Effect of Boron on Microstructure and Hardness Properties of High Entropy Alloys

İrem Burcu Algan[1], Muhammet Nasuh Arık[2], Şükrü Talaş[3], Adem Kurt[4], Fatih Akkurt [5]

[1] Department of Metallurgical and Materials Engineering, Faculty of Technology, Gazi University (irembalgan@gazi.edu.tr)

[2] BOREN (mnarik@boren.gov.tr)

[3] Department of Metallurgical and Materials Engineering, Faculty of Technology, Afyon Kocatepe University (stalas@aku.edu.tr)

[4] Department of Metallurgical and Materials Engineering, Faculty of Technology, Gazi University (ademkurt@gazi.edu.tr)

[5] BOREN (fatih@boren.gov.tr)

ABSTRACT

High entropy alloys (HEAs) are new class of metallic alloys having equiatomic or near equiatomic compositions. Unlike the traditional metallic alloys, HEAs contain several principal elements thus, exhibit significant microstructure and mechanical properties. Microstructure and hardness properties of equiatomic FeNiCoCrCu high entropy alloys with different boron content (x= 0-2 at. %) were studied in the present work. HEAs were prepared from elemental powders w of 99.95% purity by arc melting technique. After arc melting, the microstructure of HEAs were investigated using optical microscopy, scanning electron microscopy (SEM), X-ray diffraction (XRD), and Vickers micro hardness.

INTRODUCTION

In recent years, high-entropy alloys (HEAs) have been broadly studied because of their potential at replacing current commercial alloys [1]. Unlike the traditional alloys, HEAs have at least five principal elements with concentrations 5 to 35 at. %. As a result of their higher configuration entropy, HEAs may form single phase FCC, BCC, HCP or mixed phases in the microstructure [2, 3]. Their original microstructures associated with remarkable properties such as thermal stability, high strength and hardness, excellent corrosion resistance, fracture, and wear resistance [1, 2, 4, 5].

In last decade, Al-Cr-Co-Fe-Ni, Co-Cr-Fe-Mn-Ni and Al-Cr-Co-Cu-Fe-Ni HEAs widely studied since 2004 because transition metals like Fe, Ni, Co, and Cu have good thermomechanical properties, relatively low costs, similar atomic size and electronegativity. All these properties of the transition elements ease solid-solution formation in microstructure [6].

HEAs can be strengthened by adding other alloying elements as in traditional alloys [7]. Zhang et al. added a rare-earth element, Gd, in CoCrCuFeNi and found that with increasing rate of Gd in this HEA the fracture strength was increased [8]. In another study, Wong et al. added Mn in $Al_{0,3}$CoCrFeNi to increase yield and tensile strength [9].

Interstitial elements such as carbon and boron are used for phase transformation and solid solution strengthening in traditional alloys [10]. During solidification by virtue of B which has smaller atomic radius, the phase transition in microstructure is controlled by diffusion and it occurs more easily [11].

Based on the approach presented in [8-11], the purpose of this study is to investigate the influence of boron on the microstructure and hardness properties of high entropy FeNiCoCrCu alloy.

METHODS

FeNiCoCrCu and boron doped (0-2 at. %) HEAs ingots are prepared by high purity raw elements (at least 99.99 wt. %) with vacuum arc melting under argon atmosphere. Each alloy is melted three times in order to provide chemical homogeneity in microstructure.

Specimens cut from ingots etched for optical microstructure characterization. X-ray diffractometer (XRD) and scanning electron microscopy (SEM) were used to analyze the microstructures and chemical compositions of the samples. Micro hardness tests were performed with the load of 0.49 kN (HV 0.5).

RESULTS AND DISCUSSION

As HEAs produced by arc melting or induction melting which are solid state production techniques, the microstructure is dendritic [4]. Microstructures of FeNiCoCrCuBx HEAs, given in Figure 1, were attained by optical microscopy. Dendritic and inter dendritic regions can be seen through 0-2 at. % B. When the B content is at 1 at. %, (HEA-1 figure 1c-d), the dendrite size is decreased and a thinner structure was observed in the microstructure.

