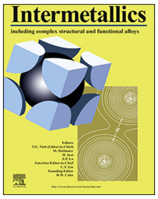
Intermetallics 103 (2018) 63–66

Contents lists available at ScienceDirect

Intermetallics

journal homepage: www.elsevier.com/locate/intermet



Pressure-induced ordering phase transition in high-entropy alloy

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ARTICLE INFO

Keywords:
High-entropy alloy
Phase transition
X-ray techniques
Powder metallurgy

ABSTRACT

The order-disorder transition has long been viewed as an important key to study materials structures and properties. Especially, pressure-induced ordering attracted the intense research interest in the recent years. In the present work, the pressure-induced ordering phase transition (disordered-fcc to ordered-fcc structures) in a CoCrCuFeNiPr high-entropy alloy (HEA) was found by employing the *in situ* high-pressure energy-dispersive X-ray diffraction (EDXRD) technique. It is interesting to note that there exists a pressure-induced fast ordering transition at the pressure ranging from 7.8 GPa to 16.0 GPa, followed by a slow transition with the pressure increase up to 106.4 GPa. We suggest that this phenomenon is caused by the presence of some short-range-order (SRO) local structures in the CoCrCuFeNiPr HEA. These SRO structures can be regarded as embryos, which will develop into the ordered phase with increasing the pressure in the prototype materials. This pressure-induced ordering may provides a new technique for tuning structures and properties of HEAs.

1. Introduction

The order-disorder phase transition, which widely exists in metals [1–3],has drawn significant attention in the research field of materials science since it is closely related to energetic and physical properties of alloys, ferroelectric materials and superconductors. Generally, the materials structure ordering was affected by its compositions and temperatures. Take Cu-Zn alloys for example, the Cu-Zn alloys are disordered at high temperatures but ordered at low temperature [4].In addition to temperatures and compositions, pressures also have significant effects on the ordering phenomenon in materials [3,5].

Over the past decade, high-entropy alloys (HEAs) [6,7]as a new strategy of materials design, which obtained the intense research interest due to their attractive and intriguing properties and manifold potential applications, such as high softening resistance at elevated temperatures [8–10],high-temperature strength and stability of nanocrystalline HEAs [11].An exceptional ductility and fracture toughness at cryogenic temperatures [12],superior soft magnetic [13,14],fatigue [15], applied a lot to the coating [16–18], superconductivity have also been reported [19]and very high hardness [20].Unlike traditional alloys, HEAs are fabricated, based on more than four principal elements in an equiatomic or near-equiatomic ratio [9]with rather simple crystal structures [e.g. body-centered cubic (bcc), face-centered cubic (fcc), hexagonal close-packed (hcp) [21]or amorphous phases] rather than with multiple phases and complex microstructures consisting of intermetallic compounds. It is worth noting that for many HEAs, except for the major phase (fcc, bcc, or hcp structure), they contain minor ordered phases B2 [22,23],and $L1_2$ [24–26].Structural stability and development are very crucial for materials properties, even strongly affecting its final applications in the extreme temperature and pressure conditions. Recently, some researchers have paid intensive attention on the high-pressure structural evolution of HEAs [27–32].It has been shown that both CoCrFeMnNi and CoCrFeNi HEAs can undergo the fcc-to-hcp phase transition [27–29].

Considering that the ordered phase and high-pressure phase transition exist in HEAs, as discussed above, and combining high-pressure ordering observed in materials with HEAs, it is reasonable to deduce that pressure-induced ordering may happen in HEAs. Up to now, high-pressure ordering in HEAs has never been reported. High-entropy alloys are an emerging alloy design. Rare earth elements, Pr, are prone to phase change under pressure. Adding rare earth element, Pr, to high-entropy alloys can better understand the high-pressure-effect on the phase transition process of high-entropy alloys. What is more, the alloying rare-earth element, Pr, and the constituent elements of CoCrCuFeNi alloy have low negative mixing enthalpy and high radius difference. Therefore, this paper focused on investigating the structural

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https://doi.org/10.1016/j.intermet.2018.10.003
Received 21 June 2018; Received in revised form 27 September 2018; Accepted 3 October 2018

evolution of the equiatomic CoCrCuFeNiPr HEA [with major disordered-fcc (D-fcc) and minor ordered-fcc (O-fcc)], under compression by using the *in situ* high-pressure energy-dispersive X-ray diffraction (EDXRD) with a synchrotron radiation source technique.

