EFFECT OF ALUMINIZING ON THE SURFACE PERFORMANCE OF ZR-ADDED COCRFENI HIGH-ENTROPY ALLOYS

Tuba YENER[1], Hasan KOTAN[2], Harun GUL[3]

[1]*Department of Metallurgy and Materials Engineering, Faculty of Engineering, Sakarya University, Sakarya, TÜRKİYE, tcerezci@sakarya.edu.tr*

[2]*Department of Metallurgy and Materials Engineering, Faculty of Engineering and Natural Sciences, Bursa Technical University Bursa, TÜRKİYE, hasan.kotan@btu.edu.tr*

[3]*Department of Metallurgy and Materials Engineering, Faculty of Engineering, Sakarya Applied Sciences, Sakarya TÜRKİYE, harungul@gmail.com*

https://doi.org/10.37904/metal.2026.5253

Abstract

Although CoCrFeNi high-entropy alloy (HEA) exhibits excellent ductility due to its face-centered cubic (FCC) crystal structure, its relatively low strength limits its applicability in certain industrial applications. To enhance its bulk mechanical performance, alloying additions can be introduced, while various surface modification techniques can be employed to improve its surface properties. In this study, CoCrFeNi HEA was produced by vacuum arc melting, followed by homogenization at 1150 °C for 24 h. Zr additions ranging from 1 to 4 wt.% were introduced to promote grain refinement and improve bulk hardness. The addition of Zr resulted in a moderate increase in hardness, from approximately 150 HV to 250 HV. To further enhance surface properties, a low-temperature aluminizing treatment was carried out at 700 °C for 4 h. This process led to the formation of Fe and Ni-based aluminide intermetallic phases on the surface, resulting in a significant increase in hardness from 250 HV to approximately 700 HV. In addition to Vickers hardness testing, scanning electron microscopy (SEM) and X-ray diffraction (XRD) analyses were performed for structural and microstructural characterizations.

Keywords: HEA, CoCrFeNi, Aluminizing, Hardness, Coating, Alloying

1. INTRODUCTION

A primary element serves as the foundation for most conventional alloys. To enhance the properties of this principal element, various alloying elements are added, forming an alloy family based on the base element. However, since the number of elements in the periodic table is finite, the number of possible alloy families is also inherently limited. What can we achieve if we design alloys using a wide variety of elements rather than relying on just one or two “base” elements? This innovative concept, first proposed in 1995, is known as a high-entropy alloy (HEA) [1], [2]. Alloys containing five or more principal elements are classified as high-entropy alloys (HEAs). In such alloys, the concentration of each primary element typically ranges between 5% and 35% [3]. Metallic materials are widely used across various fields today, depending on the required mechanical, physical, and chemical properties. These properties are directly linked to the internal structure of the materials; by introducing controlled modifications at the microstructural level, their performance can be significantly enhanced and their range of applications expanded [1], [4], [5].

Materials intended for service under demanding conditions, such as extreme temperatures, corrosive environments, wear, and mechanical loading, require continuous development and optimization. However, in material systems produced through conventional alloying methods, the limited number of alloying elements

and their restriction to low-concentration regions of phase diagrams represent one of the primary factors limiting further enhancement of their properties for advanced engineering applications [4]. The idea behind the term "high-entropy" is that these compositionally complex alloys' high mixing entropy can overcome the enthalpies of compound formation, favoring the formation of a single solid solution with body-centered cubic (BCC) and/or face-centered cubic (FCC) structures. Al, Cu, Mn, V, Ti, and Mo are added to the transition metals such as Co, Cr, Fe, and Ni in most reported HEA compositions. Their improved qualities make them viable options for structural and engineering applications when compared to traditional alloys. It is well known that mechanical qualities of HEAs can be further enhanced by reducing their grain sizes. For instance, arc-melting CoCrFeNi HEA was reported to have 141 HV hardness, but mechanical alloying of the same composition resulted in a nanocrystalline microstructure with 400 HV hardness. The CoCrFeNi HEA, which possesses a FCC structure, demonstrates outstanding ductility even at cryogenic temperatures. Nevertheless, its comparatively low strength limits its suitability for applications requiring an optimal strength–ductility balance. To address this limitation, the present study explores the systematic incorporation of Zirconium (Zr) into the CoCrFeNi HEA, aiming to improve its strength through solid solution and second-phase strengthening mechanisms.

