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Anomalous microstructure and excellent mechanical properties of $Ni_{35}Al_{21.67}Cr_{21.67}Fe_{21.67}$ high-entropy alloy with BCC and B2 structure

Lu Zhang [a], Dong Zhou [a], Bangsheng Li [a,b,c,*]

[a] School of Materials Science and Engineering, Harbin Institute of Technology, Harbin 15001, China
[b] State Key Laboratory of Advanced Welding and Joining, Harbin Institute of Technology, Harbin 150001, China
[c] Micro/Nano Technology Research Center, Harbin Institute of Technology, Harbin 15001, China

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ABSTRACT

A quarternary Co-free $Ni_{35}Al_{21.67}Cr_{21.67}Fe_{21.67}$ high entropy alloy was designed and prepared by arc melting. The $Ni_{35}Al_{21.67}Cr_{21.67}Fe_{21.67}$ high entropy alloy (HEA) possesses disordered BCC phase and ordered BCC phase (B2). A "sunflower-like" microstructure was found in $Ni_{35}Al_{21.67}Cr_{21.67}Fe_{21.67}$ high entropy alloy. B2 phase forms the continuous matrix with the disordered BCC spherical particles (200 nm–300 nm) in 'core' region. In 'petal' region, striped B2 phases are inlaid in disordered BCC matrix. Moreover, the result of mechanical property test suggests that alloy presents outstanding compressive strength and excellent ductility with the microstructure of B2/BCC phase. The alloy showed an excellent comprehensive properties at room temperature (yield strength $\sigma_{0.2}$ = 1471 MPa, compressive strength σ_b = 35 41 MPa and compression rate ε = 40%) , which was superior to some traditional metallic materials. High strength was mainly attributed to high volume fraction of hard B2 phase matrix and B2 precipitations strengthening. Dislocations motion in disordered BCC matrix provided ductility for the alloy. The $Ni_{35}Al_{21.67}Cr_{21.67}Fe_{21.67}$ HEA has promising use in future structural applications.

1. Introduction

Unique microstructure and excellent performance made high-entropy alloys become one of the most extensive researches. However, to achieve balance of high strength and high ductility is a difficult problem. It has been found that multi-phase structure is propitious to improve comprehensive property [1,2]. Recently, an ordered BCC phase (B2), which is considered to play an important role in improving strength, has been found in many HEAs [3]. For instance, in the system of $Al_xCoCrFeNi$ HEAs, B2 phase was found when x = 0.75. The harness increases and the ductility decreases when (A2 + B2) structure forms as the increase of Al content. [4]. The results of mechanical properties test showed that B2 phase is conducive to improving the strength and hardness, but reducing the ductility of the alloy. Therefore, almost no studies have reported that an alloy with BCC/B2 structure can obtain high strength and high ductility at the same time.

Our previous research [5] showed that equimolar quarternary HEA CrFeNiAl has excellent properties. In order to achieve higher properties, a Co-free $Ni_{35}Al_{21.67}Cr_{21.67}Fe_{21.67}$ (at,%) .%) quarternary HEA with BCC/B2 structure was designed. Our conclusion proved that comprehensive mechanical properties of the $Ni_{35}Al_{21.67}Cr_{21.67}Fe_{21.67}$ HEA is superior to many alloys.

2. Material and methods

Alloy ingots of the $Ni_{35}Al_{21.67}Cr_{21.67}Fe_{21.67}$ alloy were processed by arc melting and solidified in water-cooled copper crucibles under argon protection. The purity of Ni, Fe, Cr, Al raw materials is higher than 99.9% (wt, %) . The ingot was melted for five times. All the experimental samples were obtained by wire-electrode cutting. The crystal structure was characterized by a Cu Kα radiation D/max-rB X-ray diffractometer and manipulated at 45 kV and 40 mA. The range of the test angle is 20° to –100°. To observe the microstructure and analysis the composition distribution, the sample was etched using the aqua with 50% of solution concentration ($HCl:HNO_3:H_2O$ = 3:1:4). Scanning electron microscope (SEM) was used to observe the microstructure and energy dispersive spectrometry (EDS) was used to analysis the composition distribution. High magnification microstructures were observed by transmission electron microscopy (Tecnai G2 F30) operating at 300 kV. TEM specimens were made by mechanical grinding until the sample reaches the size of Φ3 mm × 60 μm. After grinding, the sample was prepared by twin-jet electropolishing device under the

* Corresponding author at: School of Materials Science and Engineering, Harbin Institute of Technology, Harbin 15001, China.
E-mail address: libs@hit.edu.cn (B. Li).

