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Corrosion behaviors of NdFeB magnets prepared by spark plasma sintering

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Abstract: The spark plasma sintering (SPS) technique was introduced into the field of NdFeB preparation due to its own advantages. High property NdFeB magnets with fine grains were prepared by SPS method. The corrosion behaviors of SPS NdFeB were studied by electrochemical measurements and 92% RH hyther tests at 353 K. The results were compared with those of the traditional sintered NdFeB magnets. It shows that both the SPS NdFeB and the traditional sintered NdFeB have good corrosion resistance in alkaline environment due to surface passivation; while, the fine grain microstructure of SPS NdFeB results in a more homogeneous phase composition distribution and thus reduces the electrochemical inhomogenity between the ferromagnetic phase and the Nd-rich intergranular phase in the magnet. Therefore, the SPS NdFeB exhibits better corrosion resistance than the traditional sintered NdFeB in neutral and weak acidic environment.

Key words: spark plasma sintering (SPS); corrosion resistance; electrochemical behaviors

1 Introduction

Sintered NdFeB magnets have been widely used in voice coil motors (VCM), magnetic resonance imaging (MRI) equipment, electric generators *etc.* [1] because of their high magnetic remanence, coercive force and energy product $(BH)_{max}$ at room temperature as well as the rich rare earth resources and low cost performance ratio. However, the poor corrosion resistance [2] of NdFeB type magnets in the course of their application is becoming a problem of great concern for their possible applications. Although there are many anticorrosive methods developed for NdFeB magnets at present, the corrosion problem is far from being solved from the aspect of magnet users [3-6]. Particularly in China, many magnet products with excellent magnetic properties lose their competitiveness due to the unqualified coatings, which are the significant barrier to the sales and applications. Problems arise from difficulties in understanding the type of the prevailing corrosion mechanism, which depends on the thermodynamic and kinetic behaviors. Therefore, it is of significance to study on the corrosion behaviors of NdFeB magnets.

NdFeB magnets are composed of $Nd_2Fe_{14}B$ matrix, Nd-rich phase and Boron-rich phase on contact with each other, which have different electrochemical potentials. The galvanic cell is then formed and electrochemical reaction is carried out. It has been commonly reported in many studies so far that the electrochemical corrosion of NdFeB magnets is of an intergranular corrosion process [7, 8].

Spark plasma sintering (SPS) is known as one of the novel sintering techniques. The SPS process utilizes the momentary local high temperature field generated by pulse energy, spark impact pressure and Joule heating throughout the sintering to heat the specimen. Thus, it has many important advantages including the lower sintering temperature, usually from 473 to 673 K and the high sintering speed, which can effectively restrain grains from growing and prepare fine grains materials in relatively short time. Moreover, this kind of technique can also be used for the preparation of large-scale or complicate-shaped workpieces *e.g.* magnet tiles and thin-wall magnet rings with high dimensional precision. Finally, the sintering process can be carried out under pressure, which is helpful for the sintered magnet to obtain higher density. High property NdFeB magnets with fine grains were prepared by SPS method in our previous work.

In this paper, the corrosion properties of SPS NdFeB magnets were studied by electrochemical measuring techniques and 92% RH hyther tests at 353 K.

2 Experimental

A casting ingot with the composition of $Nd_{15.5}Dy_1Fe_{bal}Co_{3.0}B_{6.8}Al_{1.5}$ was prepared by using a

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vacuum induction furnace. The ingot was then grinded to powders with the average granularity of 5.0 μm by airflow mill. The magnetic powders were divided into two parts. Orientating and applying slight pressure to one part of the magnetic powders after they have been enclosed in the graphite mould. The following sintering process were conducted on the SPS-1050 type sintering machine, developed by Japanese Sumitomo Coal Mining Co., followed by cooling the specimen to room temperature. The NdFeB magnets prepared by SPS technique do not have their optimal magnetic properties yet. Their magnetic properties were then greatly improved through post heat treatment under high vacuum condition (first-order post heat treatment: 1353 K for 2 h + second-order post heat treatment: 923 K for 1 h). The comprehensive magnetic properties finally obtained for the SPS NdFeB magnets were as follows: magnetic remanence (B_r): 1.2 T; coercive force (H_{ci}): 1250 kA·m^{-1}; energy product $(BH)_{max}$: 240 kJ·m^{-3}. The other part of magnetic powders were used to prepare traditional sintered NdFeB magnets for comparison.