When combined, the constituent elements in HEAs can exhibit a wide range of properties that are advantageous for various applications. Nevertheless, the strength and hardness of HEAs may sometimes fall short of the requirements for certain industrial applications [8], [9]. Enhancing their surface hardness may also help them withstand wear in a variety of settings. Thermochemical procedures like nitriding [8], [9], carburizing [10], [11], and boronizing [12], [13], [14] treatments have been studied in recent years as ways to increase the surface hardness and wear resistance of HEAs. However, although aluminizing [15], [16], [17], a thermo-reactive diffusion method in which an inert filler and a master element are prepared within a pack, enabling the deposition of the master element onto the substrate surface under the influence of temperature and time, followed by its interaction with elements diffusing from the substrate to form hard Al-based intermetallic compounds [9], [20], has been extensively studied for conventional alloys, its effect on HEAs remains limited. Another important aspect that distinguishes this study is the influence of Zr addition on the growth morphology of the coating layer thickness. Considering all these factors, the study is expected to provide valuable insights and make a meaningful contribution to the existing literature.

2. EXPERIMENTAL DETAILS

2.1 Materials Processing

(CoCrFeNi)100-xZrx (x=1, 2, and 4) HEAs were produced from elemental chunks with purities higher than 99.9 wt. % by vacuum arc melting technique under Ar atmosphere. The HEA ingots were flipped and re-melted at least 3 times to achieve the chemical homogeneity in the microstructure, before sucting casting into a water cooled copper mold. Subsequent to the casting, the HEAs were homogenized in a tube furnace at 1150 °C under controlled atmosphere for a duration of 24 h. Samples are coded seen in **Table 1**.

Table 1 Codes of the investigated alloys

Alloy	Codes	Co(at%)	Cr(at%)	Fe(at%)	Ni(at%)	Zr(at%)
CoCrFeNi	C0	25	25	25	25	0
$(CoCrFeNi)_{99}Zr_1$	C1	24,75	24,75	24,75	24,75	1
$(CoCrFeNi)_{98}Zr_2$	C2	24,5	24,5	24,5	24,5	2
$(CoCrFeNi)_{96}Zr_4$	C4	24	24	24	24	4

2.2 Aluminizing Process

CoCrFeNi HEA samples with varying Zr contents (0, 1, 2, and 4 at.%) were employed to evaluate the effect of Zr addition on aluminizing behavior. The pack aluminizing process utilized a mixture consisting of 40 wt.% Aluminum as the active source, 5 wt.% NH_4Cl as the activator, and 55 wt.% Al_2O_3 as the inert filler. Prepared substrates were ground, polished, and embedded in the pack mixture within sealed crucibles, followed by heat treatment at 700 °C for 4 h in an open atmosphere furnace. During processing, activated Al species diffused toward the substrate and reacted with alloying elements, leading to the formation of Al-based intermetallic coating layers. First reaction starts with decomposition of activator $NH_4Cl(s)$ reaction is seen as in equation (1).

$$NH_4Cl \rightarrow NH_{3(g)} + HCl_{(g)} \quad (1)$$

The dissociation of the activator yields HCl, which serves as a carrier gas by reacting with the master Al to facilitate chemical vapor transport. Upon reaching the substrate, these halides undergo reduction or substitution reactions, leading to the formation of distinct intermetallic-based phases through inward Al diffusion.

2.3 Materials Test and Characterization

Following the aluminizing treatment, cross-sectional specimens were prepared using standard metallographic procedures for structural and microstructural characterization. The analyses were conducted using a JEOL JSM-5600 scanning electron microscope (SEM). Phase identification of the aluminide coatings was performed by X-ray diffraction (XRD) using a Rigaku X-ray diffractometer with Cu Kα radiation (λ = 1.5418 Å) over a 2θ range of 10°–90°. Elemental composition and phase stoichiometry were evaluated by SEM-EDS analyses, and coating thicknesses were measured from three different regions of the SEM micrographs. Microhardness measurements were carried out on the cross-sections of the coated layers using a Leica WMHT-Mod microhardness tester under a load of 25 g, with results reported in Vickers hardness (HV).

