Heating Rate on the Influence of Characteristics of MgO/Fe Nano Particles

Yuan-yuan Kong
Department of Physics & Electronic Science
TONGREN University
TongRen, China
kyy0803@yahoo.cn

Nan-gang Ma
Department of Materials Science and Technology
Huazhong University of Science and Technology
Wuhan, China

Abstract: Nano-sized composite magnetic particles MgO /Fe were in situ-Combustion Synthesized when vacuum-sintered at 620℃ in the Mg-70.9wt%Fe_3O_4 system. In this paper, we discussed the heating rate on the influence of micro-morphology and the magnetic properties. It was indentified that: 5℃/min was the suitable heating rate, composite spherical particles with mean diameter 40nm distributed evenly. When the heating rate was 2℃/min, the heat could not aggregate effectively and the production of the intermediate product made the sample uneven distribution. nano-sized particles agglomerated to micro-sized spherical particles due to over sintering when the heating rate was 8℃/min. So the resistance was smaller when magnetized in outer magnetic field when sintered at 5℃/min, particles had better soft magnetic properties, and it was the future drug carrier materials.

Keywords: magnetic nano-particles; in-situ reaction; superparamagnetic; drug carrier

1. Introduction

Ultrafine nano particles have been subjects of intense scientific research. Surface、interface and (quantum) size effects induce properties that are significantly different from that of the bulk[1, 2]. Especially, magnetic nano particles with properties of superparamagnetism have been used in magnetic bioseparation, drug carrier, magnetic resonance imaging contrast enhancement, and hyperthermia treatment of cancer [3]. To be applied as drug carriers, the main problems are to obtain superparamagnetic particles with good magnetic resonance, high saturation magnetic value and low coercive force [4, 5]. Except that, we must have a good control of composition, particle size and morphology, a narrow size distribution, and stabilization against oxidation in case of metals [6].

Here we report the synthesis of MgO /Fe nano particles as drug carriers, which had a core-shell structure. The iron was wrapped with magnesium oxide (MgO) preventing oxidation. We used in situ reaction method to synthesize the magnetic particles. The sintered temperature below the melting point of Mg (649℃), making the production process more energy saving and cost-effective .the final products were uniformly reinforced by MgO and Fe nano particles .In this paper, we did research of the heating rate on the influence of magnetic properties.

2. Experiments

A powder mixture with certain proportion was ground for an hour under the protection of Ethanol. Powder (~5mg) was used in Differential Thermal Analysis (DTA) to determine the temperature at which the chemical reaction took place. Using the DTA result, the powder mixture was sintered in tube furnaces for an hour at 620℃ with different heating rates (2℃/min, 5℃/min, 8℃/min), Argon atmosphere was necessary during the sintering process, the samples were subsequently cooled to room temperature in furnaces with the power turned off. Some of the sintered samples were ground into fine powders, and X-ray powder diffractometry (XRD) was tested to identify the phases present. For the microstructural analysis, some samples were examined by LEO scanning electron microscope (SEM). Magnetic properties are measured by VSM.

3. Results and discussion

3.1. Calculation of the powder proportions

The chemical reaction equation between Mg and Fe_3O_4 was as followed: supposing the mass of Mg was a, the mass of Fe_3O_4 was b. Next we calculated the proportion of Mg when Mg and Fe_3O_4 were just reacted synthesized Fe and MgO completely.

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$4Mg + Fe_3O_4 = 3Fe + 4MgO$
96 232
a b

Considering the purity of raw materials: Mg (99%) and Fe_3O_4 (98%).

96 / (0.99a) = 232 / (0.98b)

a + b = 10g

From the two equations above, we could gain the results:

Mg(wt%)=29.1%，Fe_3O_4 (wt%)=70.9%.

3.2. DTA analyses

A DTA curve that was constructed as temperature was raised from ambient to about 700℃ is shown in Figure 1. Two exothermic peaks were found on the curve at 350℃ and 583℃, one endothermic peak was found at 643℃. When the powder mixture was sintered at 350℃, from the former results of our laboratory [7], some of the Fe3O4 in this sample had been reduced to FeO and Fe while some of the Mg was oxidized to MgO, that is to say, the temperature was not high enough, only some Fe_3O_4 was reduced to Fe. The endothermic peak was the melt of the pure metal Mg, which was well below the melt point of Mg (649℃). According to these results, the green samples were sintered at 620℃ in argon atmosphere for an hour before they were furnace-cooled to room temperature.

