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.

Keywords: High-entropy alloy; Mechanical alloying; High-pressure sintering; High hardness; Magnetic property

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 $\text{Co}_{0.5}\text{FeNiCrTi}_{0.5}$ [15] and $\text{CoNiFeCrAl}_{0.6}\text{Ti}_{0.4}$ [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 $\text{Co}_{0.5}\text{FeNiCrTi}_{0.5}$ 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 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 M_s 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 $\leq 45\ \mu\text{m}$ 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 to 30 h. The CS-1B type hexahedron anvils press was utilized for sintering 30 h ball-milled alloy powders at 1,273 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 $\Phi 6 \times 2\ \text{mm}$.

The structures of the samples were characterized by XRD using the

D/MAX-2500/PC diffractometer with Cu K α 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 $26 \times 8 \mu\text{m}^2$ 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 $a = 2.87 \text{ \AA}$) and CoCrFeMnNi (lattice parameter $a = 2.88 \text{ \AA}$) 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 $3.59 \text{ \AA}$ to $3.54 \text{ \AA}$ for the CoCrFeCuNi HEA, and from $3.61 \text{ \AA}$ to $3.56 \text{ \AA}$ 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 parameter during milling. While sintering, the temperature and pressure lead to the FCC phase

transforming from a larger lattice parameter in the metastable state to a smaller lattice parameter in the stable state. In addition, the diffraction peaks narrow after HPS, which indicates that the grains growth during sintering.

The morphology and size of powder particles for milled powders and grain sizes for the bulk samples were investigated using SEM and TEM shown in Fig. 2. In Figs. 2(a) and 2(b), the powder particles of the milled HEAs exhibit a lamellar morphology with a particle size of 20 μm . The particle sizes have a homogeneous distribution. Figure 2(c) and 2(d) show the SEM micrographs of the bulk HEAs after HPS. The sintering bulks possess a homogeneous, fine, and dense structure. The grain sizes could be characterized by TEM in Figs. 2(d) and 2(f). For the bulk CoCrFeCuNi and CoCrFeMnNi HEAs, the grain sizes of about 100 nm have a homogeneous distribution. The-select-area-electron diffraction patterns inserted in Figs. 2(d) and 2(f) indicate the FCC structures.

3.2. The structure of the HEAs at high pressures

The structures of the CoCrFeCuNi and CoCrFeMnNi HEAs under high pressure were investigated by in situ high-pressure synchrotron diffraction. The diffraction spectra of the alloys were displayed in Fig. 3 from ambient pressure to more than 30 GPa. With the increased pressure, the (111) and (200) diffraction peaks of FCC visibly shifted to a high angle, which shows the compression behavior of HEAs. Under the testing pressures, no new diffraction peaks were detected from the curves, indicating that the structures of the alloys were stable at high pressures.

In order to have a better understanding of their compression behavior of the

alloys, it is necessary to obtain the equation of state (EOS). Bridgman presented the EOS as follow [28]:

$$-\Delta V/V_0 = a_0 + a P + b P^2 + c P^3 + \dots \quad (1)$$

where V_0 is the volume at zero pressure, coefficients a_0 , a , b , and c can be determined, using the least-squares fitting method. One can estimate the relative volume change $-\Delta V/V_0 = V_P - V_0$ at a given pressure (V_P) to that at zero pressure (V_0). The experimental $-\Delta V/V_0$ data were shown in Fig. 4. When fitted by the Bridgman equation, EOS can be expressed as Equations (2) and (3) for CoCrFeCuNi and CoCrFeMnNi, respectively:

$$-\Delta V/V_0 = 8.51 \times 10^{-3} P - 2.73 \times 10^{-4} P^2 + 4.38 \times 10^{-6} P^3 \quad (2)$$

$$-\Delta V/V_0 = 7.35 \times 10^{-3} P - 1.80 \times 10^{-4} P^2 + 2.52 \times 10^{-6} P^3 \quad (3)$$

The bulk modulus, K , can be obtained according to the relationship [29], $K = \frac{1}{a}$.

The bulk modulus K of the HEAs are 117.5 GPa and 136.1 GPa for CoCrFeCuNi and CoCrFeMnNi, respectively. The result of the CoCrFeMnNi HEA is in good agreement Laplanche's result (137 GPa) testing in bending and torsion modes [30].

3.3. Mechanical and magnetic properties

Figure 5 shows the hardness of the CoCrFeCuNi and CoCrFeMnNi HEAs fabricated by HPS and their counterparts by casting. The hardness of the CoCrFeCuNi HEA produced by casting is 133 Hv [1]. While, the hardness increases to 494 Hv for the HEA by MA-HPS. For the CoCrFeMnNi HEA, the hardness increases from 300 Hv by casting [31] to 587 Hv by MA-HPS. The hardness of the the HEAs prepared by MA-HPS was improved greatly. The great increase of HEAs hardness prepared by MA-HPS is the reason of decreasing of grain size. The relationship between hardness

and grain size of the CoCrFeMnNi HEA was found to follow the classical Hall–Petch relationship, strengthening with a relatively high hardening coefficient of 677 MPa $\mu\text{m}^{-0.5}$ [32]. According to the Hall–Petch relationship for the CoCrFeMnNi HEA, the hardness of the CoCrFeMnNi HEA with a grain size of 100 nm in the present work is about 336 Hv. However, it is 587 Hv higher than the value calculating by the formula. This trend indicates that grain refinement plays more evident strengthening effects when the grain size is reaching the nanometer.