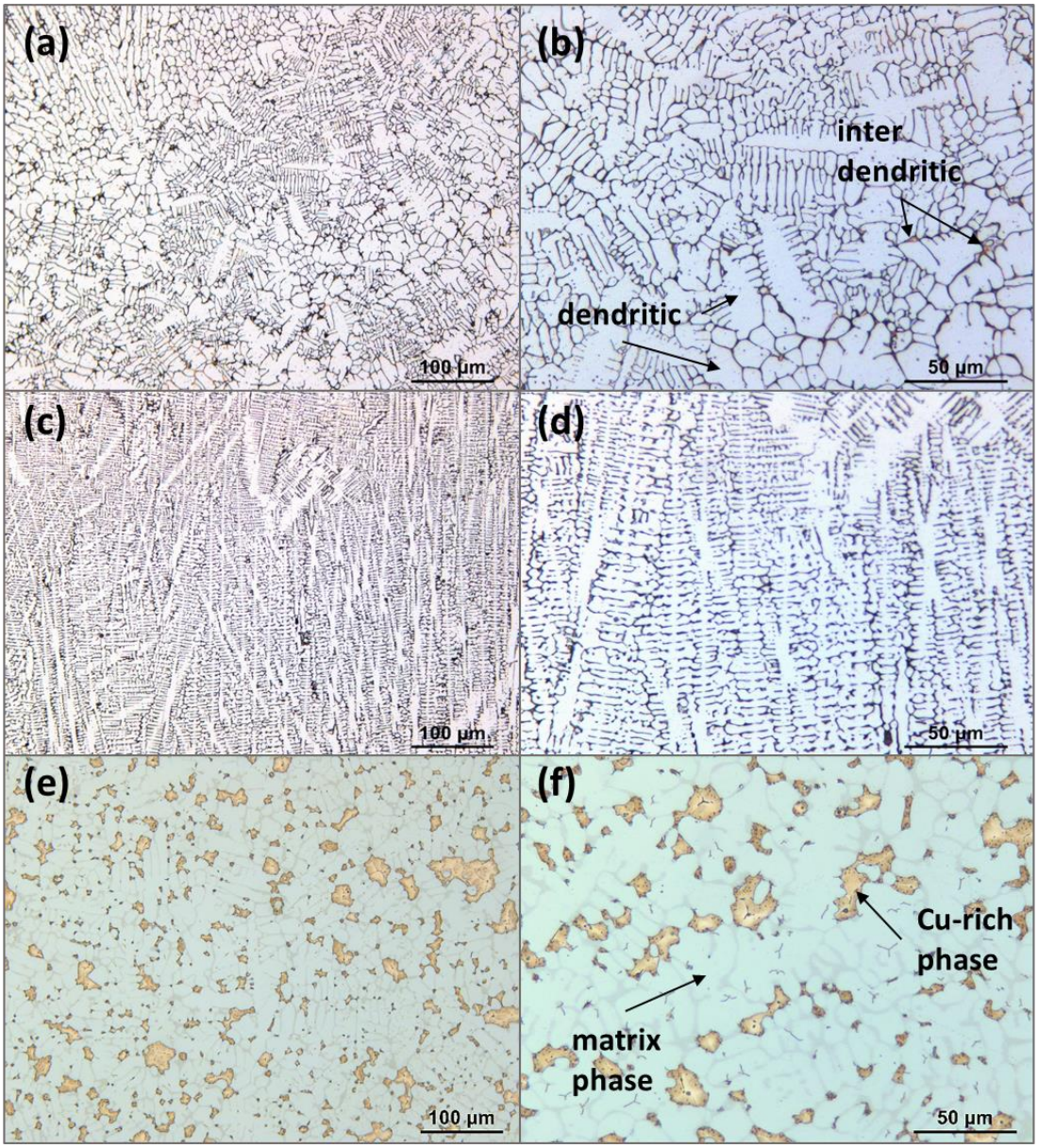


Fig. 1: The optical micrographs of 200 X and 500 X; (a) and (b) are HEA-0, (b) and (c) are HEA-1, and (e) and (f) are HEA-2

The SEM images and the results of EDS analysis are given in Figure 2 and Table 1. The results show that, Fe, Ni, Cr, and Co elements relatively equivalent distributed in dendrite regions of alloy whereas the compositions of inter-dendrite regions are Cu-rich. The reason of this dissimilarity between dendrite and inter-dendrite regions has been reported in [12] that Cu element has large positive mixing enthalpy and thus impulsive interactions occurred between Cu and other alloying elements. These impulsive interactions give rise to two-step solidification. Firstly, (Fe-Ni-Co-Cr)-rich phase nucleated from liquid phase and then Cu-rich phase occurred in inter-dendritic region with peritectic reaction (liquid + solid 1→ solid 2). On the other hand, when B content increase to 2 at. %, the size of Cu-rich inter-dendritic phase in microstructure of HEA-2 increased. Average size of Cu-rich phases is approximately 25 μm for HEA-2.