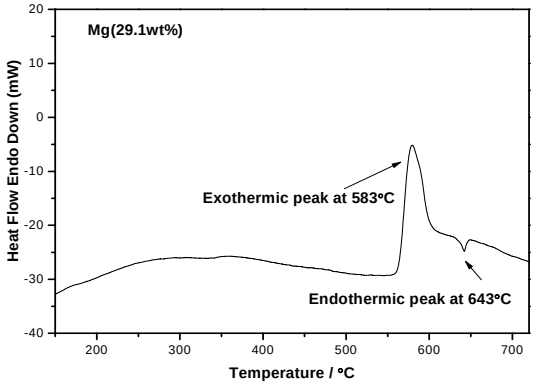

Figure 1. DTA curve of the Mg-70.9wt%Fe3O4 sample

3.3. XRD analyses

Figure 2, 3, 4 shows XRD patterns of the sintered samples at different heating rates. In figure 2, we can see that some peaks were divided into two peaks, especially at 43° and 62° , corresponded FeO and MgO respectively. Because both of FeO and MgO were all belong to face-centered cubic structure, Fe^{2+} and Mg^{2+}also have similar ionic radius, that is Mg^{2+}:0.072nm, Fe^{2+}:0.074nm, (0.074－0.072)/0.074 = 2.7%<15%, so FeO and MgO had the tendency of forming the intermediate product MgO(FeO) substitutional solid solutions. As a result, the production of pure iron was reduced. So when the heating rate was not fast enough, there was enough time to contact and react between reactants, but the production of the intermediate product impeded the further reaction; On the other hand, due to the temperature hysteresis effect of thermocouple, the raising and falling processes carried alternately all the time in the sintered furnace[8]. So the heat of the system could not aggregate effectively, most of the heat was dissipated.

In figure 3, when the heating rate was 5℃/min, there were MgO, Fe, Fe_3O_4 phases, no FeO peaks existed. In figure 4, the heating rate was 8℃/min, the phases were similar with figure 3, the difference was: the phase of Fe_3O_4 was more obvious than figure 3.

