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Synthesis of ultrafine amorphous Fe–B alloy nanoparticles using anodic aluminum oxide templates

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Abstract Ultrafine amorphous Fe–B alloy nanoparticles are self-assembled within anodic aluminum oxide templates by combining a preparation process of Fe–B nanoparticles with a template method. Scanning electron microscopy, inductively coupled plasma-atomic emission spectrometry, X-ray diffraction spectrometry, Mössbauer spectrometry, and vibrating sample magnetometry are employed to study the morphology, chemical composition, structure, and magnetic properties of the nanoparticle assemblies, respectively. The results show that the alloy particles are amorphous with a boron content of 24 at. % and can be in shape of sphere and rod by controlling the duration of preparation. There is a narrow distribution of the sizes of spherical nanoparticles with an average diameter below 35 nm in relatively short preparation time, while rods are found in longer time. The measurements of magnetic properties indicate that the nanoparticles are mostly in superparamagnetic state and the self-assembly of the nanoparticles has a weak magnetic anisotropy with an easy direction perpendicular to the template plane.

Introduction

Amorphous metallic alloys have been studied extensively and applied widely for many years due to their distinctive properties, which stem mainly from the long-range disordered and short-range ordered structure with a homogeneous single-phase nature [1]. For example, ferromagnetic amorphous metallic alloys are important soft magnetic materials which can give very low coercivity, low magnetic hysteresis losses, high magnetic permeability, and other valuable technological properties [2, 3], because they are free from magnetocrystalline anisotropy and from the defects associated with crystalline state which otherwise could pin the magnetic domain walls. Amorphous Fe–B alloy, as a basic kind of ferromagnetic amorphous material, has been researched intensively in structure, crystallization, composition, magnetism, catalysis, and so on [4–7]. Among various sample forms of Fe–B alloy, ultrafine particles have attracted much attention because they possess relatively high specific surface area, great flexibility of the variation of the composition, as well as simple pretreatment conditions [8, 9]. Normally, these particles are prepared by a chemical reduction process in an aqueous solution [10].

Anodic aluminum oxide (AAO) templates have been investigated in the past decades for assembling quasi-one-dimensional materials, such as nanowires and nanotubes. It has been proved to be a prosperous and convenient strategy to synthesize materials of metal, alloy, and oxide, by using this template in electrodeposition and sol-gel processes [11–13]. Although several amorphous alloys, such as Fe–P [14], Co–P [15] and Fe–Co–P [16], have been successfully electrodeposited into the AAO templates recently, there are few reports on the synthesis of amorphous Fe–B by template methods. In the present work, an approach to obtain ultrafine amorphous Fe–B alloy nanoparticles self-assembled within AAO templates is reported. In addition, the morphology, chemical composition, structure, and magnetic properties are studied.

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Experimental

In brief, the AAO templates were obtained in a conventional two-step anodic oxidation process in 0.3 M oxalic acid solution at 40 V_{DC} at 5 °C, which was described in detail elsewhere [11]. Then they were immersed in 0.5 M phosphonic acid for 50 min at 40 °C in order to etch off the barrier layers at the bottom of each template. Consequently the porous AAO templates with throughout hollow pores were prepared. Finally, the templates were kept in deionized water to preserve good filter properties.

In order to achieve ultrafine amorphous Fe–B nanoparticles in AAO templates, a homemade H-shaped device was employed, as illustrated in Fig. 1. A template was sealed in the middle of the device with a graphite electrode on each side. One electrode worked as cathode that connected the aqueous solution of 0.5 M KBH_4 and the other as anode that connected the aqueous solution of 0.1 M $FeSO_4$. In the experiment, a small DC voltage was applied to control the growth speed of the particles. After several minutes, the template turned black indicating the precipitation of Fe–B alloys resulting from the redox reaction between Fe^{2+} and BH_4^- in the solution and the coprecipitation of Fe and B atoms, as well. Then the template with the precipitations in it was washed carefully in a diluted HCl solution to remove any adhesion on the surface. After that, the samples were protected in ethanol to avoid oxidation before any measurements.

