Graphical Abstract

Three reversible transformations following the sequence hexagonal close-packed (hcp) → samarium type (Sm-type) → double hexagonal close-packed (dhcp) → distorted face-center cubic (dfcc) are observed at 4.4, 26.7, and 40.2 GPa in the HoDyYGdTb high-entropy alloy, respectively. The phase transitions are due to the $s \rightarrow d$ charge transfer during compression.

Pressure-induced phase transitions in HoDyYGdTb high-entropy alloy

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Abstract: The HoDyYGdTb high-entropy alloy (HEA) was synthesized and its structural phase transitions were determined under compression up to 60.1 GPa at room temperature. Three transformations following the sequence hexagonal close-packed (hcp) → samarium type (Sm-type) → double hexagonal close-packed (dhcp) → distorted face-center cubic (dfcc) are observed at 4.4, 26.7, and 40.2 GPa, respectively. The high pressure equation of state was determined for the HEA according to third-order Birch-Murnaghan equation of state. The results show that the bulk modulus and atomic volume of the alloy obey the “additivity law”.

Keywords: Rare-earth high-entropy alloys; High pressure; Phase transformation; X-ray techniques

1. Introduction

High-entropy alloys (HEAs) are loosely defined as solid-solution alloys that contain more than five principal elements in an equal or near-equal atomic percent (at.%) [1]. The structures of solid solutions include face-center cubic (fcc), body-center cubic (bcc), hexagonal close-packed (hcp), and amorphous structures. The vast majority of reports pertaining to HEAs are focused on the fcc structure, bcc structure, or their mixtures. The study on the hcp structural HEA falls behind relative to the other structured HEAs. Until 2014, Takeuchi et al. [2] found a nearly-single hcp phase in YGdTbDyLu and GdTbDyTmLu alloys. Then, Feuerbacher et al. [3] investigated a completely single phase DyGdHoTbY high-entropy alloy. The mechanical properties of GdHoLaTbY alloy were studied and indicated that there is no hardening effect from entropy [4].

The properties of the rare-earth HEAs with the hcp structure obey the rule of mixture, or the “additivity law”[4,5]. At present, few studies concerning the structure evolutions of HEAs under pressure. Li *et al.*[6,7] revealed that AlCoCrCuFeNi and CoCrFeCuNi HEAs with an fcc structure keep stable under 30 GPa. Recently, Tracy *et. al*[8] found the phase transition of CrMnFeCoNi from fcc to hcp structure at ~14 GPa. However, the structures of rare-earth HEAs under high pressures are still unclear.

Until now, the hcp structure HEAs are almost composed of heavy lanthanides. The trivalent lanthanides (La through Lu except Eu and Yb) have been shown to follow a crystal structure sequence with decreasing the atomic number or increasing pressure: hcp → samarium type (Sm-type) → double hexagonal close packed (dhcp) → fcc → distorted fcc (dfcc)[9]. Except for pure rare-earth elements, lanthanide-solvent bulk metallic glasses undergo the low-density state to high-density state transitions under high pressures[10-14]. This feature invites the questions: if the phase transition of the rare-earth-HEAs obey the route of rear-earth metatls under high pressures? What is the relationship of the phase-transition pressure values between the HEA and its constituent elements? In this study, we focus on the compressive behavior of the HoDyYGdTb HEA under high pressures by *in situ* angle-dispersive X-ray diffraction (ADXRD) with a synchrotron radiation source.

2. Material and methods

The ingots of the equiatomic HoDyYGdTb HEA was prepared by arc-melting mixtures of pure metals (weight purity $\geq 99.9\%$) in a Ti-gettered high-purity argon atmosphere and remelted at least four times. The sample was scraped and loaded into the T301-stainless-steel gasket hole with a diameter of 180 μm . Silicone oil was used as a pressure-transmitting medium, while for the pressure calibration, ruby pieces were dispersed inside. In-situ high-pressure XRD experiments with a wavelength of 0.6199 Å were performed at the 4W2 beam line of the Beijing Synchrotron Radiation Facility (BSRF), Chinese Academy of Sciences. 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[15].

3. Results and discussion

Figure 1 shows the integrated X-ray diffraction patterns of all four phases (hcp, Sm-type, dhcp, and dfcc) seen in the HoDyYGdTb HEA under compression with different pressures. The ADXRD pattern of the starting material indicates an hcp structure with a small oxide peak, which is connected by a dotted line. With increasing pressures, the diffraction peaks shift to a higher angle. In this experiment, we noticed that the hcp phase to be stable under 4.4 GPa. A peak of Sm-type indicated by an arrow begins upon further compression. With increasing the pressure to 13.6 GPa, the (102) diffraction peak of the hcp phase disappears, and the transition from the hcp to Sm-type phase is completed.

Fig. 1. Representative ADXRD spectra of the HoDyYGdTb HEA under different pressures during compression.

The transition to dhcp starts around 26.7 GPa. This phase persists to 38.3 GPa. It is known that the fcc phase-stability field is narrow usually about 5 GPa in heavy rare-earth metals. Thus, many experiments never observe a pure fcc phase in heavy rare-earth metals (Dy[16], Y[17], and Gd[18,19]). For Ho[20], the transition goes directly from the dhcp to dfcc structure. In our experiment, there is no obvious fcc phase during compression. The dfcc phase structure obtained at 40.2 GPa is identified with the trigonal space group of $R\bar{3}m$ [21] with lattice parameters, $a = 0.61$ nm and $c = 1.42$ nm. The dfcc phase exists to the highest pressure of our test (60.1 GPa).

