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Short communication

Alloying behavior and novel properties of CoCrFeNiMn high-entropy alloy fabricated by mechanical alloying and spark plasma sintering

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ABSTRACT

An equiatomic CoCrFeNiMn high-entropy alloy was synthesized by mechanical alloying (MA) and spark plasma sintering (SPS). During MA, a solid solution with refined microstructure of 10 nm which consists of a FCC phase and a BCC phase was formed. After SPS consolidation, only one FCC phase can be detected in the HEA bulks. The as-sintered bulks exhibit high compressive strength of 1987 MPa. An interesting magnetic transition associated with the structure coarsening and phase transformation was observed during SPS process.

1. Introduction

For centuries, the design concept of alloy systems has been based on utilizing one or two elements as the principal components, with minor amounts of other elements for property enhancement, such as steels and NiAl intermetallics [1,2]. However, this paradigm has been broken by the suggestion of high-entropy alloys (HEAs) developed by Yeh et al. [3]. A HEA is originally defined as an alloy system composed of at least five principal elements in an equimolar or near equimolar ratio (varying 5–35 at.%) with a small difference in atom radii (<15%). The high mixing entropy of multi-principle elements will induce lattice distortion and sluggish cooperative diffusion. As a consequence, HEAs often possess simple solid-solutions or amorphous structure rather than intermetallics [4] and exhibit high hardness, excellent strength as well as promising resistances to wear, oxidation and corrosion [5].

Among HEA systems, the equi/non-equiatomic CoCrFeNiMn has attracted great interest for its unique characteristics. Liu et al. investigated the grain growth behavior of CoCrFeNiMn HEA during annealing [6]. Yao and his colleagues studied the exceptional phase stability and tensile ductility of $Co_5Cr_2Fe_{40}Ni_{26}Mn_{27}$ HEA [7]. Moreover, the microstructure, texture evolution and dislocation nucleation of CoCrFeNiMn HEAs fabricated by vacuum arc-melting have been investigated systematically [8,9]. However, the CoCrFeNiMn HEA system has been prepared mainly by arc melt/casting. But those fabrication routes are unsuitable for industrial manufacturing due to the disadvantages of diseconomy and limitations in shape and size of final products [10]. By contrast, mechanical alloying (MA) is a more convenient way, which has been widely used for the synthesis of nanocrystalline materials with uniform microstructure. Thus MA is expected to reduce the cost of preparing nanocrystalline materials and widen the application of HEA [11,12]. Combined with the new spark plasma sintering (SPS) technique, high-entropy alloys can be easily obtained from the as-milled powders [13–15]. What's more, the novel magnetic properties, which can be usually observed in traditional alloy systems containing Mn element [16–18], have not been investigated for the CoCrFeNiMn HEA. This scope is also an academic issue and required to be revealed and discussed.

In this work, we focused on the high-entropy alloy system of CoCrFeNiMn synthesized by mechanical alloying and spark plasma sintering, and studied on the alloying behavior, microstructure, mechanical and magnetic properties.

2. Experiment details

High purity (>99.5 wt.%) Co, Cr, Fe, Ni and Mn powders with particle size less than 45 μm were used as starting materials. The elemental powders were mixed in equiatomic composition and

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milled in a planetary ball-miller for 60 h at 250 rpm in an argon atmosphere. Stainless steel vials and balls were utilized as the milling media with a ball-to-powder mass ratio of 15:1. N-heptane was introduced as the processing controlling agent (PCA) to avoid cold welding as well as preventing metal oxidation. The MA process was monitored by regular powder extraction at an interval of 6 h. Subsequently, the as-milled powder was consolidated by SPS (Dr. Sinter-3.20 MKII, SCM) at 800 °C for 10 min under 50 MPa uniaxial pressure in argon atmosphere.

The crystal structure of the as-preserved alloy prepared was examined by X-ray diffractometer (XRD, Rigaku Ultima III) with CuKα radiation. The microstructure of the powders was observed using scanning electron microscopy (SEM, Hitachi 3400) and transmission electron microscopy (TEM, JEOL JEM-2010HT). Density of the bulk HEA was calculated using the Archimedes principle. Bulk hardness of the sectioned and polished specimens was measured using Vickers hardness tester (Wolpert-430SV). The compressive properties at room temperature were measured by a MTS810 testing machine. The magnetic properties of the HEAs were characterized on a Physical Property Measurement System (PPMS, Quantum Design PPMS-9T).

3. Results and discussion

The XRD patterns of as-milled CoCrFeNiMn HEAs powders and consolidated bulks were shown in Fig. 1. The primary blending powder includes diffraction patterns of all alloying elements. After 6 h MA, the diffraction peaks of the principle elements can still be observed with a dramatic decrease in intensity. With prolonged milling time to 30 h, peak broadening is obvious and some peaks become invisible. As the milling time increases to 60 h, only peaks belongs to a BCC structure ((110), (200), (211)) and an FCC structure ((111), (200)) can be identified, by which is deduced the formation of a simple solid solution. Throughout the milling process, the decrease in intensity, broadening of the peak and its subsequent disappearance may result from the three following factors: refined crystal size, high lattice strain and decreased crystallinity.