The AAO templates with and without nanoparticles were observed by a scanning electron microscopy (SEM, Hitachi S4800). The chemical composition of the nanoparticles was investigated by an energy dispersed X-ray spectrometer (EDS) attached to SEM and an inductively coupled plasma-atomic emission spectrometer (IRIS, ER/S), qualitatively and quantitatively, respectively. X-ray diffraction (XRD, X'Pert PRO PHILIPS, with Cu Kα radiation) was employed to study the structure of the nanoparticles. The magnetic properties of nanoparticles confined in AAO templates were characterized by using a Mössbauer spectrometer (MS, under transmission geometry in a constant-acceleration mode with a source of ^{57}Co in rhodium) and a vibrating sample magnetometer (VSM, Lakeshore 7304) with the applied field parallel and perpendicular to the template plane at ambient temperature.

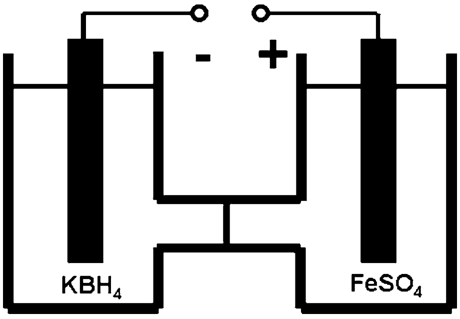

Fig. 1 The device utilized to fabricate the assembly of Fe–B nanoparticles. The AAO template is in the middle of the device and contacted by the solutions from two sides

Results and discussion

The SEM images of a porous AAO template with throughout hollow pores taken from transverse and top view are shown in Fig. 2(a) and its inset, respectively. It can be seen obviously that the nanopores are rather uniform along the length and highly ordered in a hexagonal array. It is also found that the average diameter of the pores is about 75 nm, a little larger than 65 nm, which was gotten when the pores were not widened in H_3PO_4 (pictures are not shown here). The AAO template with nanoparticles prepared in a short time of 40 s is shown in Fig. 2(b). It can be seen that there are a large number of nanoparticles within AAO nanopores adhering to the walls. A narrow size distribution of the particles with an average diameter of 35 nm is found. In fact, at the beginning of the precipitation, nucleation takes place randomly on the walls of the pores, and particles in shape of sphere grow subsequently, which results in small diameters and relatively narrow size distribution of the particles. Smaller particles will be obtained by shortening the growth duration further. It should be noted that the filterability of the AAO template is preserved when the ultrafine nanoparticles are self-assembled in it. It is reasonable to conclude that, due to this characteristic, our samples will have potential applications in catalysis aspect. Figure 2(c) and (d) illustrate the AAO templates with particles prepared in longer time, i.e., 2 min and 6 min, respectively. Bigger particles, having the same average diameter of 75 nm as the AAO pores have, and some short rods are obtained, as a result of the transverse confinement of the pore walls. The following work is performed in order to control the morphology of the nanoparticles precisely.

The EDS measurements consistent with the SEM observations indicate that Fe and B are the main elemental components, although there is a relatively poor sensitivity in detecting the lighter element of boron. Quantitative analysis of the composition using an inductively coupled plasma-atomic emission spectrometer shows that the alloy possesses a chemical formula of $Fe_{76}B_{24}$. The content of B is in the range stated in a previous report [4] on amorphous Fe–B alloys.

Figure 3 illustrates the XRD pattern of the self-assembly of $Fe_{76}B_{24}$ ultrafine particles in the AAO template. The particles were synthesized in 40 s. It can be seen that there are no sharp diffraction peaks but only smooth amorphous