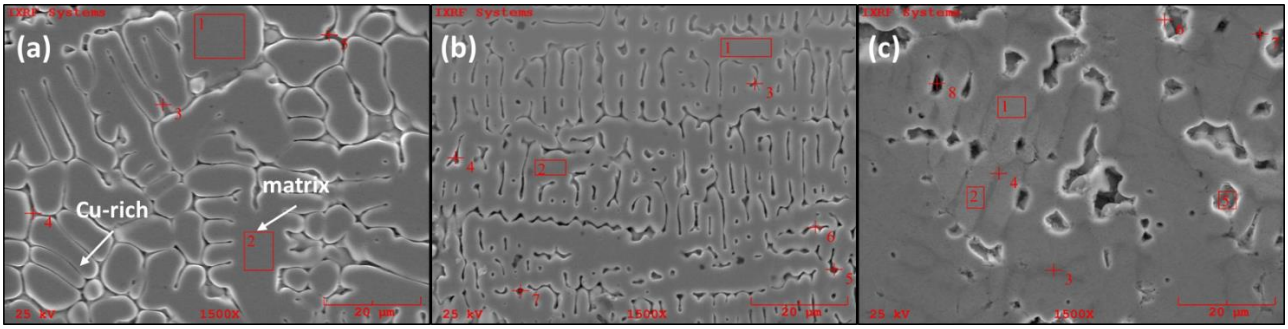


Fig. 2: SEM images of (a) HEA-0, (b) HEA-1 and (c) HEA-2

Table 1. Chemical compositions of $FeNiCoCrCuB_x$ HEAs

Element %	HEA-0 Points		HEA-1 Points		HEA-2 Points		
	1-2 dendrite	3-4-5 inter dendrite	1-2 dendrite	3-4-5-6 inter dendrite	1-2 dendrite	3-4 inter dendrite	5-6-7-8 Cu- rich
Fe	21-23	15-19	20-21	15-22	20-22	18-20	19-21
Ni	20-22	21-24	19-21	14-21	21-23	22-24	18-24
Co	24-26	14-20	22-24	13-23	21-23	21-27	22-24
Cr	20-22	16-22	20-23	16-24	20-22	23-25	23-31
Cu	9-12	15-34	12-14	13-45	10-12	7-12	9-12

Boron content and distribution in microstructure cannot be detected by EDS analysis due to small atomic weight of boron. For this reason, our future work will involve wavelength dispersive spectrometry (WDS) analysis.

XRD results of HEAs are shown in Fig. 3. It can be clearly seen that the crystal structures have two type of FCC phase: one is Cu-rich and the other is (Fe-Ni-Co-Cr)-rich FCC phase which is identified by the peaks. Previous studies in literature indicate that while Cu, Ni, and Co elements are FCC

structure and stabilize FCC; Fe and Co are BCC and stabilize BCC structure in HEAs [13]. In contrast to literature, no BCC phase were seen in XRD patterns in this study.

