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The high-entropy alloys with high hardness and soft magnetic property prepared by mechanical alloying and high-pressure sintering

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ABSTRACT

The equiatomic multiprincipal CoCrFeCuNi and CoCrFeMnNi high-entropy alloys (HEAs) were consolidated via high pressure sintering (HPS) from the powders prepared by the mechanical alloying method (MA). The structures of the MA'ed CoCrFeCuNi and CoCrFeMnNi powders consisted of a face-centered-cubic (FCC) phase and a minority body-centered cubic (BCC) phase. After being consolidated by HPS at 5 GPa, the structure of both HEAs transformed to a single FCC phase. The grain sizes of the HPS'ed CoCrFeCuNi and CoCrFeMnNi HEAs were about 100 nm. The alloys keep the FCC structure until the pressure reaches 31 GPa. The hardness of the HPS'ed CoCrFeCuNi and CoCrFeMnNi HEAs were 494 Hv and 587 Hv, respectively, much higher than their counterparts prepared by casting. Both alloys show typical paramagnetism, however, possessing different saturated magnetization. The mechanisms responsible for the observed influence of Cu and Mn on mechanical behavior and magnetic property of the HEAs are discussed in detail.

1. Introduction

The high-entropy alloys (HEAs) consisted with a minimum of five principal elements each of them with an atomic concentration between 5 and 35 at% were firstly proposed by Yeh et al., in 2004 [1]. The alloy design [2], properties optimization [2,3], the atomic distributions of HEA [4], phase formation rules [5], and the sample preparation method were widely studied. At present, typical processing routes for HEAs can be summarized according to the starting states for the alloy preparation [6], mainly (1) from the liquid state: the arc melting [7], (2) from the solid state: the high-energy ball mill [8,9], (3) from the gas state: the sputtering method [10,11], and (4) from electrochemical process [12]. For the same components, different methods produce distinct microstructures especially for grain sizes, leading to different properties. A small grain size will result in high hardness and high strength according to Hall–Patch relationship [13]. The grain size usually reaches several hundred micrometers even several millimeters by the arc melting and then casting. However, the mechanically alloying (MA) could prepare alloy powders with nanocrystalline particles [14]. Then, the powders could be sintered by spark-plasma sintering (SPS). Fu et al. fabricated the inequi-atomic $Co_{0.5}FeNiCrTi_{0.5}$ [15] and $CoNiFeCrAl_{0.6}Ti_{0.4}$ [16] HEAs by MA–SPS. Zhang et al. synthesized the equiatomic multicomponent CoCrFeNiCuAl [17] and CoCrFeNiTiAl [18] HEAs with the same method. The grain size after SPS is nearly 300–400 nm [16] hard to reach less than 100 nm. Even though the grain size doesn't reach less than 100 nm, the yield stress of $Co_{0.5}FeNiCrTi_{0.5}$ alloy has been measured to be 2.65 GPa while the compressive strength reaches 2.69 GPa higher than most of the HEAs prepared by casting [16,19,20].

When the HEAs prepared by SPS, the pressure is usually dozens of MPa. In order to gaining high density, the sintering temperature will be high leading to a large grain size. When the pressure applied to sintering comes to several GPa, not only restraining the grain growth to acquiring a small grain size, but also increasing the density of the alloy bulk. Therefore, mechanical alloying (MA) and then sintered by high pressure sintering (HPS) is an efficient way to produce fine-grain alloys.

There has been expectation that some HEAs may also possess

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excellent magnetic properties for several ferromagnetic elements with high magnetic moments known to form HEAs [21,22]. The magnetic properties is strongly composition dependence. The saturation magnetization Ms drops almost monotonically upon the additions of Al and Si in $FeCoNi(AlSi)_x$ ($0 \leq x \leq 0.8$) [22]. Therefore, magnetic properties of the alloys were tested in the present work.

In the present work, with the aim to obtain excellent mechanical properties of HEAs with the nanoscaled grain size, equi-atomic CoCrFeCuNi and CoCrFeMnNi HEAs powders were fabricated by MA and then sintered by HPS. The structure of the powders prepared by MA and subsequent consolidation bulks were carefully investigated by X-ray diffraction (XRD), scanning electron microscopy (SEM), and transmission electron microscopy (TEM). The compression behavior of the samples was investigated by *in situ* high-pressure synchrotron diffraction. The hardness and magnetic properties of the HEAs after HPS were investigated by a Vickers hardness instrument and vibrating sample magnetometer (VSM). This study provides a valuable method to prepare nanocrystalline HEAs with excellent properties.

2. Experimental

The CoCrFeCuNi and CoCrFeMnNi HEAs were prepared by MA and HPS with elemental powders of Co, Cr, Fe, Ni, Cu, Mn, with diameter $\leq$ 45 μm and 99.7 wt.% purity. The elemental powders were milled in a planetary ball mill (Fritsch Pulverisette P-5) with the tungsten-carbide grinding media in toluene. The ball-to-powder weight ratio is 10:1, and a 450 rpm speed was used under the argon atmosphere. The powders were dry milled for 25 h. Then, the ethanol was used as a process-controlling agent in order to avoid excessive cold welding and also act as a reducing medium to avoid oxidation of the alloy within 25 h–30 h. The CS-1B type hexahedron anvils press was utilized for sintering 30 h ball-milled alloy powders at 1273 K and 5 GPa for 15 min. A graphite tube and pyrophyllite were taken as the heating device and pressure-transmitting medium. The size of the bulk alloys we produced by this equipment is about Φ 6 × 2 mm.