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environment of 10% perchloric acid solution. The shape of the mechanical property specimens were cylinders (Φ3 mm × 5 mm) and Instron 5569 testing machine was used to test the compressive properties with the strain rate of $1 \times 10^{-3}\,s^{-1}$ at room temperature.

3. Results and discussion

The X-ray diffraction pattern of the $Ni_{35}Al_{21.67}Cr_{21.67}Fe_{21.67}$ HEA are shown in Fig. 1(a). Result shows disordered BCC phase and B2 phase (ordered BCC phase) are detected in the alloy. This is mainly related to the high content of Al in the alloy. With the increase of Al content, the lattice strain will increase because of its large atomic radius. The BCC phase, which don't have a close-packed structure, will tend to form for the sake of reducing the lattice distortion [6]. Furthermore, it shows high intensity diffraction peak in {100}, which indicates the high fraction of B2 phase. Fig. 1(b) shows the microstructures of the $Ni_{35}Al_{21.67}Cr_{21.67}Fe_{21.67}$ HEA at as-cast state. The microstructure is composed of sunflower-like morphologies, which are divided into the 'core' and 'petal' region. A radiating structure can be found in 'petal'. The section morphology of the radiating structure is reticular structure as Fig. 1(c) shows. In 'core' region, spherical precipitated phase with the size 200–300 nm are uniform distributed in matrix, as Fig. 1(d) shows.

Fig. 2 shows the elemental distribution maps of "sunflower-like" microstructure, where Ni and Al are enriched in the matrix while Fe and Cr are concentrated in the precipitated phase in 'core' region. Guo et al. [6] proved that B2 phase is Ni-Al riched and disordered BCC is Fe-Cr riched. Therefore, we can confirm that B2 phase forms the continuous matrix with the spherical nano-precipitated phase (200 nm–300 nm) in "core" region, which is disordered BCC phase. Fig. 3(b) shows the diffraction spots of two phases. It indicates that striped B2 phases are inlaid in disordered BCC matrix.

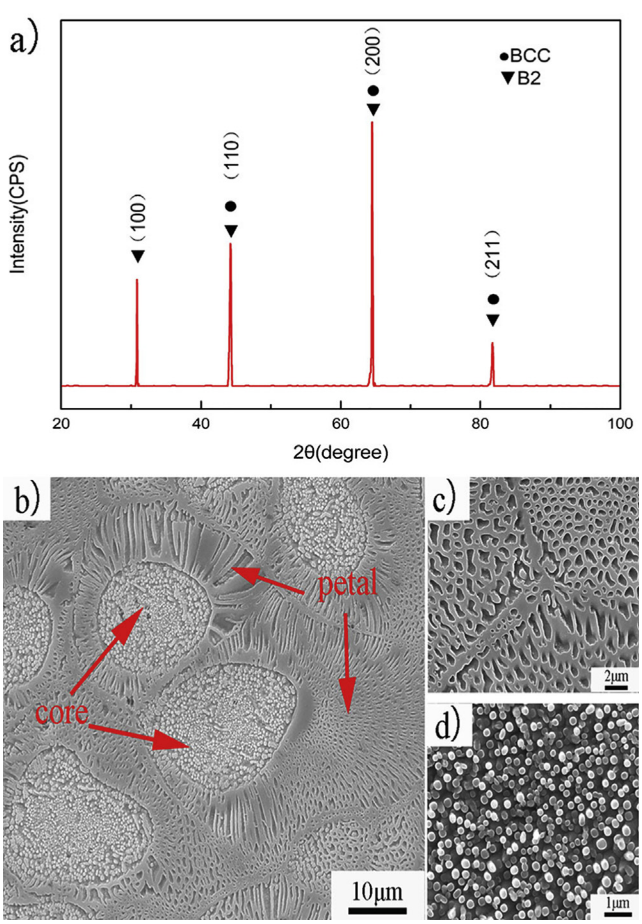

Fig. 1. (a) The XRD patterns of the $Ni_{35}Al_{21.67}Cr_{21.67}Fe_{21.67}$ high-entropy alloy. (b), (c), (–d) SEM morphologies of $Ni_{35}Al_{21.67}Cr_{21.67}Fe_{21.67}$ HEA.