The electrochemical testing and 92% RH hyther tests at 353 K were then conducted for traditional NdFeB magnets, SPS NdFeB magnets and the SPS NdFeB magnets after post heat treatment. The microstructures of the specimens were observed using S-250MK scanning electron microscope (SEM) and the chemical analysis of different phases in SPS NdFeB and traditional sintered NdFeB were performed by energy dispersive X-ray (EDX) analysis respectively.

3 Results and discussions

3.1 Corrosion potential and corrosion process

In the electrochemical reactions of NdFeB magnets, the anodic reactions of the electrode are usually the oxidation of Nd, Fe and Boron in the magnets, dissolving in the solutions in form of Nd^{3+}, Fe^{2+} and H_3BO_3 [9]. Meanwhile, the cathodic reaction of the electrode is the reduction of H^+ to H_2 in acid solution and the formation of OH^- in alkaline solution. In neutral solution, both kinds of the cathodic reactions mentioned above can be carried out either.

The electrostatic potentials (*vs.* SCE) of NdFeB magnets in different solutions are shown in **table 1**. It is found that the potential of traditional sintered NdFeB is the most negative in all three solutions. The results from the thermodynamics aspect show that the traditional sintered NdFeB magnets are more prone to electrochemical corrosion compared with SPS NdFeB.

Table 1 Electrostatic potentials (*vs.* SCE) of NdFeB magnets in different solutions V

NdFeB magnets	3.0% NaOH solution	3.5% NaCl solution	0.025% H_2SO_4 solution
Traditional sintered NdFeB	−0.654	−0.909	−0.785
SPS NdFeB	−0.246	−0.750	−0.779
SPS NdFeB after post heat treatment	−0.560	−0.797	−0.768

3.2 Polarization characteristics

The polarization characteristics of SPS NdFeB magnets and traditional sintered NdFeB magnets were tested using electrochemical methods. The electrochemical testing was conducted in a three-electrode system, *i.e.* the specimen was used as the working electrode, and the saturated calomel electrode and the graphite electrode were used as reference electrode and auxiliary electrode, respectively. Before the experiment, the surface of the working electrode was mechanically abraded to an 800-grade emery paper followed by thorough rinsing in acetone and deionized water. Then the surface is cleaned. The testing equipment is PARC M273 Potentiostat and the testing software is M352 SoftCorr III corrosion measurement software. The dynamic potential scanning method was used for polarization curves with the scanning rate of 2 mV/s. The polarization curves of NdFeB magnets in three kinds of solutions are shown in **figure 1**.

Figure 1 shows that the polarization characteristics of NdFeB magnets are quite different in the solutions with different acidity and alkalinity. In alkaline solution, the passivation region is shown evidently for the SPS NdFeB magnets and traditional sintered NdFeB magnets. Therefore, all the SPS NdFeB magnets and traditional sintered NdFeB magnets have better corrosion resistance in alkaline solution. However, there is no passivation occurred in the neutral and acid solutions. It also can be seen that traditional sintered NdFeB magnets have greater polarization current density than SPS NdFeB magnets under the same applied potential in the anodic branch of the polarization curve.

3.3 Corrosion rate

The corrosion rate of NdFeB magnets can be expressed in form of corrosion current density. Using PARC calculation functions in the M352 SoftCorr III corrosion measurement software, we fit the polarization curve of NdFeB magnets in 0.025% (mass fraction) H_2SO_4 solution. The corrosion rate of NdFeB magnets were then calculated (**table 2**). It can be seen that the corrosion rate of traditional sintered NdFeB magnets is the biggest (more than one time bigger than that of SPS NdFeB after post heat treatment). However, after post heat treatment, the corrosion resistance of SPS NdFeB is greatly improved.

