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Preparation of Fe–Ni–P–B metallic nano-ribbons

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ABSTRACT

Nano-ribbons of $(Fe,Ni)_3(P,B)$ intermetallic compound have been prepared by a so-called selective etching method from the precursor $Fe_{40}Ni_{40}P_{14}B_6$ alloys. These precursors, with a eutectic structure constituting of $(Fe,Ni)_3(P,B)$ phase and γ-(Fe,Ni) phase, were prepared in a rod shape by the rapid quenching method. Then, the γ-(Fe,Ni) phase was dissolved off from the eutectic structure through selective etching with aqua regia, resulting in nano-ribbons, with about 10–50 nm thickness, 300–1000 nm width and about 10 μm or more length, having been obtained under the action of etching and polishing effects. Based on the experimental results, the possible evolution process of $(Fe,Ni)_3(P,B)$ nano-ribbons from eutectic structures was proposed. The present result shows that the selective etching method is an easy and effective approach for preparing metallic nano-ribbons.

1. Introduction

In recent years, nanostructured materials have attracted great attention due to their excellent catalytic, electrical, magnetic and optical properties [1–4] resulting from their nanosized structures. At the same time, many techniques have been developed to prepare nanostructured materials, such as chemical vapor deposition (CVD) [5], electric-arc and arc-discharge methods [4,6,7], aqueous solution method [8], mechanical exfoliation [9], selective etching [10], vapor–liquid–solid (VLS) method [11], dealloying method [12] and so on. With these techniques, many types of nanoparticles, nanotubes, nanowires, nanosheets, nanofibers and nano-ribbons of inorganic materials have been successively prepared. However, the preparation of nanowires or nano-ribbons of metallic materials has been scarcely reported due to the fact that metallic materials are quite easily oxidized during preparing process. Then, it is meaningful to develop new techniques and new methods to synthesize nanostructured metallic materials since many metallic nanomaterials possess good functional properties, such as catalytic, electrical and magnetic properties. Here we report a simple and low cost method for preparing metallic nanomaterials. Magnetic $(Fe, Ni)_3(P, B)$ nano-ribbons were prepared through selective etching of the eutectic Fe–Ni–P–B alloys and the possible mechanism has been discussed.

2. Experimental procedure

In the present work, a classic $Fe_{40}Ni_{40}P_{14}B_6$ glassy alloy [13] was selected as the precursor alloy, because it is quite easy to obtain an ultrafine eutectic structure by increasing the undercooling of the alloy melt before solidification [14,15]. The ingots of the $Fe_{40}Ni_{40}P_{14}B_6$ alloy were prepared by melting the mixtures of high purity Fe (99.9%) and B (99.9%) blocks, Ni (99.9%) plates and Ni_2P (99.95%) powders within a high-purity argon gas condition. The ingots were subsequently purified with the fluxing medium B_2O_3 in a quartz tube at about 1423 K for more than 10 h. After purification the rod samples were quenched onto a copper plate cooled by liquid nitrogen.

The structures of the prepared rod samples were examined by Rigaku D/max-RB X-ray diffraction (XRD) with monochromatic CuKα radiation. Then the alloy samples were immersed in aqua regia for selective etching. The etched specimens were examined by a LEO1530 scanning electron microscope (SEM) integrated with a field emission gun. The microstructure of the obtained nano-ribbons was examined by JEOL 200CX and JEOL 2011 transmission electron microscopes (TEMs). The TEM samples are prepared by two methods: a thin foil specimen of as-prepared $Fe_{40}Ni_{40}P_{14}B_6$ alloy was prepared by a standard twin-jet electropolishing method for TEM observation. After corrosion by the aqua regia, the obtained nano-ribbons were dispersed in ethanol by ultrasound vibration and then collected by a copper grid with holey carbon films.

3. Results and discussion

The XRD spectrum of an as-prepared $Fe_{40}Ni_{40}P_{14}B_6$ rod sample is shown in Fig. 1. As indicated in Fig. 1, the diffraction peaks have been indexed as the tetragonal $(Fe,Ni)_3(P,B)$ intermetallic compound and the face centered cubic (FCC) γ-(Fe,Ni), which is consistent with the result reported by Zhang and Yao [14]. The diffraction peaks are somehow broad, indicating the existence of

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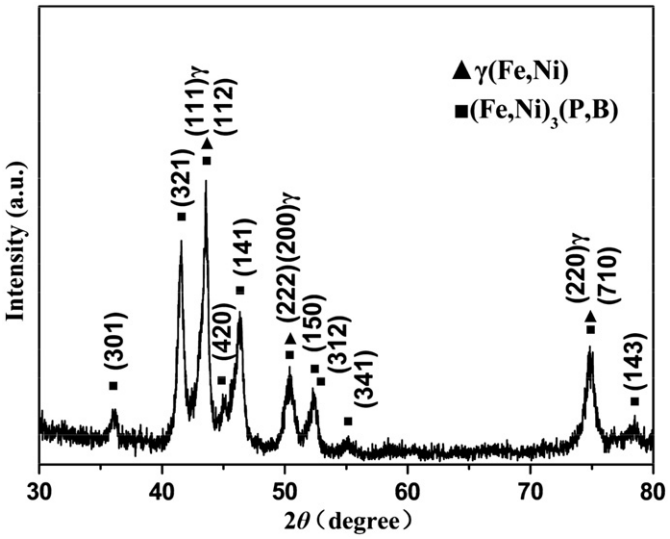

Fig. 1. XRD spectrum of the as-prepared $Fe_{40}Ni_{40}P_{14}B_6$ sample.

Table 1
Calculated grain sizes of the pristine $Fe_{40}Ni_{40}P_{14}B_6$ sample.