The crystallite sizes (CS) during MA were present in Table 1 calculated by Scherrer's formula after eliminating the instrumental and the strain contributions. As shown, the CS of the BCC phase is significantly refined to 13.4 nm after 42 h MA and then slightly decreases to 12.7 nm after 60 h milling. The results reveal that the balance between crystalline refinement and cold welding

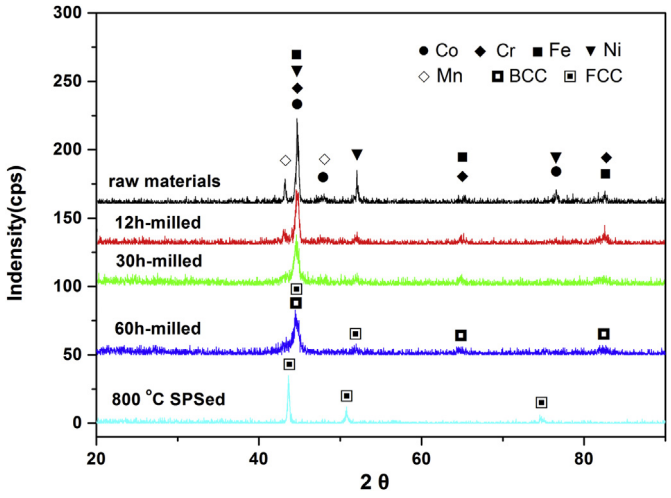

Fig. 1. XRD patterns of CoCrFeNiMn HEAs powders milled under different time and CoCrFeNiMn HEA bulk consolidated by SPS.

Table 1
The crystalline size (CS) and lattice parameter (LP) of the BCC and FCC phases with different milling time.

Milling time (h)	CS (nm)		LP (Å)	
	BCC	FCC	BCC	FCC
12	21.3 ± 0.02	21.1 ± 0.02	2.866 ± 0.01	3.519 ± 0.01
30	16.1 ± 0.02	16.5 ± 0.02	2.871 ± 0.02	3.524 ± 0.01
42	13.4 ± 0.01	13.9 ± 0.02	2.876 ± 0.01	3.534 ± 0.01
60	12.7 ± 0.01	9.8 ± 0.01	2.878 ± 0.01	3.536 ± 0.02

of BCC phase might have been achieved when the milling time reaches 42 h. Further increase of the milling time has no vital influence on the crystallite size of the BCC phase, but the FCC phase can still be refined after 42 h of milling. The CS of the FCC phase for 42 h MA and 60 h MA are 13.9 nm and 9.8 nm, respectively.

Table 1 also lists the lattice parameters (LP) of the BCC and FCC phases with varying milling time. The lattice parameters of both BCC and FCC phases increase as the milling time prolongs. At the initial stage of milling, the LP of BCC (2.866 Å) and FCC (3.519 Å) phases are rather closed to that of highly pure iron (2.866 Å) and nickel (3.524 Å), respectively. As MA processing, the simple solid-solutions are gradually formed from the principle components. The corporation of elements with larger atomic size, e.g. Cr and Mn, results in the enlargement in lattice parameter.

The XRD pattern of the SPSed HEA bulk shows only an FCC solid solution structures, seen in Fig. 1. The crystallite structure is different from that of the as-milled alloy but similar with the as-cast one [7]. Compared with the XRD patterns of as-milled HEA powder, a peak shift can be clearly observed for the as-sintered bulk. The peak shifting towards lower Bragg angle (2θ) indicates that the lattice parameter of as-sintered HEA bulk is larger than that of as-milled HEA powder. The phase transition is resulted from the converting to more stable phases of as-milled alloy powder during subsequent consolidation at higher temperatures [19,20].

Moreover, due to the non-equilibrium state of the MA process, a large amount of internal stress would be stored in the lattice, as well as defects, i.e. lattice distortion and twins. The internal stress was released when the HEA was sintered at high temperature and the metastable state transformed to stable one. Both would contribute to the expansion of the crystal lattice.

The microstructures of obtained CoCrFeNiMn HEA powders after 60 h MA were shown in Fig. 2(a)–(b). As shown in Fig. 2(a), as-milled powder agglomerates into elliptical shape of ~2.36 μm and less than 1 μm in thickness. The nanocrystalline nature of CoCrFeNiMn HEA powder has been further characterized by the TEM bright field image and the SAED patterns, seen in Fig. 2(b). The average grains with size of ~10 nm can be observed in the bright field TEM image, and the rings in the SAED pattern of Fig. 2(b) reveal that the nanocrystalline HEA powder consists of a BCC phase and a FCC phase, which is in good agreement with the XRD analysis. The results confirm that the CoCrFeNiMn high-entropy alloy with a structure of simple solid solution has been successfully fabricated by mechanical alloying.

The TEM bright field image and corresponding SAED patterns of bulk CoCrFeNiMn HEA by SPS are shown in Fig. 2(c). It can be observed that there are two different sizes of grains, one is 100–200 nm with twin crystals and the other one is approximate 50 nm. Corresponding SAED patterns indicate that the grains both have a structure of FCC, with similar calculated lattice parameters of 3.589 Å and 3.590 Å, respectively. Available literatures indicate that only a single FCC phase exist in the CoCrFeNiMn high-entropy alloy [8,9] and so the grains with different size can be considered as one FCC phase. The result can better account for the only FCC crystal