The structures of the samples were characterized by XRD using the D/MAX-2500/PC diffractometer with Cu Kα radiation. The microstructure of the powders and the bulk samples were studied by SEM using Hitachi-S4800 and TEM using JEM-2010.

Some powders were carefully scraped from the bulks of HEAs with a 4Cr13 stainless-steel scalpel for pressure experiments. In-situ high-pressure XRD experiments with a wavelength of 0.6199 Å and a focused beam size of about 26 × 8 μm^2 were performed at the beamline 4W2 of Beijing Synchrotron Radiation Facility in China. The powders were loaded into diamond anvil cells with the sample chamber about 180 μm in diameter, drilled in a T301-stainless-steel gasket. Silicone oil was used as a pressure-transmitting medium, while for the pressure calibration ruby pieces were dispersed inside. The pressure applied to the sample was calculated from the positions of ruby-fluorescence levels. The XRD patterns were acquired in the pressure range of 0–31 GPa upon compression with a transmission mode through the diamonds with a 20-min interval for each pressure point to allow for the stress relaxation. Debye rings were recorded using an image plate in a transmission mode, and the XRD patterns were integrated from the images using the FIT2D software [23].

Hardness measurements were conducted employing a Vickers hardness tester with an applied load of 300 g for 10 s. At least ten tests were conducted to obtain the average value. The hysteresis loops of the HEAs at room temperature were measured by using the Lakeshore 7407 VSM.

3. Results and discussion

3.1. Crystal structures and morphologies of powders and bulks

The XRD patterns shown in Fig. 1 reveal the phase of the MA powders and HPS bulks of both CoCrFeCuNi and CoCrFeMnNi HEAs. From the XRD results it is clear that the structure of the HEAs powders is a main face-centered-cubic (FCC) phase and a minor body-centered cubic (BCC) phase. After HPS, the BCC phase disappears for the bulk CoCrFeCuNi (lattice parameter a = 2.87 Å) and CoCrFeMnNi (lattice parameter a = 2.88 Å) HEAs. Therefore, phase transition from BCC to FCC occurred during sintering of the HEAs powders. Phase evolution during sintering may be attributed to the metastable supersaturated solid-solution phases transforming to equilibrium phases [8,24]. In the milled powders, a substantial amount of energy is stored because of the high dislocation density and the significant volume fraction of grain boundaries [25,26]. Accordingly, the excess energy may reduce the activation energy for phase evolution and, therefore, in favor of its occurrence during sintering [8,27]. Thus, metastable supersaturated solid-solution BCC phases transform to equilibrium FCC phases under the effect of temperature and pressure. Compared with the powders XRD, the diffraction peaks of FCC phases shift to high angles. It means that the lattice parameters become smaller. The lattice parameters of the FCC phases transform from 3.59 Å to 3.54 Å for the CoCrFeCuNi HEA, and from 3.61 Å to 3.56 Å for the CoCrFeMnNi HEA shown in Table 1, respectively. And they are smaller than their counterparts prepared by casting. The reason is similar to the phase transition from BCC to FCC. The substantial amount of stored energy induce the lattice of the FCC phase highly distortion with a larger lattice

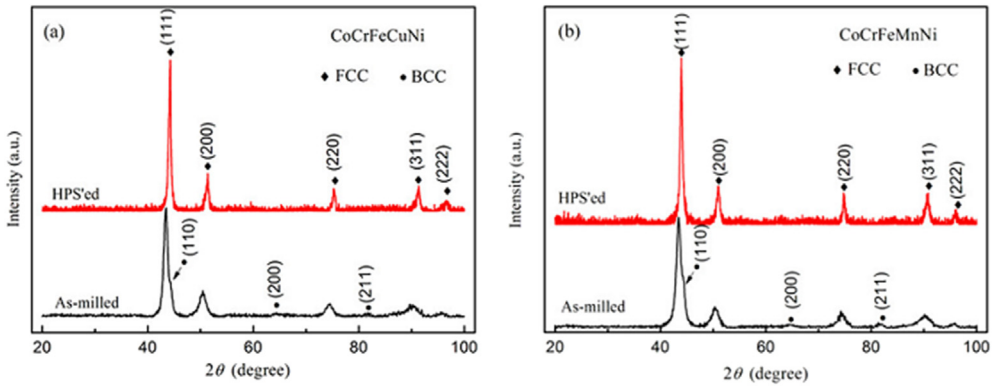

Fig. 1. XRD patterns of powders and bulk alloys; (a) As-mill'ed and HPS'ed CoCrFeCuNi, (b) As-mill'ed and HPS'ed CoCrFeMnNi.