2θ (deg.)	Crystal indices	Full width of half maximum (deg.)	Calculated grain size (nm)
41.52	(321)	0.45	18.7
43.54	(112)	0.47	17.9
50.39	(222)	0.80	10.8
74.88	(710)	0.68	14.6

size-limited phases. After deconvoluting the beam size effect, the grain sizes could be calculated based on the Scherrer Formula. The results are listed in Table 1. It is found that the calculated grain sizes vary from 10.8 nm to 18.7 nm, indicating that the $Fe_{40}Ni_{40}P_{14}B_6$ sample possesses nanosized grains.

Fig. 2(a) shows the SEM image of a well etched $Fe_{40}Ni_{40}P_{14}B_6$ sample, exhibiting a lamellar structure, or called ribbons. The obtained nano-ribbons possess similar thicknesses, which have been estimated to be about 50 nm by examining the high-magnification image. As shown in the inset of Fig. 2(a), the edges of lower buried ribbons can be also observed. It indicates that the thicknesses of the top ribbons and thereby all ribbons are very low, while the widths of the ribbons vary from about 300 nm to about 1000 nm with an average value of about 500 nm, and the length is in a few tens of micrometers scale, according to the measurement results of different areas. Fig. 2(b) shows the morphology of a sample not etched heavily. In the lower part of the image, honeycomb morphology could be observed, while in the top-left part of the image nano-ribbons could be observed. It is known that the Fe–Ni–P–B alloy is still constituted by eutectic structures of $(Fe,Ni)_3(P,B)$ intermetallic phase and γ-(Fe,Ni) phase even at very large undercooling [14]. And the γ-(Fe,Ni) phase assumes a rod-like shape, like those obtained from $Fe_{40}Ni_{40}P_{14}B_6$ glassy ribbon [16]. During corrosion the γ-(Fe,Ni) phase would be preferentially corroded due to its weaker corrosion resistance. So the honeycomb morphology is believed to result by selective etching of the γ-(Fe,Ni) phase. With the increase of the etching time, the honeycomb structure would be broken and nano-ribbons as shown in Fig. 2(a) and in the top-left part of Fig. 2(b) are obtained. In the top-right part of Fig. 2(b), a eutectic cell boundary is observed to separate the two neighboring eutectic cells, indicating that the length of the nano-ribbons is as large as the size of the eutectic cells, which is around 10 μm or more.

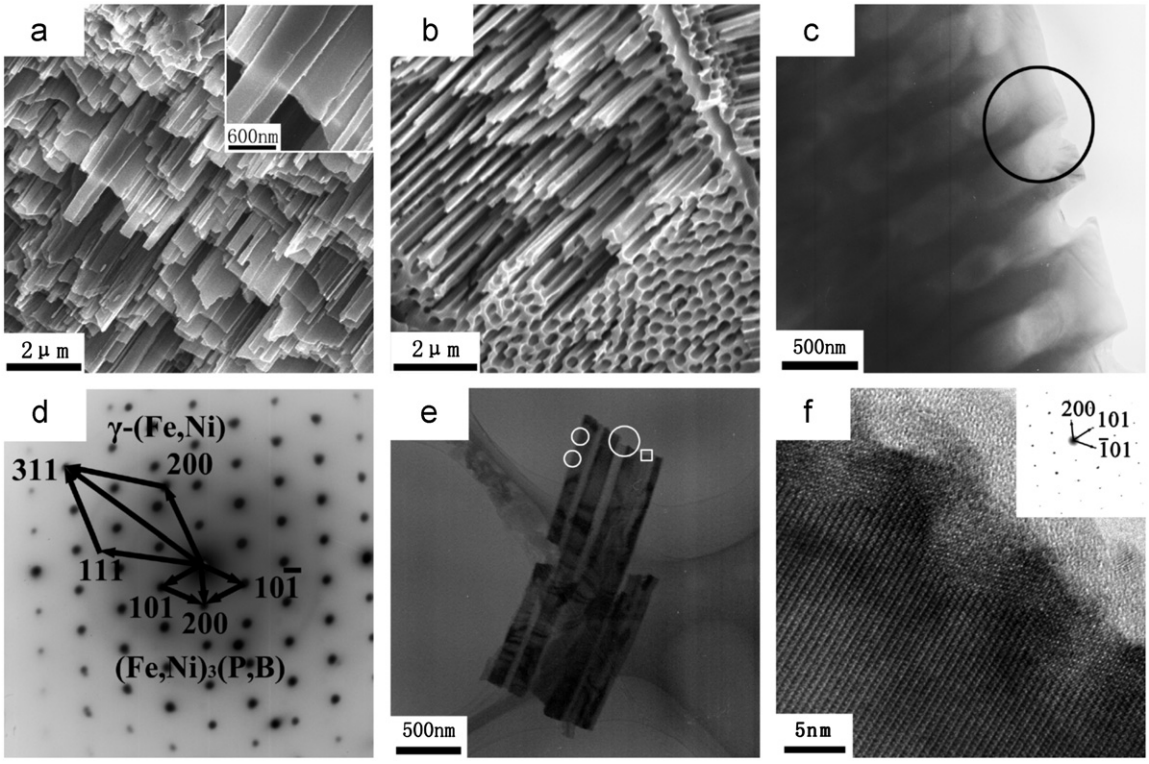

Fig. 2. SEM images of samples (a) well etched with high-magnification image (inset) and (b) partially etched. (c) Bright field TEM image of an as-prepared sample and (d) its selected-area electron diffraction (SAED) pattern. (e) Bright field TEM image of a nano-ribbon and (f) its high resolution TEM (HRTEM) image with SAED pattern (inset).