3. RESULTS AND DISCUSSION

The SEM micrographs of the cross-sectional morphology obtained after the aluminizing process at 700°C for 4 h are presented in **Figure 1**. The images reveal the successful formation of a continuous and uniform diffusion layer on the Co, C1, C2 and C4 sample substrates. Examination of **Figure 1a** reveals an initial coating thickness of roughly 18 μm for the specimen without Zr addition. The observed interfacial diffusion layer is characteristic of thermo-reactive deposition processes. It is widely recognized that the formation of such an interdiffusion zone significantly contributes to the improvement of mechanical performance, particularly regarding surface hardness and wear characteristics [19].

The experimental results indicate that Zr addition significantly enhances the coating kinetics under identical temperature and time conditions. Specifically, the coating thickness exhibited a progressive increase with each increment of Zr, reaching a maximum of 40 μm with the 4 wt.% Zr addition. This substantial growth, doubling the thickness of the Zr-free sample, is attributed to the catalytic effect of the alloying element in accelerating the diffusion rate and promoting intermetallic formation. The observed trend aligns with similar findings in the HEA literature regarding minor alloying additions. For instance, Polat et al [20]. investigated the microstructural and mechanical evolution of Yttrium (Y) added CoCrFeNi HEAs. They reported that increasing the Y content from 2 at. % to 4 at. % led to a dramatic enhancement in mechanical performance, with hardness rising from 143 (±2) HV to 335 (±7) HV and yield strength soaring from 130 MPa to 1025 MPa. In the present study, the role of Zr mirrors this behavior. It not only facilitates a thicker coating through enhanced diffusion but also contributes to the formation of a superior hardness profile, reaching 700 HV, by establishing a dense network of FeNiAl, NiAl, and AlCr-based intermetallics **Figure1e**. Additionally, the SEM-MAP analysis of the C2 sample

clearly demonstrates the transport of other elements in addition to the aluminum present on the surface **Figure 2**.

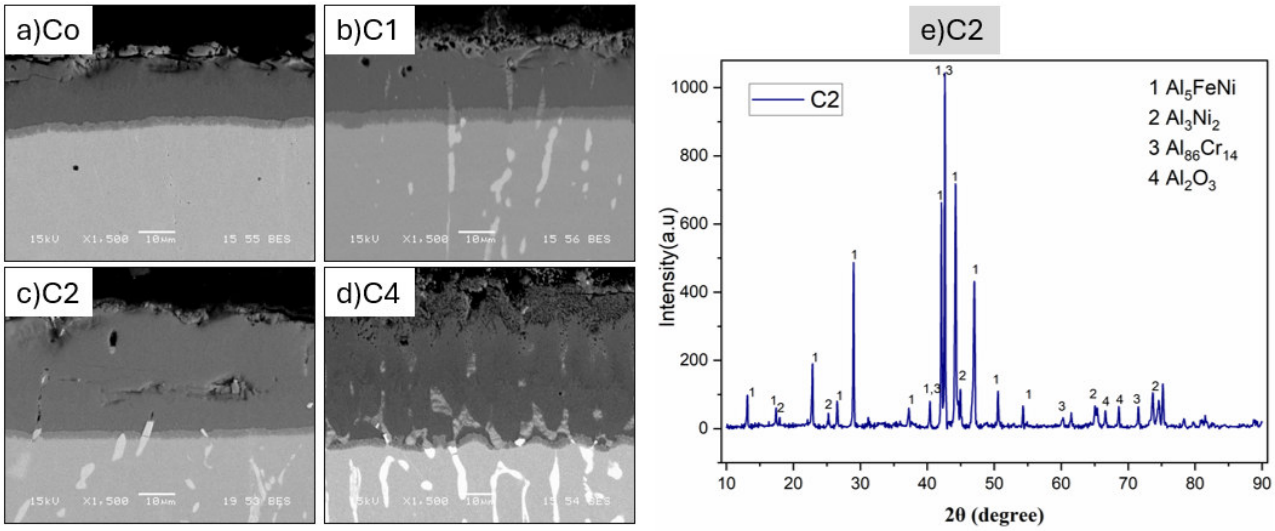

Figure 1 SEM images of aluminized samples a) C0, b) C1, c) C2, d) C4 and XRD pattern of e) C2