The CoCrFeCuNi and CoCrFeMnNi HEAs were consolidated with the same procedures including MA and HPS except for elements difference. Because of their similar grain sizes, the difference of grain-boundary strengthening effect on bulk modulus and hardness could be ignored. The atomic radii of Cu and Mn are 1.27 Å and 1.32 Å, respectively. The HEAs are different from traditional alloys because of different-sized atoms randomly distributed in the crystal lattice with the same probability to occupy the lattice sites [6]. Mn atoms with a larger atomic radius lead to larger lattice distortion and more evident solution strengthening. Therefore, the CoCrFeMnNi HEA will show a higher resistance to compression than the CoCrFeCuNi HEA during high pressure procedure. In addition, the higher hardness of CoCrFeMnNi HEA is also likely responsible for more evident solution strengthening.

The magnetic hysteresis loops of the CoCrFeCuNi and CoCrFeMnNi HEAs were presented in Fig. 6 measured by VSM at room temperature. The CoCrFeCuNi HEA show excellent soft magnetic property. The saturated magnetizations (M_s), remanence ratio (M_r/M_s), and coercivity (H_c) of the CoCrFeCuNi HEA are estimated to be 53.41

emu/g, 58.09%, and 166 Oe, respectively. The M_s of the CoCrFeCuNi HEA is higher than the CoCrFeNiCuAl HEA (38.18 emu/g) by casting [33]. However, the M_s of the CoCrFeMnNi HEA is 1.34 emu/g, similar to the value of CoCrCuFeNiTi alloy (1.368 emu/g) [34]. Compared with the magnetic properties of CoCrFeMnNi HEA prepared by SPS in Ji's paper [35], the HEA in this paper show lower saturated magnetizations for structure coarsening. The structure coarsening and phase transformation could result in magnetic property changes [6]. On the other hand, according to our results, the elements play a crucial role in the magnetic properties of HEAs. The CoCrFeCuNi and CoCrFeMnNi HEAs with a similar grain size, however, their saturated magnetizations vary widely. Therefore, the magnetic property of HEAs could be designed by choosing different elements.

4. Conclusions

In this study, two equiatomic CoCrFeCuNi and CoCrFeMnNi HEAs were prepared by MA-HPS. The bulk alloys exhibits a simple FCC solid solution structure with a grain size of about 100 nm. The HEAs remained stable up to 31 GPa, and the bulk modulus are 117.5 GPa and 136.1 GPa for CoCrFeCuNi and CoCrFeMnNi, respectively. The CoCrFeCuNi and CoCrFeMnNi HEAs show high hardness of 494 Hv and 587 Hv, respectively. Meanwhile, the CoCrFeCuNi HEA exhibits a high M_s value of 53.41 emu/g, whereas the CoCrFeMnNi HEA shows a low M_s value of 1.34 emu/g. This study reveals that MA-HPS can be used as an effective way to design HEA materials with the high hardness, high bulk modulus, and controllable magnetic property.

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Table caption

Table 1 The lattice parameters of the CoCrFeCuNi and CoCrFeMnNi HEAs prepared by the as-milled, HPS'ed, and as-cast (Å) conditions.

Figure captions

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.

Fig. 2 SEM micrographs of powders and bulk alloys after sintering; (a), (c) CoCrFeCuNi and (b), (d) CoCrFeMnNi; TEM micrographs of bulk alloys after HPS, (e) CoCrFeCuNi and (f) CoCrFeMnNi.

Fig. 3 Angle-dispersion X-ray diffraction patterns; (a) CoCrFeCuNi and (b) CoCrFeMnNi.

Fig. 4 Pressure dependence of relative volumetric change at room temperature; (a) CoCrFeCuNi and (b) CoCrFeMnNi.

Fig. 5 The hardness of the CoCrFeCuNi and CoCrFeMnNi HEAs prepared by MA-HPS and by casting from references [1,32].

Fig. 6 The hysteresis loops of the CoCrFeCuNi and CoCrFeMnNi HEAs prepared by MA-HPS.

Table 1 The lattice parameters of the CoCrFeCuNi and CoCrFeMnNi HEAs prepared by the as-milled, HPS'ed, and as-cast (Å) conditions.

Alloy	As milled		HPS'ed		As cast	
	FCC	BCC	FCC	BCC	FCC	BCC
CoCrFeCuNi	3.59	2.87	3.54	–	3.57 ^[1]	–
CoCrFeMnNi	3.61	2.88	3.56	–	3.59 ^[31]	–

Figure 1

Figure 2

Figure 3

Figure 4

Figure 5

Figure 6