2. Material and methods

Equiatomic elementals, Co, Cr, Cu, Fe, Ni and Pr powders, with 99.9% (weight percent) higher purity were mechanically alloyed to fabricate the experimental prototype material of an equiatomic CoCrCuFeNiPr HEA. The milling was carried out up to 25 h, later with the added alcohol. It continues milling up to 5 h in a high energy planetary ball mill (QM-3SP4) at 450 rpm with a ball to powder ratio of 20:1. High strength stainless steel vials and balls were utilized for mechanical alloying protected under an Ar atmosphere.

The X-ray diffraction experiment on the HEA with a wavelength of $\lambda = 0.6199$ Å and *in situ* high pressures was carried out, using the synchrotron radiation with a diamond anvil cell (DAC) in the 4W2 beam line of the Beijing Synchrotron Radiation Facility (BSRF). Some prepared CoCrCuFeNiPr HEA powders were used and loaded into the T301-stainless-steel gasket hole with a diameter of 140 μm. Silicone oil was used as a pressure-transmitting medium, while for the pressure calibration, ruby pieces were dispersed inside. Two dimensional diffraction patterns were recorded, employing an image plate in a transmission mode, and the XRD patterns were integrated from the images using the FIT2D software [33].

3. Results and discussion

The X-ray diffraction (XRD) patterns of the CoCrCuFeNiPr HEA sample under compression with various pressures at room temperature are shown in Fig. 1. As seen in the lower degrees, there are two phases' diffraction peaks, which are the major D-fcc phases (shown in black rhombs) and minor O-fcc phases (shown in red solid circles). It can be clearly seen that at 16.0 GPa, the O-fcc peaks suddenly become strong (conversely, in the meantime, peaks corresponding to the D-fcc phase are abruptly weakened), which suggest that in the pressure range from 7.8 GPa to 16.0 GPa, there exist a sharp disorder-order phase transition. Additionally, despite that the intensity of the (200) peak of the D-fcc phase gradually lower and almost completely disappear when the pressure increases up to 45.1 GPa, the patterns change slowly with increasing the pressure to 106.4 GPa, and no other new phase peaks occurred, it indicates that the coexistent state of the major O-fcc and minor D-fcc phases is stable at high pressures. It is worth noting that all diffraction peaks of both O-fcc and D-fcc phases shift toward higher 2Theta values, and their intensities are reduced with a further increase of the applied pressure, which is an expected result induced by pressure [28,30].We should note that the peaks marked with the black-asterisk symbols do not shift or little change with increasing pressures. Therefore, they are not related with the peaks of the studied materials.

Fig. 2 presents the pressure dependence of d_{111}-spacing and pressure-volume relations for D-fcc and O-fcc phases of the present HEA under different pressures via the *in situ* high-pressure EDXRD technique. It is found from Fig. 2(a), respectively, that the O-fcc phase always has the lower d_{111} than the D-fcc phase. It should be noted that, at the outset, the d_{111} of the O-fcc phase increases a little with increasing the pressure, abnormally. This trend might be caused by the pressure-induced solidification of the transmitting media silicon oil, which was used in the DAC (a diamond anvil cell). When the pressure reaches around 26 GPa, the d_{111} of all these two phases decreases smoothly with a further increase of the applied pressure. The relationships of the pressure and volume for both phases are shown in Fig. 2(b), and the atomic volumes as a function of pressure for D-fcc and O-fcc phases are fitted, using the third-order Birch-Murnaghan equation of state (3rd order B-M EOS), which can be written as follows [34].