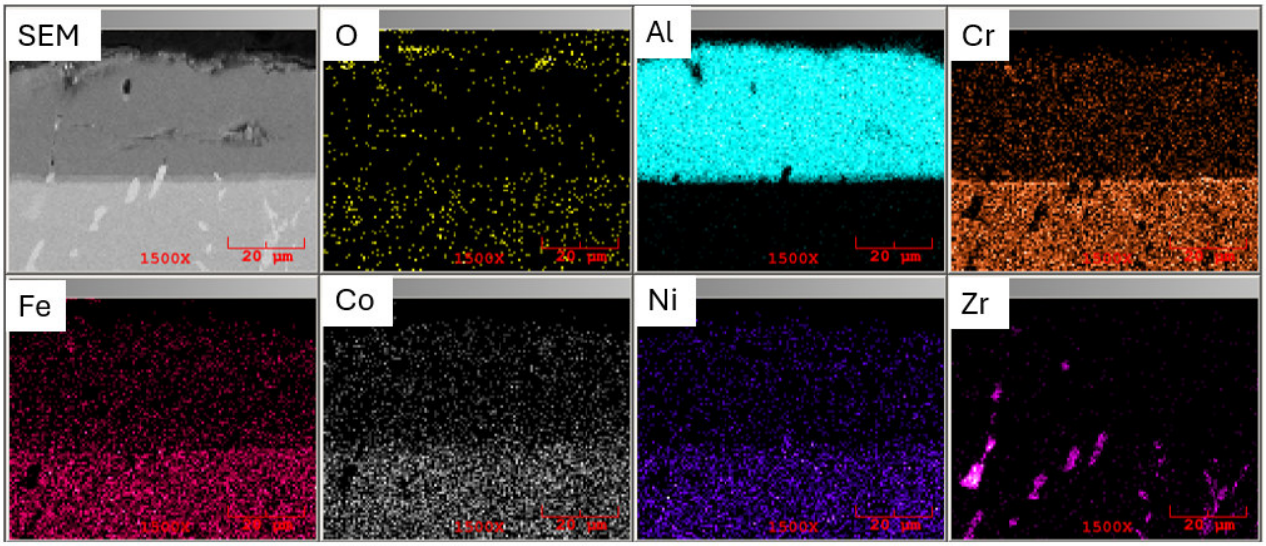

Figure 2 SEM -MAP analyses of aluminized “C2” coded sample

Regarding the hardness results, surface hardness values of 700 HV were achieved due to the formation of hard intermetallic layers. While the substrate hardness was 150 HV for the C0 sample, it increased to 250 HV with the addition of Zr. In addition to the significant increase in the coatings, hardness values of 400 HV were also reached at the interface. The observed hardness profile is consistent with the literature on aluminide intermetallics. Ambali et al [21] reported that different iron-aluminum phases exhibit distinct hardness levels, with Fe_2Al_5 reaching up to 1010 HV, while FeAl and Fe_3Al show values around 570–630 HV and 320–410 HV, respectively. In the present study, the surface hardness of 700 HV suggests the predominant formation of hard NiAl and FeNiAl-based intermetallics. Furthermore, the hardness value of 400 HV measured at the interface aligns closely with the values reported for the Fe_3Al phase, indicating a gradual phase transition and a well-bonded diffusion zone

4. CONCLUSION

In this study, an aluminum-based coating was successfully deposited on a CoCrNiFe HEA substrate at a relatively low temperature of 700 °C for 4 h. The primary conclusions drawn from the experimental results are as follows:

