PRODUCTION OF Fe-Co-Cr-Ni-Al HEAS VIA ECAS AND EFFECTS OF HEAT TREATMENT ON SINTERED ALLOY MICROSTRUCTURE

IPEK Mediha, YENER Tuba, ZEYTIN Sakin

Sakarya University, Engineering Faculty, Department of Metallurgy and Materials Engineering, Esentepe Campus, 54187, Adapazari, Sakarya, Turkey
tcerezci@sakarya.edu.tr

Abstract

In this study, it was investigated fabrication of high entropy alloy containing 25 wt.% Fe, 25 wt.% Co, 25 wt.% Cr, 15 wt.% Ni, 10 wt.% Al via Electric Current Activated (Assisted) Sintering (ECAS) process and effect of heat treatment (annealing) on sintering samples. Heat treatments were performed in open atmospheric furnace at 900, 1000 °C for 10 hours. Microstructures of sintered and heat treated samples were investigated by optic and scanning electron microscopes, phases in samples were analyzed by XRD and their hardness was measured by Vickers hardness tester ranged from 291 to 977 HV.

Keywords: High entropy alloys, FeCoCrNiAl alloy, ECAS, heat treatment, hardness

1. INTRODUCTION

High-entropy alloys (HEAs) (some other names are multi-principal-element alloys, equi-molar alloys, equi-atomic ratio alloys, substitutional alloys, and multi-component alloys) emerge as a new research frontier in materials science and engineering [1, 2]. Traditional alloys are typically composed of one principal element, with minor additions of other elements to tailor the microstructures and properties (such as iron based, aluminum based, and nickel based super alloys). HEAs differentiate with conventional alloys in that they have at least four principal elements, instead of one or two elements. Moreover, HEA is defined as an alloy containing n principal elements, where n is between 5 and 13, and the molar ratio of each element ranges from 5 to 35 at.% in an equimolar or near equimolar ratio with a small difference in atomic radius (<15%) [3- 5]. Due to the multi-principal-element composition, HEAs have more pronounced entropic effects than conventional alloys, i.e. “high-entropy effect” [3, 6]. The high-entropy effect states that the higher mixing entropy (mainly configurational) in HEAs lowers the free energy of solid solution phases and facilitates their formation, particularly at higher temperatures. The number of phases present in HEAs can be evidently reduced because of enhanced mutual solubility among constituent elements. According to Gibbs free energy ($G=H-TS$, where G is the Gibbs free energy, H is enthalpy, T is temperature, and S is entropy), entropy can stabilize a phase with higher entropy, provided that temperature is sufficiently high. As a consequence, HEAs often possess simple solid-solutions or amorphous structure rather than intermetallics and exhibit high hardness, excellent strength as well as promising resistances to wear, oxidation and corrosion. To synthesize methods used for high entropy alloys are generally arc melting, mechanical alloying followed by isostatic pressing and surface coating (plasma spray and laser coating) [3, 9, 10]. The objective of the present work is to fabricate high entropy alloy containing Fe-Co-Cr-Ni-Al elements via Electric Current Activated (Assisted) Sintering (ECAS) process which less used method for producing HEAs and to investigate effect of heat treatment (annealed) on microstructure and mechanical properties of sintered samples [6-10].

2. EXPERIMENTAL DETAILS

The starting materials are Fe-Co-Cr-Ni-Al elemental powders with high purity (99 wt.%) and particle size of ~45 μm (-325 mesh). 25 wt.% Fe, 25 wt.% Co, 25 wt.% Cr, 15 wt.% Ni, 10 wt.% Al (23 Fe, 21 Co, 24 Cr, 13 Ni, 19 Al in atomic percent) containing powders are ball milled 4 h then cold-pressed before sintering to form a cylindrical compact under a uniaxial pressure of 200 MPa. The production of HEAs is performed via electric current activated sintering technique in an open atmosphere with a current of 2500 A for 150 s. After sintering, sintered samples are annealed in an open atmospheric furnace at 900 and 1000 °C for 10 h. Phase analysis of sintered and heat treated samples are performed by XRD analysis technique using Cu Kα radiation with a wave length of 15.418 nm over a 2θ range of $10° \leq 2\,\theta \leq 90°$. The microstructures of the products are examined by means of scanning electron microscopy with energy dispersive spectroscopy (SEM-EDS). The microhardness of polished specimens is measured by using Vickers indentation technique with a load of 50 g for 15 s.