The detailed phase-transition sequence and pressures for the HoDyYGdTb HEA and its

constituent elements are listed in Table 1. The constituent elements undergo similar structural transitions, and the transition pressures increase with increasing the atomic number (except for Y). According to Table 1, it is noticeable that the phase transition sequence of the HoDyYGdNb HEA follows a similar route with its constituent elements. The phase transition pressure values of the HEA are between the minimum and maximum pressure values of its constituent elements phase transformation.

Table 1. Phase transition routes and pressures of Gd[18,19], Tb[20], Dy[16], Ho[20], Y[17], and HoDyYGdNb HEA in the present work.

Elements and Alloy	hcp→Sm-type	Sm-type→dhcp	dhcp→fcc	fcc→dfcc
Gd	1.5	6.5	24	32
Tb	2	16	28	38
Dy	6	15	38	43
Ho	7	20	-	52
Y	14	32	-	50
HoDyYGdNb	4.4	26.7	-	40.2

The atomic volumes for different phases of HoDyYGdNb HEA as a function of pressure were calculated and fitted using the third-order Birch-Murnaghan equation of state (EOS), which is given by[22],

$$P = \frac{3}{2} K_0 \left[\left(\frac{V_0}{V} \right)^{\frac{7}{3}} - \left(\frac{V_0}{V} \right)^{\frac{5}{3}} \right] \left\{ 1 + \frac{3}{4} (K_0' - 4) \left[\left(\frac{V_0}{V} \right)^{\frac{2}{3}} - 1 \right] \right\}, \quad (1)$$

where K_0 , K_0' , and V_0 are the isothermal compressibility, the first derivative of K_0 , and the atomic volume at ambient conditions, respectively. Figure 2 presents the compressional volume data of different phases and the fitting red solid curve with the Birch-Murnaghan EOS. Through fitting the atomic volume to 60.1 GPa by Eq. (1), we calculate the bulk modulus of the HEA, $K_0 = 45.8$ GPa, its pressure derivative, $K_0' = 3.0$, and atomic volume at ambient conditions, $V_0 = 19.3$ cm³/mol. The bulk modulus and atomic volume of the HEA agree extremely well with the estimated average values of 45.4 GPa and 19.3 cm³/mol, respectively, using the rule of mixture, or the

“additivity law”[5], which is suitable for mechanical properties.

$$p = \sum_{i=1}^n c_i p_i, \quad (2)$$

where c_i and p_i are the atomic percentage and the mechanical properties of each constituent elements, respectively. In this letter, we could consider that p_i is the bulk modulus and atomic volume of each rare-earth elements.

Fig. 2. The measured pressure-volume relations for various phases of the HoDyYGdTb HEA to 60.1 GPa at room temperature. The red solid curve is the fit to the Birch-Murnaghan equation of state.

It is widely believed that the occupancy of the d band and the d -band contribution to the total energy determine the crystal structure of rare-earth elements[9]. Fig. 3 is the schematic illustration of phase transition in the HoDyYGdTb HEA related to the d -band electronic state. The elements composed the HoDyYGdTb HEA have different d -band occupancy states expressed with different colors. After alloying, the d -band occupancy state of the HEA is determined by its constituent elements, and it is expressed with another color. During compression, the volumes of each rare-earth atoms become smaller. Meanwhile, the $s \rightarrow d$ charge-transfer of the HEA induces the number of d electrons in the conduction band n_d increasing[23]. As the d band are progressively filled with electrons (the “color” changing), the structure of the HEA move through the sequence $hcp \rightarrow \text{Sm-type} \rightarrow dhcp \rightarrow dfcc$ as is experimentally observed. Very recently, Tracy *et. al*[8] found the pressure-induced fcc-to-hcp transformation of CrMnFeCoNi HEA at ~14 GPa, which has not been previously observed in any transition metal at ambient temperature. This indicates that the CrMnFeCoNi HEA exhibits different phase transformation behavior as to its constituent

elements. However, in our experiment, the HoDyYGd Tb HEA show a similar phase transition sequence with its constituent elements. These suggest that the properties of the HEA depend on its constituent elements and their interactions.

Fig. 3. Schematic illustration of phase transition in the HoDyYGd Tb HEA related to the d -band electronic state.

4. Conclusions

In summary, we have carried out angle-dispersive high pressure X-ray diffraction studies on the HoDyYGd Tb HEA with an hcp structure to 60.1 GPa at ambient temperature. The HEA is shown to follow the trivalent rare-earth crystal structure sequence of hcp $\rightarrow$ Sm-type $\rightarrow$ dhcp $\rightarrow$ dfcc correlated $s \rightarrow d$ charge transfer of the HEA. Finally, an EOS for HoDyYGd Tb HEA was obtained at room temperature under nearly hydrostatic conditions with bulk modulus $K_0 = 45.8$ GPa, pressure derivative of $K_0' = 3.0$, and atomic volume $V_0 = 19.3 \text{ cm}^3/\text{mol}$. The bulk modulus and atomic volume of the HEA agree extremely well with the calculated values with the “additivity law”.

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