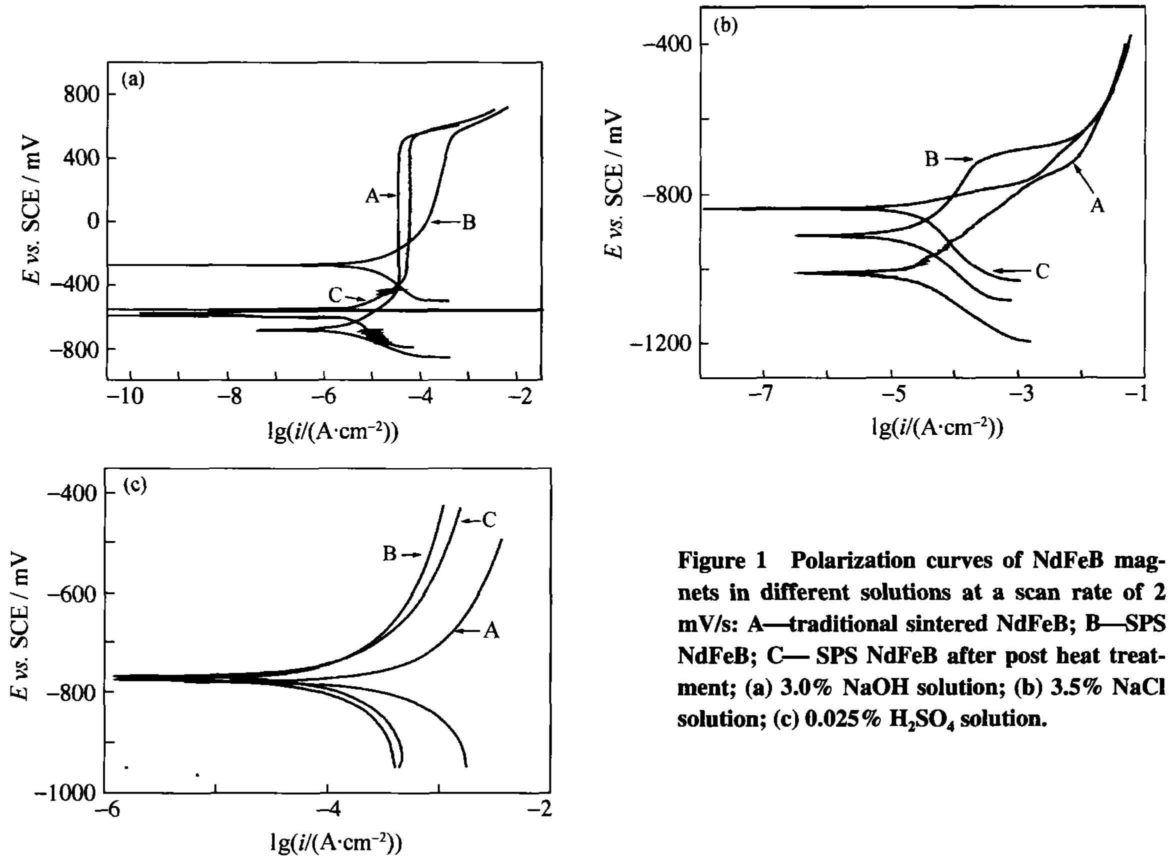

Figure 1 Polarization curves of NdFeB magnets in different solutions at a scan rate of 2 mV/s: A—traditional sintered NdFeB; B—SPS NdFeB; C— SPS NdFeB after post heat treatment; (a) 3.0% NaOH solution; (b) 3.5% NaCl solution; (c) 0.025% H_2SO_4 solution.

Table 2 Corrosion current densities (i_{corr}) of NdFeB magnets in 0.025% H_2SO_4 solution

NdFeB magnets	i_{corr} / (mA·cm^{-2})
Traditional sintered NdFeB	5.236
SPS NdFeB	5.024
SPS NdFeB after post heat treatment	2.457

Similar results were obtained with the mass gain in the 92% RH hyther gain tests at 353 K on the NdFeB magnets in the same period. **Figure 2** shows that the mass gain of both SPS NdFeB magnets in the 92% RH hyther tests at 353 K is smaller than that of traditional sintered NdFeB magnets. The SPS NdFeB magnets after post heat treatment has the smallest mass gain, which is about 35% of traditional sintered NdFeB magnets (after 75 h).

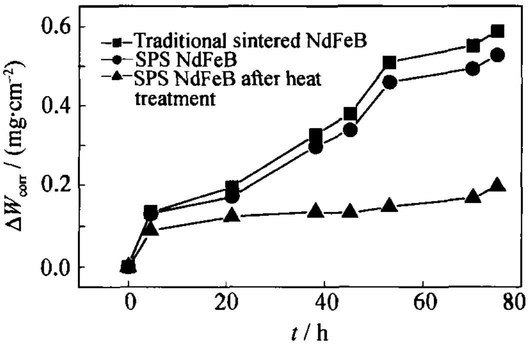

Figure 2 Corrosion rates of NdFeB magnetic materials (353 K, 92% RH).