3. RESULTS AND DISCUSSION

SEM micrographs of sintered, sintered and annealed for 10 h polished samples are given in **Figure 1**. Sintered sample micrograph is different than sintered-annealed samples and the microstructures of sintered annealed samples at different temperature are similar to each other. In sintered sample, the distribution of elements is inhomogeneous and especially Cr together with O concentrates individually different from the other constituents. With the annealing, the distributions of elements get homogenous (**Figures 2** and **3**). ECAS is very short time process and does not give opportunity for diffusion due to sluggish diffusion of elements in HEAs. At the same time, ECAS process temperature cannot reach required process temperature for single phase formation. Also the amount of dark gray areas which is rich in aluminum (Mark 7 in **Figure 2a**) decreases by the annealing heat treatment.

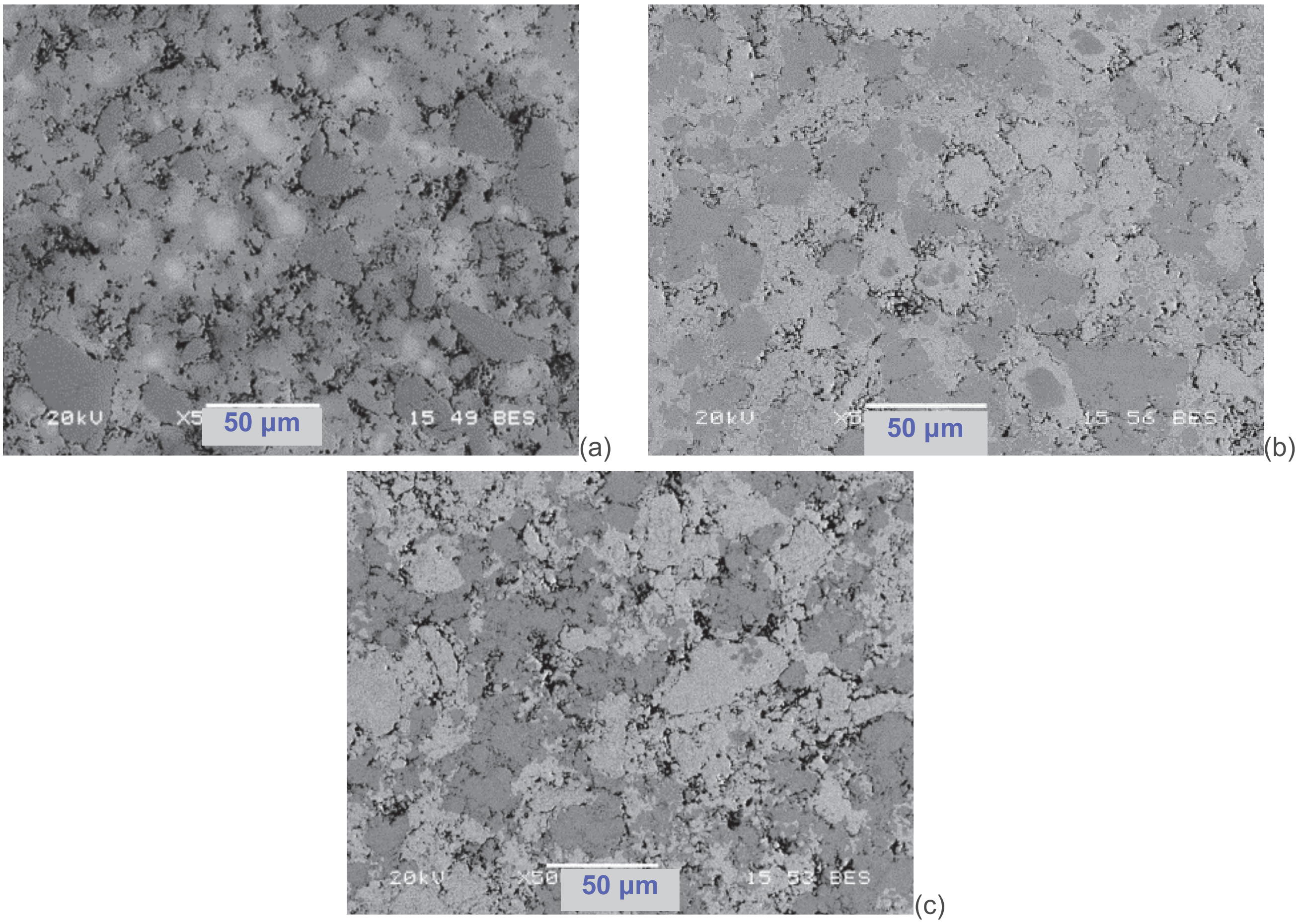
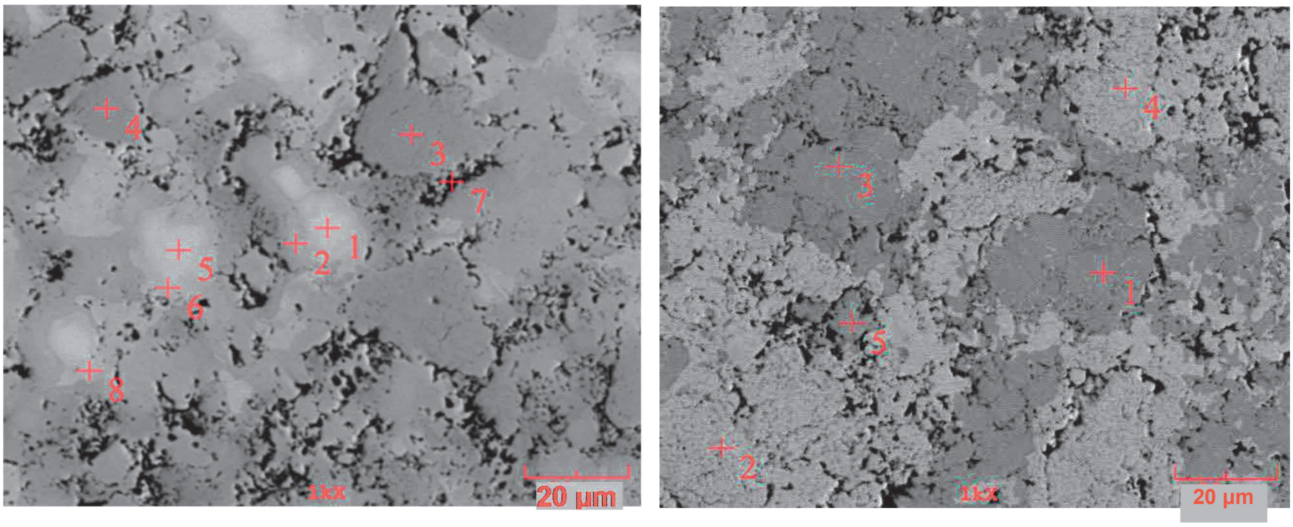


Figure 1 SEM micrographs of a) sintered, b) sintered and annealed at 900 °C and c) sintered and annealed at 1000 °C