- Microstructural Evolution: The coating process facilitated significant aluminum accumulation and the formation of a dense intermetallic layer on the surface. Specifically, the coating was composed of FeNiAl, NiAl, and AlCr-based intermetallic phases, which are responsible for the enhanced surface properties.
- Effect of Zr on Coating Thickness: The addition of Zr played a critical role in coating kinetics. While the thickness of the Zr-free coating was measured at 18–20 μm, each increment of Zr addition (1, 2, and 4 wt.%) led to a progressive increase in thickness, ultimately reaching 40 μm with the 4 wt.% Zr addition.
- Grain Growth Inhibition: A significant finding of this work is that Zr additions effectively inhibited grain growth within the substrate, demonstrating the potential of Zr as a microstructural stabilizer during high-temperature processing.
- Hardness Profile: The base hardness of the substrate increased from 150 HV (Zr-free) to 250 HV with Zr addition.
- Due to the formation of hard intermetallic phases, the surface hardness reached approximately 700 HV. Notably, the interface exhibited an intermediate hardness of 400 HV, indicating a controlled transition zone between the coating and the HEA substrate.

ACKNOWLEDGEMENTS

This work was supported by the Sakarya University Scientific Research Projects (BAP) under Project No. 2026-29-85-82.

REFERENCES

[1] TSAI, M.-H. AND YEH, J.-W., “High-Entropy Alloys: A Critical Review,” *Mater. Res. Lett.* 2014, vol. 2, no. 3, pp. 107–123, Available from: https://doi.org/10.1080/21663831.2014.912690.

[2] MIRACLE, D. B. and SENKOV, O. N., “High entropy alloys: A focused review of mechanical properties and deformation mechanisms,” *Acta Mater.*, Apr. 2020, vol. 188, pp. 435–474, Available from: https://doi.org/10.1016/j.actamat.2016.08.081.

[3] ERDOGAN, A., “Boriding Temperature Effect on Micro-Abrasion Wear Resistance of Borided Tool Steel,” *J. Tribol.*, Dec. 2019, vol. 141, no. 12, Available from: https://doi.org/10.1115/1.4044859.

[4] FU, Z.*et al.*, “Fcc nanostructured TiFeCoNi alloy with multi-scale grains and enhanced plasticity,” *Scr. Mater.*, vol. 143, pp. 108–112, Jan. 2018, Available from: https://doi.org/10.1016/j.scriptamat.2017.09.023.

[5] TEKIN, M., POLAT, G., AND KOTAN, H., “An investigation of abnormal grain growth in Zr doped CoCrFeNi HEAs through in-situ formed oxide phases,” *Intermetallics*, Jul. 2022, vol. 146, p. 107588, Available from: https://doi.org/10.1016/J.INTERMET.2022.107588..

[6] GÜNEN, A., “Tribocorrosion behavior of boronized Co1.19Cr1.86Fe1.30Mn1.39Ni1.05Al0.17B0.04 high entropy alloy,” *Surf. Coatings Technol.*, 2021, vol. 421, no. June, p. 127426, Available from: https://doi.org/10.1016/j.surfcoat.2021.127426.

[7] YILMAZ, T. T., ERDOGAN, A., DOLEKER, K. M.and KALLEL, M., “Wear response of laser remelted and aluminized CoFeNiCr0.5Mo0.1 medium entropy alloy,” *Surf. Coatings Technol.*, 2025, vol. 504, no. January, p. 132040, Available from: https://doi.org/10.1016/j.surfcoat.2025.132040.

[8] MENG, F. and BAKER, I., “Nitriding of a high entropy FeNiMnAlCr alloy,” *J. Alloys Compd.*, Oct. 2015, vol. 645, pp. 376–381, Available from: https://doi.org/10.1016/j.jallcom.2015.05.021.

[9] WANG, Y., YANG, Y., YANG, H., ZHANG, M., and QIAO, J., “Effect of nitriding on the tribological properties of Al1.3CoCuFeNi2 high-entropy alloy,” *J. Alloys Compd.*, Nov. 2017, vol. 725, pp. 365–372, Available from: https://doi.org/10.1016/j.jallcom.2017.07.132.