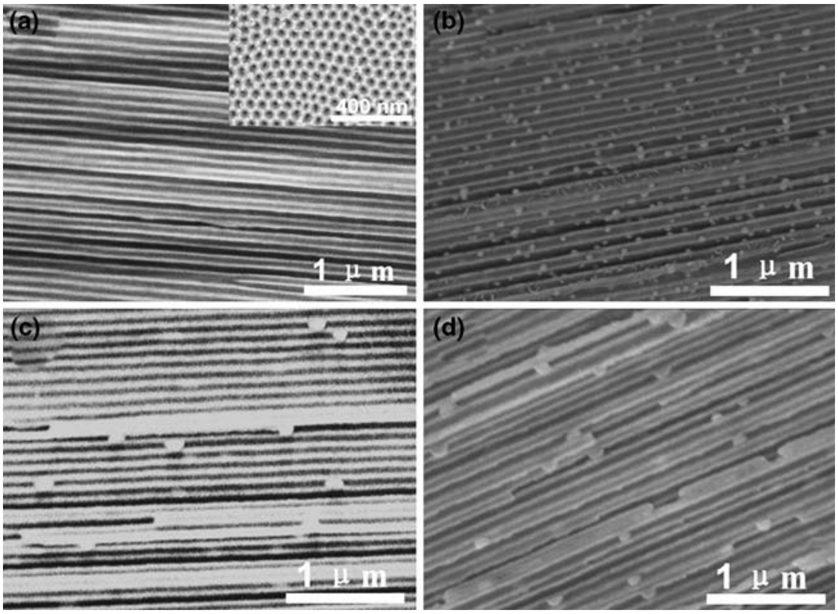

Fig. 2 SEM images of (**a**) transverse and top view of a porous AAO template with throughout hollow pores, and transverse view of the templates confining Fe–B nanoparticles with preparation duration of (**b**) 40 s, (**c**) 2 min and (**d**) 6 min, respectively

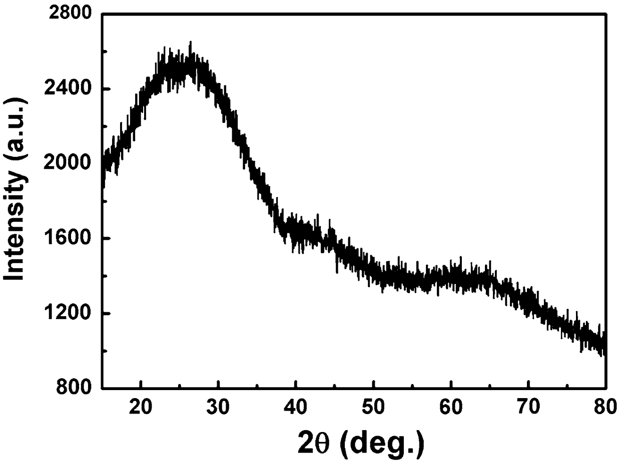

Fig. 3 X-ray diffraction pattern of the self-assembly of amorphous $Fe_{76}B_{24}$ nanoparticles synthesized in 40 s in AAO templates

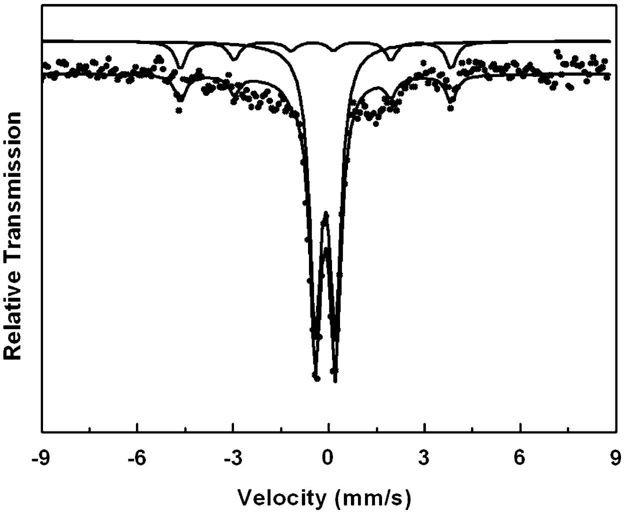

Fig. 4 Mössbauer spectrum of the self-assembly of amorphous $Fe_{76}B_{24}$ nanoparticles at ambient temperature

broad peaks, which may come from the Al_2O_3 film and the Fe–B alloy. This indicates that the Fe–B particles are amorphous in nature.