3.4 Effects of microstructure

Heat treatment evidently betters the distribution of Nd-rich phase in SPS NdFeB and reduces the space and holes between crystal grains, hence increases the density of the magnets. In addition, one advantage is that the SPS technique can effectively restrain grains from growing during the sintering process and prepare fine grains magnets. **Figure 3** shows the microstructure comparison of SPS NdFeB magnets and traditional sintered NdFeB magnets. It shows that the granularity of SPS NdFeB magnets is about 5 μm and evenly distributed (figure 3(a)). In comparison, the granularity for traditional sintered NdFeB is relatively larger for about 20 μm and not evenly distributed (figure 3(c)). The average grain size of SPS NdFeB magnets remains almost unchanged after post heat treatment (as shown in figure 3(b)). Meanwhile, the chemical analysis of different phases in SPS NdFeB and traditional sintered NdFeB were performed by EDX analysis respectively, as shown in **table 3**. The results show that there is less Nd and more Fe in Nd-rich phase of SPS NdFeB than that of traditional sintered NdFeB. In the electrochemical reaction of

NdFeB magnets, the Nd-rich intergranular phase is the anodic area of the reaction, however, the ferromagnetic phase is the cathodic area. This kind of composition (less Nd and more Fe) reduces the reaction activity of the anodic Nd-rich phase, thus reduces the electrochemical inhomogenity between the Nd-rich phase and the ferromagnetic phase of the magents. In another word, the fine grain microstructure can make more homogeneous phase composition distribution in the magnets, which results in less electrochemical inhomogenity. As the poor corrosion resistance of the NdFeB magnets just arises from this kind of electrochemical inhomogenity, the fine grain microstructure is good for their anticorrosive behavior.

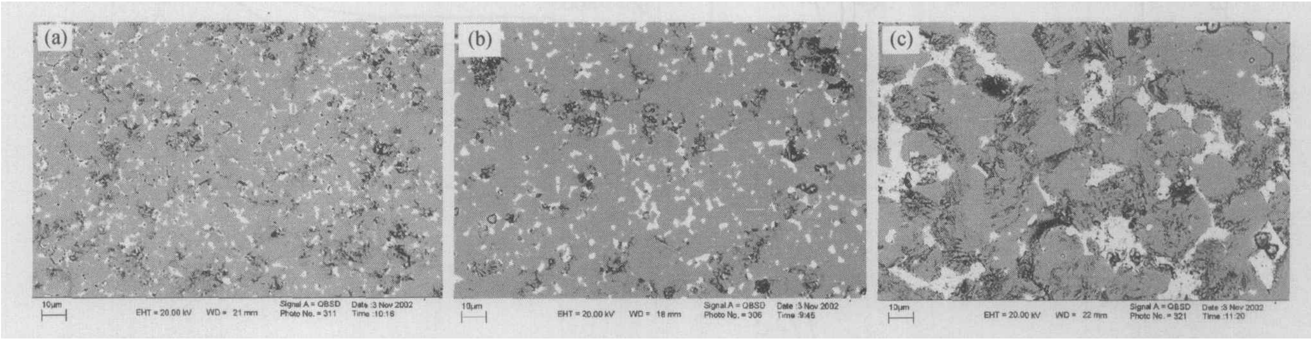

Figure 3 Microstructures of SPS NdFeB and traditional sintered NdFeB (SEM Photos): (a) SPS NdFeB; (b) SPS NdFeB after post heat treatment; (c) Traditional sintered NdFeB; A—Ferromagnetic phase; B—Nd-rich phase.

Table 3 The compositions (mass fraction) of the main contents in SPS NdFeB and traditional sintered NdFeB %

Content	SPS NdFeB after post heat treatment		Traditional sintered NdFeB	
	Ferromagnetic phase	Nd-rich phase	Ferromagnetic phase	Nd-rich phase
Nd	26.48	80.34	26.22	89.47
Fe	69.75	15.73	73.78	3.53

4 Conclusions

(1) A new type high property NdFeB magnets with fine grains and good anticorrosive ability can be prepared by SPS method.

(2) Both SPS NdFeB and traditional sintered NdFeB have good corrosion resistance in the alkaline environment due to the surface passivation; while, the fine grain microstructure of SPS NdFeB results in a more homogeneous phase composition distribution and thus reduces the electrochemical inhomogenity between the ferromagnetic phase and the Nd-rich intergranular phase in the magnet. Therefore, SPS NdFeB exhibits better corrosion resistance than traditional sintered NdFeB in neutral and weak acidic environment.

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