEOS and 2 ml aqueous ammonia (25 wt%) were injected simultaneously into the mixture by injection pump (LSP01-2A) at a constant speed at 60 °C for 10 h. And then the mixture was stirred for another 6 h. Finally, the suspension was filtered, washed with ethanol absolute several times, and then dried at 60 °C for 24 h.

2.3. Preparation of Fe_3Si/Al_2O_3 composite core

The collected powders were pressed under 2000 MPa into toroidal shape with outer diameter of 20.3 mm, inner diameter of 12.7 mm and thickness of 6.35 mm. Finally, the Fe_3Si/Al_2O_3 composite core was obtained by sintering at 1100 °C for 2 h in Ar atmosphere. To investigate the effect of insulating coatings on the electrical and magnetic properties, the raw $Fe_3Si_{0.7}Al_{0.3}$ core without SiO_2 coatings were also prepared under the same conditions.

2.4. Characterization

X-Ray diffraction (XRD) were analyzed on an X-Pert Philips diffractometer with Cu Kα radiation (λ=1.5418 Å). The morphology and local chemical homogeneity of the as-prepared samples were observed by scanning electron microscopy (SEM) (Nova400) equipped with an energy dispersive X-ray spectrometer EDS (IE350PentaFETX-3). The real density of the $Fe_3Si_{0.7}Al_{0.3}@SiO_2$ core–shell particles were measured using an automatic density analyzer (AccuPyc 1330). The thermal behavior of $Fe_3Si_{0.7}Al_{0.3}@SiO_2$ core–shell particles was carried out on a NETZSCH STA-499 C differential scanning calorimeter (DSC) under argon atmosphere from 40 °C to 1450 °C with a 10 °C/min heating rate. The resistivity was obtained by a four probes method by SB100A-2. The hysteresis loops were recorded by a vibrating sample magnetometer (VSM) (JDAW-2000) under an applied maximum field of about 7000 Oe. The inductance (L) was measured under a constant voltage of 0.3 V in a frequency range from 50 Hz to 1000 kHz by impedance Analyzer (HIOKI 3532-50 LCR HiTESTER). The number of turns of inductor is one turn. The effective permeability (μ_{eff}) was calculated using the following formula (1) [26,27]:

$$\mu_{eff} = \frac{\bar{l}L}{\mu_0 N^2 A} \tag{1}$$

where $\bar{l}$ means the average length of the magnetic circuit, N refers to the number of turns of inductor, A stands for the effective area of magnetic circuit, μ_0 represents the permeability of vacuum, its value is $4\pi\times10^{-7}$ H/m. Core loss at high-frequency was measured by an wide band power analyzer (CH2335A).

3. Results and discussion

Fig. 1(a–d) shows the SEM images of $Fe_3Si_{0.7}Al_{0.3}$ particles before and after chemical coating process. The raw $Fe_3Si_{0.7}Al_{0.3}$ particles before chemical coating process are spherical morphology and their surfaces are relatively clean and smooth (Fig. 1(a and b)), while they tend to be rougher after chemical coating process (Fig. 1(c and d)). The magnified image of selected region in Fig. 1(c) clearly indicates that the particles are uniformly and entirely coated by a thick layer, which is comprised of nano-scaled clusters as illustrated in Fig. 1(d). The phase structures of $Fe_3Si_{0.7}Al_{0.3}$ particles before and after chemical coating process are characterized by XRD and their diffraction patterns are shown in Fig. 1(e). The crystalline $Al_{0.3}Fe_3Si_{0.7}$ phase can be detected in $Fe_3Si_{0.7}Al_{0.3}$ particles before and after chemical coating process, which has a face-centered cubic structure [space group $Fm3m$ (225), JCPDS 00-045-1206]. Besides, the XRD pattern of $Fe_3Si_{0.7}Al_{0.3}$ particles after chemical coating process also exhibits a characteristic of another amorphous phase at 2θ of about 15–30°. No other characteristic peaks of impurities, such as iron oxide or aluminum oxide, are detected.

The EDS analysis of $Fe_3Si_{0.7}Al_{0.3}$ particles before and after chemical coating process is shown in Table 1. The surface layer of $Fe_3Si_{0.7}Al_{0.3}$ particles after chemical coating process consists of Fe, Al, Si and O elements. Compared with raw $Fe_3Si_{0.7}Al_{0.3}$ particles, after coating, the concentration of Fe and Al elements significantly decrease, while the concentration of Si and O elements increase. In addition, the $Fe_3Si_{0.7}Al_{0.3}$ particles after chemical coating process show a density of 5.88 g/cm^3, which is obviously lower than that of raw $Fe_3Si_{0.7}Al_{0.3}$ particles (7.0 g/cm^3). The above mentioned analysis results demonstrate that the coating layer may be amorphous phase SiO_2 and the new $Fe_3Si_{0.7}Al_{0.3}@SiO_2$ core–shell particles are successfully prepared through a modified stöber method.