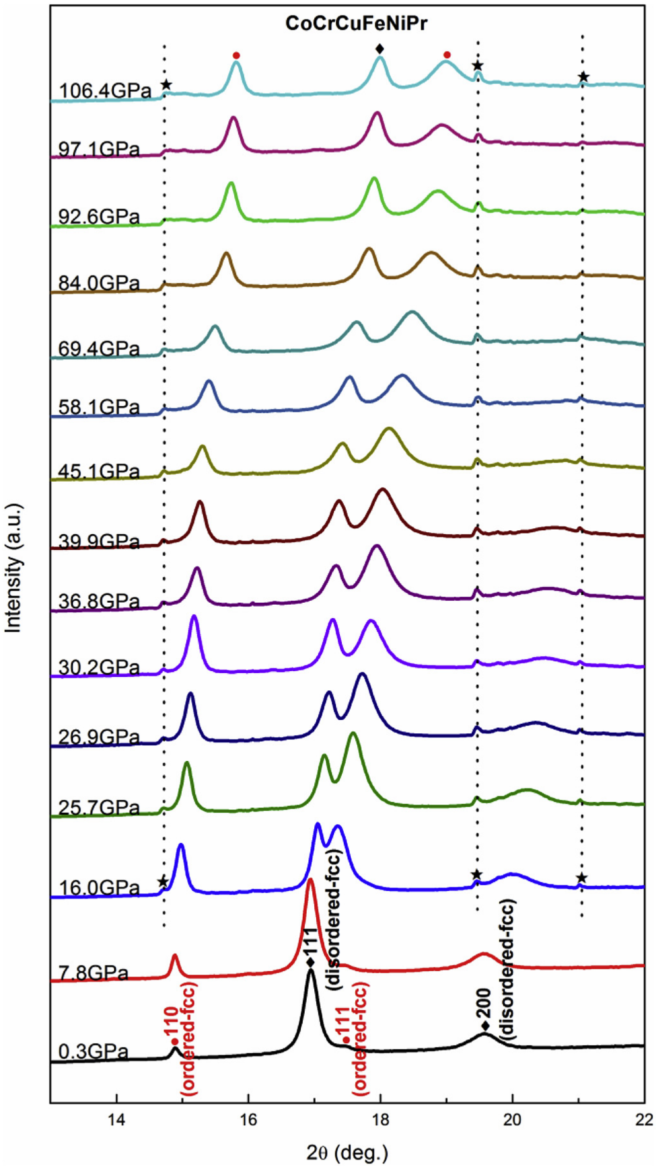

Fig. 1. *In situ* high-pressure X-ray diffraction patterns of the CoCrCuFeNiPr HEA under various pressures. Peaks marked with black asterisks which do not belong to the studied material. Black dash lines are guides for the eye.

$$P = \frac{3}{2}B_0\left[\left(\frac{V_0}{V}\right)^{\frac{7}{3}} - \left(\frac{V_0}{V}\right)^{\frac{5}{3}}\right] \times \left\{1 - \frac{3}{4}(4 - B_0')\left[\left(\frac{V_0}{V}\right)^{\frac{2}{3}} - 1\right]\right\} \tag{1}$$

Where P is the applied pressure, V is the atomic volume at the pressure, P, V_0 is the atomic volume in ambient conditions, and the isothermal bulk modulus, B_0, and its pressure derivative, B_0', are commonly derived by fitting the pressure-volume data.

Herein, through the fitting phases of P-V/V_0 curves by Eq. (1) [marked as red solid lines in Fig. 2(b)], we obtained the isothermal bulk modulus of $B_0 = 448.40 \pm 24.5$ GPa and its pressure derivative of $B_0' = 2.62 \pm 0.55$ for the D-fcc phase, and $B_0 = 295.43 \pm 15.7$ GPa and its pressure derivative of $B_0' = 2.08 \pm 0.57$ for the O-fcc phase, and these relative fitting parameters are listed in Table 1. According Table 1, it is noticeable that the bulk moduli of D-fcc phases are larger than these of O-fcc phases. It indicates that upon compression, the decrease in the cell-volume of the O-fcc phase is larger than the D-fcc phase in the studied HEA. From Fig. 2, we could analyze the change of d_{111} and V/V_0 for D-fcc and O-fcc phases under various applied pressures quantitatively. With the increased pressure up to 106.4 GPa, the