[10] ZHANG, L. J. *et al.*, “Effect of solid carburization on the surface microstructure and mechanical properties of the equiatomic CoCrFeNi high-entropy alloy,” *J. Alloys Compd.*, Nov. 2018, vol. 769, pp. 27–36, Available from: https://doi.org/10.1016/j.jallcom.2018.07.329.

[11] PENG, Y.J. GONG, CHRISTIANSEN, T. L.and SOMERS, M. A. J. “Surface modification of CoCrFeNi high entropy alloy by low-temperature gaseous carburization,” *Mater. Lett.*, Jan. 2021, vol. 283, p. 128896, Available from: https://doi.org/10.1016/j.matlet.2020.128896.

[12] DÖLEKER, K. M., GÜNEN, A. and ERDOĞAN, A. “Boriding influence on cyclic oxidation of CrFeMnNbNi high entropy alloy,” *Surf. Coatings Technol.*, 2025, vol. 495, Available from: https://doi.org/10.1016/j.surfcoat.2024.131564.

[13] ATAM, D. SUNBUL, S. E. ICIN, K. DÖLEKER, K. M. GÖK, M. S. and ERDOĞAN, A. “Boriding effect on CrFeMnNbNi high entropy alloy: Microstructure, micro-nano properties, wear behaviour,” *Tribol. Int.*, 2025, vol. 203, no. Available from: https://doi.org/10.1016/j.triboint.2024.110410.

[14] GÜNEN, A. “Tribocorrosion behavior of boronized Co1.19Cr1.86Fe1.30Mn1.39Ni1.05Al0.17B0.04 high entropy alloy,” *Surf. Coatings Technol.*, Sep. 2021, vol. 421. Available from: https://doi.org/10.1016/J.SURFCOAT.2021.127426.

[15] TONG, L. DENGZUN,Y. and CHUNGEN, Z. “Low-temperature Formation of Aluminide Coatings on Ni-base Superalloys by Pack Cementation Process,” *Chinese J. Aeronaut.*, 2010, vol. 23, pp. 381–385. Available from: https://doi.org/10.1016/S1000-9361(09)60231-4.

[16] XIANG, Z. D. and DATTA, P. K. “Low temperature aluminisation of alloy steels by pack cementation process”, Available from: https://doi.org/10.1179/174328406X118366.

[17] FELCA GLÓRIA, CHAIA, R., WESLEI DA CRUZ, ALCKMIN, N. A. L. B. C. A. NUNES, and G. RODRIGUES, “Aluminide coating on Mar-M246 nickel superalloy by halide activated pack cementation (HAPC),” *Surf. Coat. Technol.*, 2021, vol. 411, p. 126999. Available from: https://doi.org/10.1016/j.surfcoat.2021.126999.

[18] KEERATIMAS, P. VISUTTIPITUKUL, P. and WANGYAO, P. “Improvement of surface properties of nickel-based superalloys grade Haynes 214 by Pack aluminizing,” *Mater. Test.*, Nov. 2013,. 55, no. 11–12, pp. 824–829. Available from: https://doi.org/10.3139/120.110515/MACHINEREADABLECITATION/RIS.

[19] DÖLEKER, K. M. *et al.*, “Enhancing the wear and oxidation behaviors of the Inconel 718 by low temperature aluminizing,” *Surf. Coatings Technol.*, 2021, vol. 412. Available from: https://doi.org/10.1016/j.surfcoat.2021.127069.

[20] POLAT, G. and KOTAN, H. “Microstructural Evolution and Mechanical Properties of Y Added CoCrFeNi High-entropy Alloys Produced by Arc-melting,” *Hittite J. Sci. Eng.*, 2024, vol. 11, no. 1, pp. 25–31. Available from: https://doi.org/10.17350/hjse19030000328.

[21] AMBALI,I. O. SEMAN,A. KATRINA,A. BRIJ, T. A. and DHINDAW, K. “Formation and Growth Kinetic of Intermetallic Layers on 304SS at Different Slurry Aluminizing Temperature and Time Using Si - Al 2 O 3 - Modified Aluminide Coating,” *Trans. Indian Inst. Met.*, 2025. Available from: https://doi.org/10.1007/s12666-025-03590-2.