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ARTICLE

# Microstructure and Properties of AlCoCrFeNiB$_x$($x$=0, 0.1, 0.25, 0.5, 0.75, 1.0) High Entropy Alloys

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**Abstract:** The influences of B element on the microstructure and properties of AlCoCrFeNiB$_x$ ($x$=0, 0.1, 0.25, 0.5, 0.75, 1.0, mol ratio) high entropy alloys were investigated. The AlCoCrFeNi high entropy alloy exhibits equiaxed grain morphology, and then turns to dendritic structures when B content $x$=0.1. The spinodal decomposition microstructure can be clearly observed in equiaxed grains. When $x$>0.1, both of the dendrite and the spinodal decomposition microstructure gradually disappear, but much borides form instead. The transformation is attributed to the high negative mixing enthalpy of Cr-B and Co-B. The microstructures of AlCoCrFeNiB$_x$ high entropy alloys change from B2+bcc structures to B2+bcc+fcc structures, and finally formed B2+bcc+fcc and borides mixing structures with the increased B elements. The hardness HV declines from 4860 to 4607 MPa, then rises to 6157 MPa with the addition of B element. The lowest hardness value is obtained when $x$=0.1. The compressive fracture strength shows a distinct decrease with B addition. The maximum compression strength is 2227 MPa when $x$=0.25. But when $x$ reaches 0.75, the samples fracture during the elastic deformation due to the formation of hard and brittle borides. The coercive forces and the specific saturation magnetizations of the alloys decrease as the contents of B element increase. The decreasing coercive forces show a better soft magnetic behavior.

**Key words:** high-entropy alloys; microstructures; microhardness; compressive properties; magnetic behavior

Conventional alloy-design strategy is mainly based on one or two elements as the principal components, while other elements are regarded as minor components to improve the properties[1,2]. Differing from the conventional one, a new alloy-design strategy was proposed by Cantor et al[3] and Yeh et al[4], which was called high-entropy alloys (HEAs) or multi-principal element alloys. At present, HEAs have become a new research hotspot in the field of materials science[5-7].

A lot of researches about the effects of elemental additions in the AlCoCrFeNi alloy system have been done, for example, AlCoCrFeNiTi$_x$[8], AlCoCrFeNiMo$_x$[9], AlCoCrFeNiSi$_x$[10], AlCoCrFeNiNb$_x$[11], AlCoCrFeNiC$_x$[12], AlCoCrFeNiV$_x$[13] alloys and so on. However, in the AlCoCrFeNi alloy system, B element additions were little studied[14].

In the present study, B was selected based on the following several reasons: firstly, B and many elements have very negative mixing enthalpies (the values of B and Co, B and Cr, B and Fe, B and Ni atomic pairs are −24, −31, −26 and −24 kJ/mol, respectively)[15,16], which would lead to the formation of borides, and the borides can improve the compression strength and wear resistance of alloys, such as CoCrCuFeNi-Al0.5B$_x$ alloys[17], AlTiNiMnB$_x$ alloys[18], Al0.5CoCrCuFeNiB$_x$ alloys[14] and FeCoNiCrCuTiMoAlSiB0.5 alloy[19]; secondly, the atomic radius of B element is much smaller than that of other elements, which can make B atoms easy to diffuse during solidification. And diffusion is a key factor of controlling phase transition[20]. The transition of the morphologies and microstructure is crucial to mechanical properties. Moreover, some alloys containing B element may possess good soft magnetic property[21].Therefore, in this paper, the effects of B element from $x$=0 to $x$=1.0 in molar fraction on the microstructures and properties of the AlCoCrFeNiB$_x$ HEAs were investigated in detail.

## 1 Experiment

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The HEAs ingots of AlCoCrFeNiB$_x$ ($x$=0, 0.1, 0.25, 0.50, 0.75, 1.0, denoted by B0, B0.1, B0.25, B0.5, B0.75 and B1.0, respectively) were prepared by vacuum arc furnace under a Ti-gettered high-purity argon atmosphere. The purity of all the raw materials (Al, Co, Cr, Fe, Ni, B) was above 99.9 wt%. The alloys were flipped and remelted at least five times. The button ingots ~30 g were directly solidified in a water-cooled cold copper hearth. X-ray diffractometer (XRD, Shimadzu XRD-6000) with Cu Kα radiation was used for the phase analysis, and scanning angle ranged from 20° to 100° at a speed of 4(°)/min. Microstructures and phase compositions were observed by a scanning electron microscope with energy dispersive spectrometry (SEM, Zeiss supra55). The samples for the tests of compressive properties was made into $\Phi 5$ mm×10 mm, prepared from as-cast alloy button. The tests were conducted at a strain rate of $1.0\times10^{-3}$/s. Vickers microhardness tester model (MH-60) with 1000 g for 15 s was used for hardness measurements. Five measurements were made for each sample to obtain the average experimental data. The magnetization curves were measured with JDM-13T vibrating sample magnetometer.