Fig. 3(a) presents the compressive properties of the $Ni_{35}Al_{21.67}Cr_{21.67}Fe_{21.67}$ HEA. The compressive test showed that the alloy possesses a yield strength of 1471 MPa, a compressive strength of 3541.88 MPa, and a compression rate of 40% in engineering stress-strain condition at room temperature. In the true stress-strain condition, these values were transformed to 1372 MPa, 2110 MPa, and 51%, respectively. As listed in Table 1, the comprehensive compressive properties of the $Ni_{35}Al_{21.67}Cr_{21.67}Fe_{21.67}$ HEA is better than other high-entropy alloys with more principal elements, conventional high-strength stainless steels and even amorphous alloys.

In fact, B2 phase is (Ni,Al)-riched intermetallic compound (IMC). IMCs are easiliy formed in many HEA systerms. If the mixing enthalpy has greater influences on the total Gibbs free energy than the configurational entropy, it will tend to form IMCs. The configurational entropy of the $Ni_{35}Al_{21.67}Cr_{21.67}Fe_{21.67}$ HEA is low (ΔS_{conf} = 11.31 J/K·mol) and the mixing enthalpy is more negative (ΔH_{mix} = −13.53 KJkJ/mol). The contribution of mixing enthalpy becomes dominant, therefore the IMC forms. The ability of forming compounds between each constituent elements decides the type of IMCs [7]. It is reasonable to infer that Ni and Al formed (Ni,Al)-rich IMC firstly during the solidification because Ni and Al have the the greater negative formation enthalpy (−22 KJkJ/mol) than other elements combination. As a result of high formation temperature, (Ni, Al)-rich B2 phase formed firstly as the matrix phase in 'core' region. In 'petal' region, the formation of striped B2 phase can be explained by phase wetting. It has been reported that second solid phase layers will form along the grain boundary when second phase can wet primary phase completely. And particles will appear when partial wetting happens [13,14]. In 'petal' region, it is visible that the disordered BCC phase is perfectly wetted by B2 phase, just as Fig. 2 shows. Therefore, striped B2 phase (can be treated as a thicker layer) form instead of particle. The (Fe,Cr)-rich particles formed via a spinodal transformation from the primary B2 phase.

The outstanding mechanical properties can be put down to the high content B2 phase, which is considered as a high strength phase. B2 phase forms high strength matrix which provides primary strength in "core" region. Moreover, dislocations can be found around the B2 phase in "petal" region, as Fig. 3(b) shows. It suggests that striped B2 phase in "petal" region acts as strong obstacles to the dislocation motion. It indicates that dislocation motion can be occured in continuous disordered BCC matrix, which provides ductility.

4. Conclusions

The present study has investigated the microstructure and properties of $Ni_{35}Al_{21.67}Cr_{21.67}Fe_{21.67}$ HEA. We successfully designed a new $Ni_{35}Al_{21.67}Cr_{21.67}Fe_{21.67}$ HEA with an excellent comprehensive mechanical properties. The alloy consists of Fe-Cr riched disordered BCC phase and Ni-Al riched ordered BCC phase (B2). An unconventional 'sunflower-like' microstructure appeared in this alloy, where B2 phase forms the continuous matrix with the disordered BCC spherical precipitated phase in "core" and striped B2 phase in disordered BCC matrix in "petal". The alloy achieves excellent compressive yield strength of 1471 MPa, compressive strength of 3541 MPa and a compression rate of 40% in as-cast condition at room temperature. The high strength of the $Ni_{35}Al_{21.67}Cr_{21.67}Fe_{21.67}$ HEA is due to the hard B2 phase, which provides primary strength and prevents dislocation from moving.