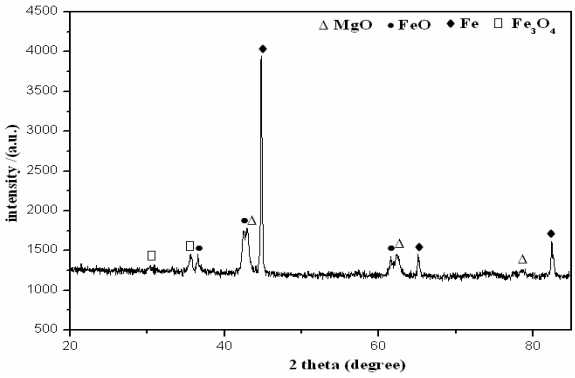

Figure 2. XRD patterns of the sintered samples at 2℃/min heating rate

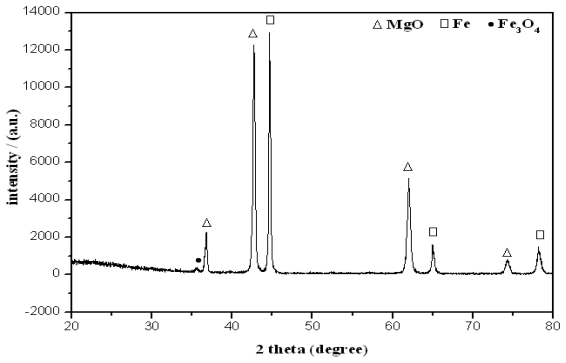

Figure 3. XRD patterns of the sintered samples at 5℃/min heating rate

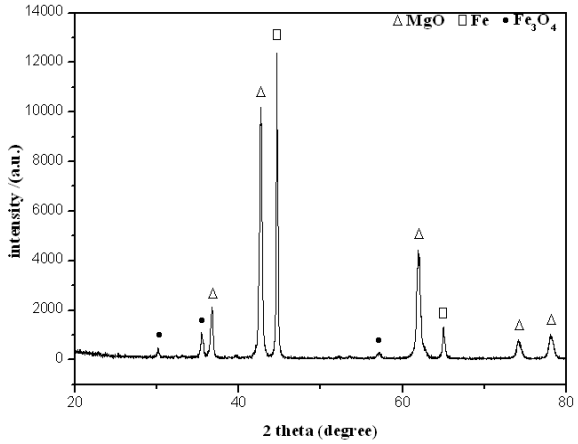

Figure 4. XRD patterns of the sintered samples at 8℃/min heating rate

3.4. Microstructural analyses

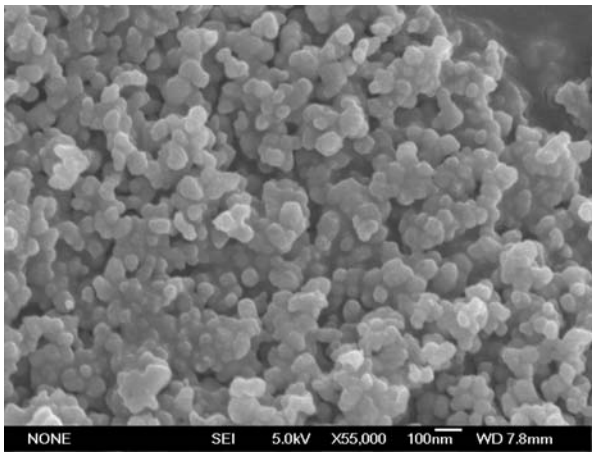

Figure 5. SEM micrograph of the Mg-70.9 wt.% Fe_3O_4 samples at 5℃/min heating rate

Figure 5 shows the SEM micrograph of the Mg-70.9 wt% Fe_3O_4 samples sintered at 5℃/min heating rate, nano-sized grey white spherical particles with mean diameter 40nm distributed evenly. From Figure 5, we also see few silvery white particles dispersed sporadicly among grey white particles. Some nano particles agglomerated severely in some places. There were two reasons for the phenomenon: On the one hand, the system reacted fiercely, accompanying generation of plenty of calories, so there would be part of Mg in liguid state; On the other hand, vander waals force aggravated agglomeration among nano-sized particles.

Figure 6 shows the SEM micrograph of the Mg-70.9 wt.% Fe_3O_4 samples sintered at 8℃/min heating rate, largely different from Figure 5, Obvious interface existed among micron-sized spherical particles, that was to say, particles had been occurred over sintered, several nano-sized spherical particles had been sintered together. On the surface of micron-sized spherical particles, white particles with different diameters distributed evenly, we can infer that, the smaller nano-sized particles was Fe, while the larger white nano-sized particles was Fe_3O_4, it was the result of later growth of nano-sized Fe. The main components of the grey colored micron-sized spherical particles were MgO. From this figure, we knew that, some nano-sized white particles were also found in the interface among micron-sized spherical particles, even few cuboid structure, stepladden piled polyhedron existed on the interface. The material composition was Fe and Fe_3O_4. It was induced by the large enough energy of the system.