## 2 Results and Discussion

### 2.1 X-ray diffraction analysis

Fig.1 shows the XRD patterns of the AlCoCrFeNiB$_x$ HEAs. When $x$=0, the alloy exhibits a B2 and bcc mixing structure. But when $x$ exceeds 0.1, fcc phases begin to appear. And the intensities of fcc diffraction peaks increase as B contents increase, until B0.25. From B0.25, the intensities of both bcc and fcc phases begin to decrease as a result of the formation of borides, and distinct diffraction peaks of (Cr, Co)-borides phase could also be observed from Fig.1. Combined with the XRD diffraction patterns, a conclusion can be obtained that both Cr-borides and Co-borides are formed during $x$=0.1~0.25.

### 2.2 Microstructure and characterization

Fig.2 and Fig.3 display the SEM images of the microstructures of the AlCoCrFeNiB$_x$ HEAs. The morphologies of AlCoCrFeNiB$_x$ HEAs are sensitive to alloying contents. B0 exhibits a typical equiaxed grain morphology, accompanying with obvious intragranular segregation, as shown in Fig.3a. The bright segregation area and the dark segregation area are denoted as A and B, respectively. The typical spiondal decomposition microstructure can be observed in the interior of the grains. According to the previous research[22], the bright section and the dark section of interconnected microstructure are composed of (Fe, Co, Cr)-rich element and (Al, Ni)-rich element whereas section A has a higher amount of Al and Ni than section B.

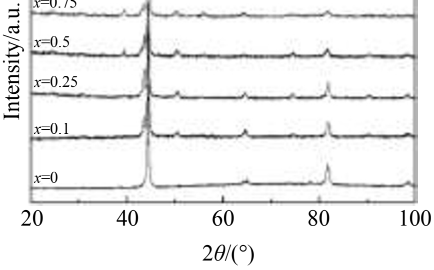

Fig.1 XRD patterns of the AlCoCrFeNiB$_x$ HEAs ($x$=0, 0.1, 0.25, 0.5, 0.75, 1.0)

When $x$=0.1, the alloy exhibits dendrite structures. The atomic radius of B element is far smaller than that of Al, Co, Cr, Fe and Ni elements, which may lead to the large strain energy of the crystal lattice when B atoms are further added. During the solidification, the B atoms are discharged in front of the solid-liquid surface to reduce the strain energy, which facilitates the constitutional undercooling that is beneficial to the formation of dendrites. The dendritic region is a mixture of rod-like and interlaced spinodal decomposition structures, marked by DA and DB, respectively. Their spinodal decomposition structure is composed of (Fe, Co, Cr)-rich elements and (Ni, Al)-rich elements, respectively[23]. When $x$=0.25, the spinodal decomposition structures disappear completely. The change can be due to the high negative enthalpy of Cr-B, Co-B and Fe-B, and the formation of borides. According to the previous studies, the spinodal decomposition in AlCoCrFeNi HEAs system can be divided into two parts, one is rich in (Al,Ni), and the other is rich in (Fe, Co, Cr). But with B contents increasing, Cr and Co atoms tend to integrate with B to form borides, which breaks the composition of spinodal decomposition. As a result, the spinodal decomposition inside the grains disappears. From $x$=0.5, the needle-like structures appear in the region rich in (Al, Ni), as seen in Fig.3c. The interdendritic regions are mainly composed of both B and Cr elements. The reason is that Cr-B has a much lower mixing enthalpy (–31 kJ/mol) than among other elements[23,24], which leads to the Cr and B atoms segregating together. Moreover, the interdendritic rod-like and long strips precipitates grow up, and connect together as B contents increase, as shown in Fig.3. When $x$ exceeds 0.5, the interdendritic regions still consist of two parts, one is boride phase rich in Cr-B and Co-B, marked as S1, but the other part is rich-(Fe, Co, Cr) elements with the fcc solid solution structures, marked as S2. The interdendritic region of sample B1.0 can be divided into three parts. Combining the XRD patterns and EDS results (as seen in Table 1), it could be concluded that S1 and S3 are mainly composed of Cr borides and Co borides, respectively. And the S4 is rich-(Fe, Co) elements with bcc solid solution structures.

With the incorporation of B element, the grain size is refined obviously, such as sample B0, 200~300 μm, sample B0.1, 20~50 μm, until B0.75 and B1.0, 5~10 μm, as seen in Fig.2.