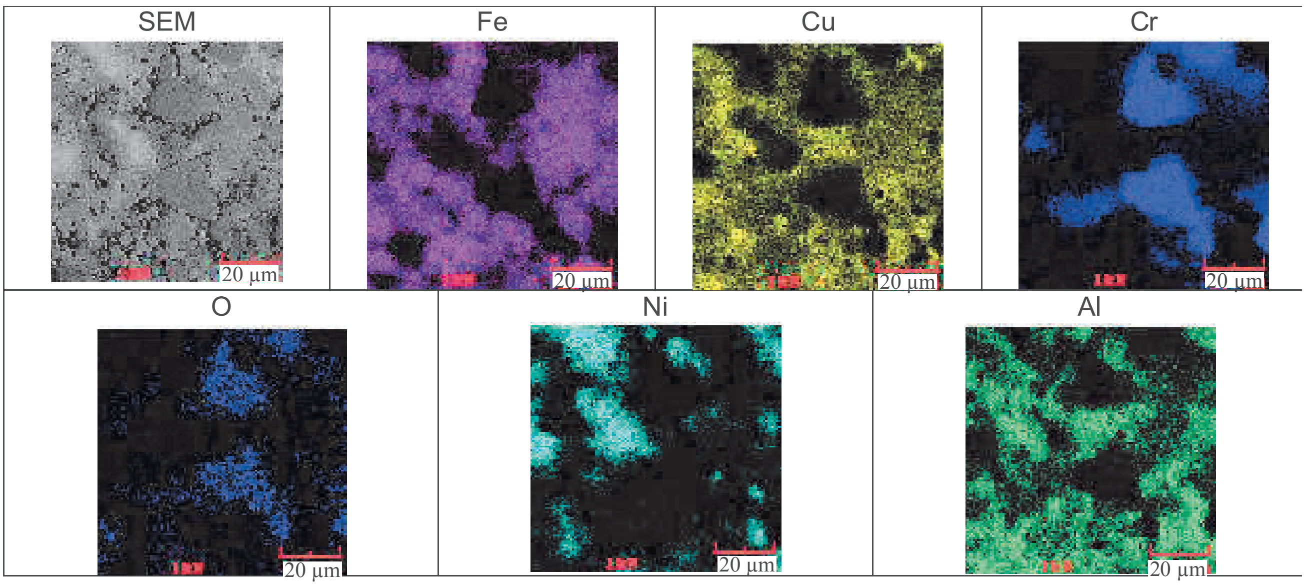
Marks	wt. %					
	O	Al	Cr	Fe	Co	Ni
1	-	0.82	1.29	1.13	0.25	**96.51**
2	-	**23.74**	0.95	2.75	5.55	**67.01**
3	12.56	0.24	**86.26**	0.34	0.31	0.29
4	13.46	0.15	**85.22**	0.82	0.31	0.04
5	-	0.43	1.53	2.19	0.78	**95.07**
6	5.34	-	6.49	9.43	**57.78**	**20.96**
7	4.89	**19.74**	7.70	**31.97**	**34.45**	1.25
8	7.30	**4.62**	0.62	**31.04**	**46.98**	**9.44**

(a)

Marks	wt. %					
	O	Al	Cr	Fe	Co	Ni
1	2.05	**21.62**	**8.78**	**16.66**	**27.70**	**23.19**
2	4.84	7.87	33.26	25.99	20.14	7.90
3	-	**23.63**	**7.71**	**16.51**	**27.43**	**24.72**
4	4.29	4.93	27.58	30.14	26.64	6.42
5	-	23.88	9.72	16.69	24.12	25.59