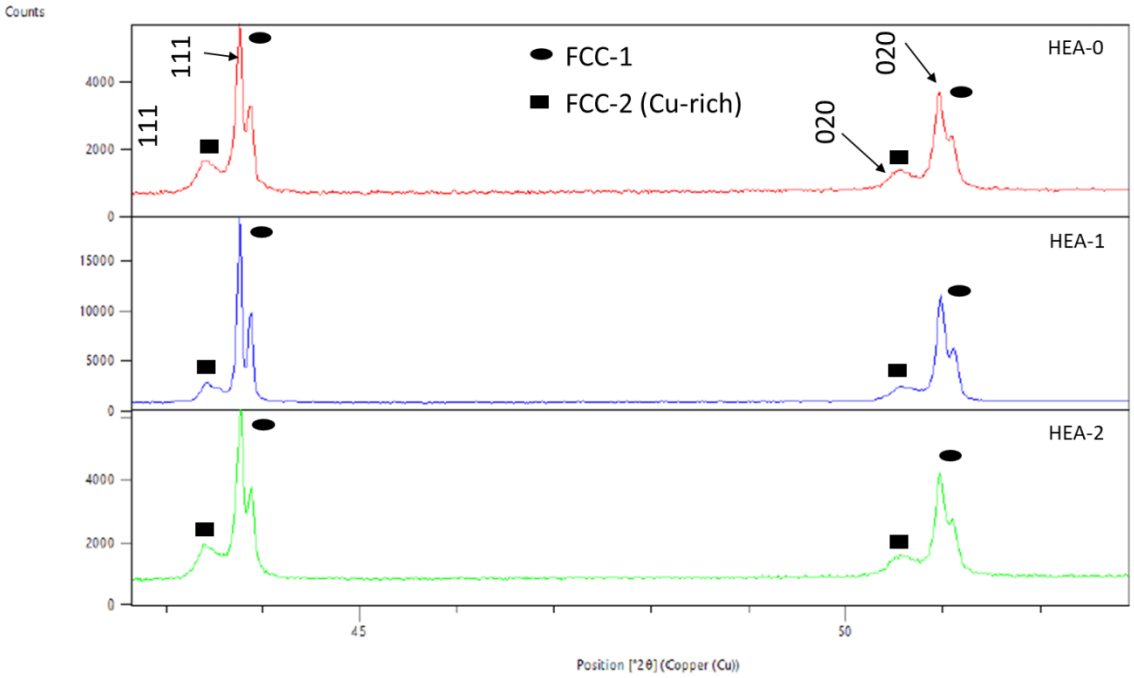


Fig. 3: XRD patterns of $FeNiCoCrCuB_x$ HEAs

The micro hardness results are given in Fig. 4. The results show that, with the increasing B content in HEA, the hardness values was increased. It can be seen that the maximum hardness values are 182 HV, 192 HV and 257 HV for HEAs 0-2, respectively. The hardness values increased as a result of solid solution strengthening of B which is interstitial atom and dispersed in microstructure [10, 14, 15].

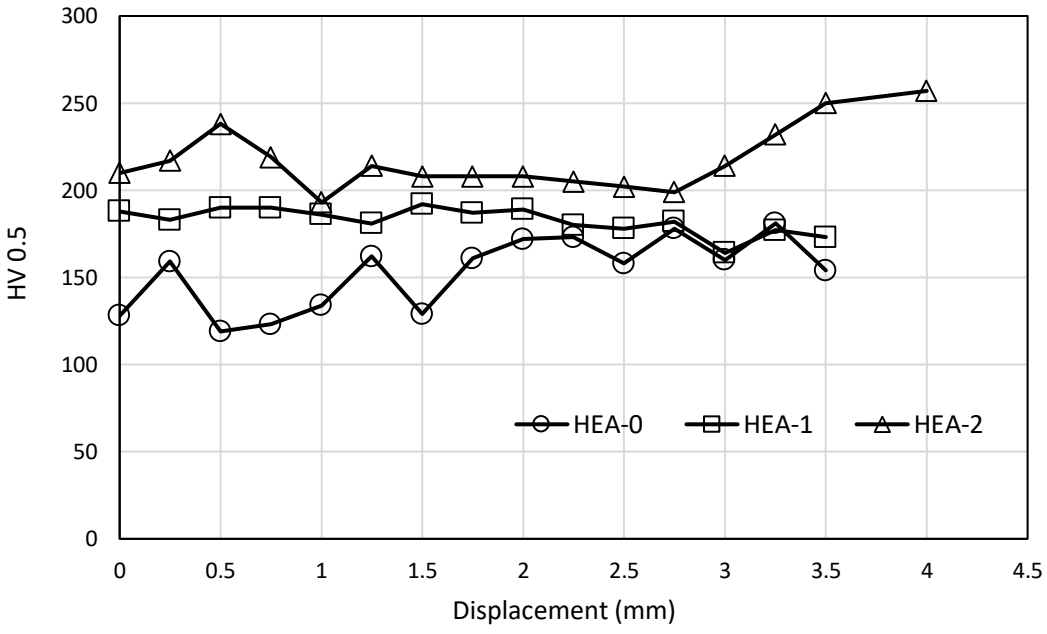


Fig. 4: Micro hardness values of $FeNiCoCrCuB_x$ HEAs

CONCLUSIONS

The aim of this study is to investigate the effects of boron on the microstructure and hardness properties of $FeNiCoCrCuB_x$ (x=0-2) HEAs. The following conclusions could be drawn:

- Cu-rich inter-dendritic phase and (Fe-Ni-Co-Cr) - rich dendritic phase occurred in microstructure as a result of liquid phase separation.
- The size of Cu-rich phase increased with the increasing B content.
- Due to small radius, B content of HEAs cannot be detected by EDS and thus WDS analysis will be performed in future work.
- XRD results show that Cu-rich and (Fe-Ni-Co-Cr)-rich FCC phases occurred in microstructure because of FCC stabilizer elements like Cu, Ni and Co.
- Because of solid solution strengthening of boron, micro hardness values of HEAs increased with the increasing of B content.

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