In Fig. 4 is shown the room-temperature MS of the ultrafine amorphous Fe–B alloy nanoparticles confined in AAO templates, which can be best fitted with a sextet and a doublet. The sextet consists of six broad absorption lines, yielding a magnetic hyperfine field of about 32.7 T, an isomer shift of about –0.261 mm/s and a negligible quadrupole splitting shift. The broadened peaks indicate the characteristic of amorphous structure of our sample, which is in accord with the XRD results quite well. Having an isomer shift of about 0.17 mm/s and a quadrupole splitting shift of about 0.78 mm/s, the doublet is convinced to originate from the superparamagnetism of ultrafine particles. Much larger than that of the sextet, the relative intensity of the doublet is about 84%, which makes the doublet dominant. We attribute the large number of particles in superparamagnetic state to the utilization of a template, because the finite volume of individual AAO nanopores limits the growth speed of the alloy particles.

The hysteresis loops of the nanoparticle assembly investigated by VSM at room temperature are shown in Fig. 5, where $H_{\perp}$ and $H_{//}$ represent the applied fields perpendicular and parallel to the template plane, respectively. The fact that the saturation field for $H_{\perp}$ is smaller than that for $H_{//}$ and the coercivity for $H_{\perp}$ is larger than that for $H_{//}$ supports that the ultrafine particle assembly confined in the AAO template has a weak uniaxial magnetic anisotropy

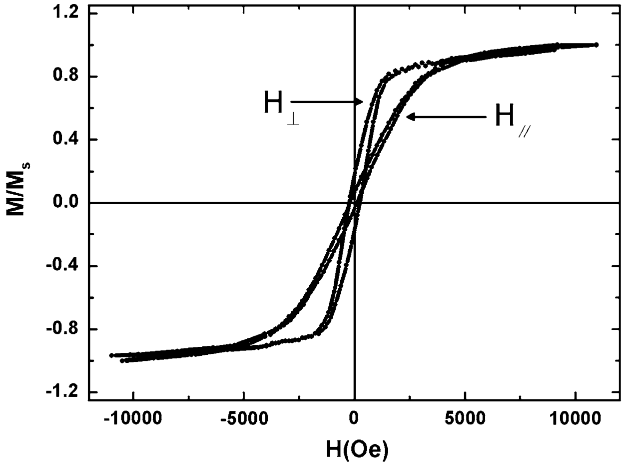

Fig. 5 Hysteresis loops of the self-assembly of amorphous $Fe_{76}B_{24}$ nanoparticles at room temperature. $H_\perp$ and $H_{//}$ represent the applied fields perpendicular and parallel to the template plane, respectively

with an easy direction normal to the template plane. This weak anisotropy can be interpreted by the following two reasons: first, the static magnetic interactions between the particles within a same pore can align their magnetic moments to the perpendicular direction; second, some big particles may be in an elongated sphere shape with its long axis parallel to the pore axis. The two loops have the coercivities of 220 Oe and 152 Oe and remanence ratios of 0.15 and 0.05 for $H_\perp$ and $H_{//}$, respectively. The coercivities are larger and the remanence ratios are smaller than those of bulk $Fe_{80}B_{20}$ sample [17]. Differing from the bulk counterpart and other particle systems, this assembly form of nanoparticles is believed to account for these characteristics.

Conclusion

In conclusion, ultrafine amorphous Fe–B alloy nanoparticles are self-assembled within AAO templates by combining a preparation process of Fe–B nanoparticles with a template method. The alloy particles are amorphous with a boron content of 24 at. %. By controlling the reaction time, a narrow distribution of the sizes of spherical particles with an average diameter below 35 nm can be obtained and the filterability of the AAO template is preserved at the same time. The assembly of the ultrafine particles has a weak uniaxial magnetic anisotropy with the easy direction perpendicular to the template plane, although most nanoparticles are in superparamagnetic state. It is believed that this synthesis strategy is a convenient and efficient way to prepare ultrafine nanoparticles, and their self-assembly has potential applications in magnetic devices and especially in catalysis.

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