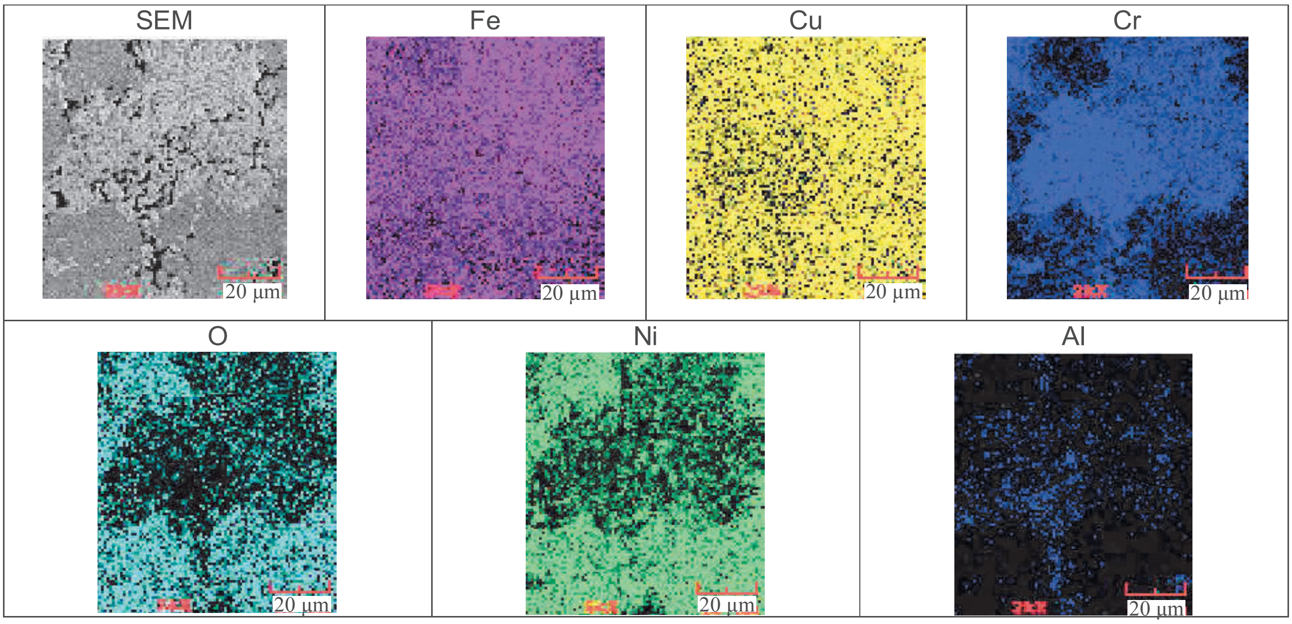
(b)

Figure 2 SEM-EDS micrographs and EDS point analysis of samples a) sintered, b) sintered and annealed at 1000 °C



(a)

Figure 3 SEM-EDS dot maps on samples a) sintered, b) sintered and annealed at 900 °C



(b)

Figure 3 SEM-EDS dot maps on samples a) sintered, b) sintered and annealed at 900 °C

The hardness of the all samples, sintered and sintered-annealed, varies in a wide range (**Table 1**) because of the different phase hardness being in HEAs. Also, with the annealing, the hardness range increase due to presence of NiCoCr (σ) and intermetallic phases [11].

Table 1 The microhardness value of HEAs (HV), 50 g load, 15 s

Sintered	**Sintered + annealed**	
	900 °C	**1000 °C**
291-533	406-903	376-977

XRD analysis (**Figure 4**) shows that sintered sample has Fe, Co, Cr, Ni elements and AlNi intermetallic phase. After the heat treatment, sintered-annealed samples at both temperatures (900 and 1000 °C) have similar phases and consist of dominantly NiCoCr phase and less amount of AlNi, $AlNi_3$, Fe_3Ni_2, Cr, Co, Fe phases. Many HEAs tend to form simple face-centered cubic (fcc) and/or body-centered cubic (bcc)-type solid solution phases which

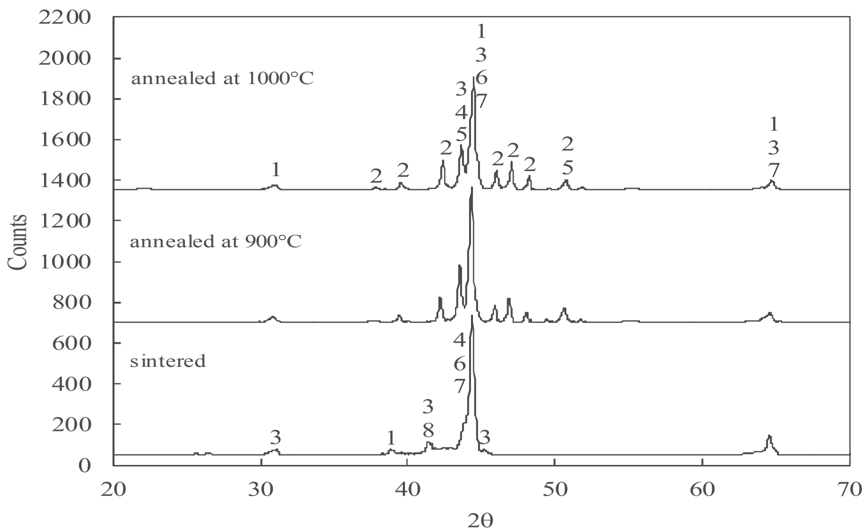


Figure 4 XRD patterns of sintered and sintered-annealed samples, 1: AlNi, 2: NiCoCr, 3: Cr, 4: $AlNi_3$, 5: Fe_3Ni_2, 6: Co, 7: Fe, 8: Ni