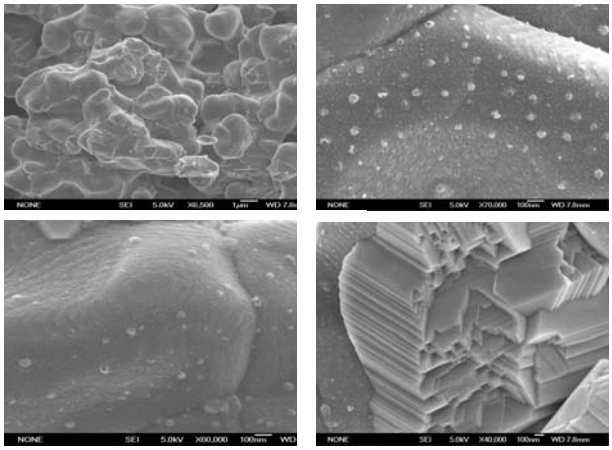

Figure 6. SEM micrograph of the Mg-70.9wt%Fe_3O_4 samples at 8℃/min heating rate

3.5. Magnetic analyses

Figure 7 is the M-H hysteresis loops of the Mg-70.9 wt% Fe_3O_4 samples sintered at different heating rates. The curves were nearly single S shape, magnetic particles were saturated when the outer magnetic field was about 7000 Oersted (Oe). From the M-H hysteresis loops, we can see that, coercivity and residual magnetism were in low grade. When the heating rate was 5℃/min, the nano-sized particles displayed good soft magnetic properties, its coercivity was 7.492 Oe, Ms: 78.815emu/g, Mr: 0.2094 emu/g, that was close to superparamagnetization. Magnetic parameters of the other samples with different heating rates were as follows:

2℃/min：Hci: 163.860 Oe, Ms: 52.444 emu/g, Mr: 3.7653 emu/g,

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5℃/min : Hci: 7.492 Oe, Ms: 78.815 emu/g, Mr: 0.2094 emu/g

8℃/min : Hci: 17.513 Oe, Ms: 67.475 emu/g, Mr: 0.571 emu/g.

Compared the magnetic properties of three samples with different heating rates, we could conclude that: sample heated at 5℃/min possessed the best soft magnetic properties, magnetic particles were prone to magnetization and demagnetization. When the heating rate was 2℃/min, the heating rate was not high enough, the heat of the system could not aggregate effectively, the production of the intermediate product influenced the magnetic properties. When the heating rate was 8℃/min, the heating rate was much higher, nano-sized particles agglomerated to micro-sized spherical particles due to over sintering. So the 5℃/min was the most appropriate heating rate. After sintering, nano-sized spherical particles distributed more evenly, so the resistance was smaller when magnetized in outer magnetic field.

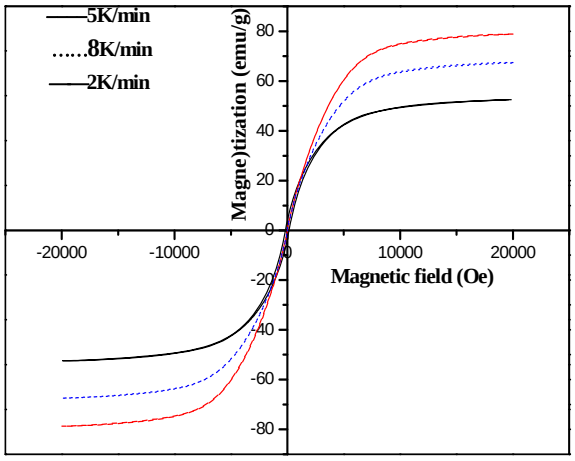

Figure 7. M-H hysteresis loops of the Mg-70.9 wt.% Fe_3O_4 samples sintered at diferent heating rates

4. Conclusions

Through the analysis above, we could conclude that: the In Situ-Combustion Synthesis method was an ideal preparation method, Preparation technology was simple, save energy and cost compared with other preparation methods. For the Mg-Fe_3O_4 system, through calculation, we gained the reactant ratio when reacted into Fe and MgO. In this paper, we discussed the heating rate on the influence of the magnetic properties, from XRD pattern analysis and SEM micrograph observation of the samples sintered at different heating rates, we discovered that 5℃/min was the most appropriate heating rate. After sintering, nano-sized spherical particles distributed more evenly, so the resistance was smaller when magnetized in outer magnetic field. On the contrary, when the heating rate was 2℃/min, the intermediate product hindered the generation of the final product Fe, so the resultant composition concluded Fe, FeO, MgO, Fe_3O_4.the complexity and nonuniformity distribution increased the resistance when magnetized in outer magnetic field, so the samples soft magnetic properties decreased. When the heating rate was 8℃/min, particles had been sintered together due to over sintering, the soft magnetic properties was also decreased.

5. Acknowledgment

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