often attributed to their high entropies of mixing that are thought to suppress the formation of intermetallic compounds or other equilibrium phases. Configurational entropy alone is not sufficient to explain the formation of simple random solid solutions in cases where the atomic size differences between atoms are large or when there is a strong attraction between certain elements in the multicomponent alloy. In such cases, various intermetallic phases (or intermediate phases) and under some processing conditions even amorphous phases have been observed. Among the intermetallic phases, the crystal structures most commonly observed are B2, sigma (σ) phase, and Laves phases. In this study, with the heat treatment after the sintering, NiCoCr sigma (σ) phase and intermetallic phases (AlNi, $AlNi_3$, Fe_3Ni_2) are also observed. These phases are thought to be due to precipitation from the solid solutions in HEAs during slow cooling or thermal annealing of these alloys [1, 10].

ACKNOWLEDGEMENTS

The authors thank to Prof. Dr. Cuma Bindal for his notable support.

REFERENCES

[1] BUTLER, T. M., ALFANO, J. P., MARTENS, R. L., WEAVER, M. L. High-temperature oxidation behavior of Al-Co-Cr-Ni-(Fe or Si) multicomponent high-entropy alloys. *The Journal of the Minerals, Metals & Materials Society (TMS)*, 2015, vol. 67, no. 1, pp. 246-259.

[2] LI, D. Y., ZHANG, Y. The ultrahigh charpy impact toughness of forged AlxCoCrFeNi high entropy alloys at room and cryogenic temperatures. *Intermetallics*, 2016, vol. 70, pp. 24-28.

[3] CHEN, Z., CHEN, W., WU, B., CAO, X., LIU, L., FU, Z. Effects of Co and Ti on microstructure and mechanical behavior of Al0.75FeNiCrCo high entropy alloy prepared by mechanical alloying and spark plasma sintering. *Materials Science & Engineering A,* 2015, vol. 648, pp. 217-224.

[4] KAO, Y. F., CHENA, T. J., CHEN, S. K., YEH, J. W. Microstructure and mechanical property of as-cast, homogenized and deformed AlxCoCrFeNi ($0 \leq x \leq 2$) high-entropy alloys. *Journal of Alloys and Compounds*, 2009, vol. 488, no. 1, pp. 57-64.

[5] JI, W., WANG, W., WANG, H., ZHANG, J., WANG, Y., ZHANG, F., FU, Z. Alloying behavior and novel properties of CoCrFeNiMn high-entropy alloy fabricated by mechanical alloying and spark plasma sintering. *Intermetallics*, 2015, vol. 56, pp. 24-27.

[6] TSAI, M. H., YEH, J. W. High-Entropy Alloys: A Critical Review. *Materials Research Letters*, 2014, vol. 2, no. 3, pp. 107-123.

[7] GAO, M. C., YEH, J. W., LIAW, P. K., ZHANG, Y. *High-Entropy Alloys Fundamentals and Applications*. 1st ed. Switzerland: Springer, 2016.

[8] QIU, Xing-Wu Microstructure and properties of AlCrFeNiCoCu high entropy alloy prepared by powder metallurgy. *Journal of Alloys and Compounds*, 2013, vol. 555, pp. 246-249.

[9] ALANEME, K. K., BODUNRIN, M. O., OKE, S. R. Processing, alloy composition and phase transition effect on the mechanical and corrosion properties of high entropy alloys: a review. *Journal of Materials Research and Technology*, 2016, vol. 5, no. 4, pp. 384-393.

[10] SVENSSON, D. O. *High entropy alloys: Breakthrough materials for aero engine applications*. Chalmers University of Technology, Department of Materials and Manufacturing Technology, Gothenburg, Sweden 2015, Diploma work 2014.