

AlCoNiFeCrTiV_x High-Entropy Coatings Prepared by Electron-Beam Cladding

A. Yurkova, V. Chernyavsky, A. Matveev, M. Sysoyev

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Igor Sikorsky Kyiv Polytechnic Institute, Kyiv, Ukraine
E-mail: alexmatveev1994@gmail.com

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Abstract This study reports the investigation of high-entropy coatings obtained by electron-beam cladding in a vacuum of Al-Co-Ni-Fe-Cr-Ti-V_x powder blend on a steel substrate. V was added to the Al-Co-Ni-Fe-Cr-Ti equiatomic system and the effects of this added element on structure, phase composition and microhardness of AlCoNiFeCrTiV_x high entropy coatings resulted from electron beam cladding were studied. The AlCoNiFeCrTiV₀ coatings consist of two solid solutions with BCC1 and BCC structure with different lattice parameters and a small volume fraction of σ -phase. It was shown that with increase in V content from $x = 0$ to $x = 1.5$, the phase composition of the coatings transforms from two solid solutions to a single BCC solid solution and σ -phases of different composition. The σ -phase volume fraction increased with an increase in the V content. The addition of V to AlCoNiFeCrTi shows the strengthening effect of the AlCoNiFeCrTiV_{0.5-1.5} coatings and the Vickers hardness increased from 8,4 to 11 GPa. Microhardness of the coatings was affected by the sigma phase. The hardness enhancement can be likely attributed to the effect of solid solution strengthening and to the presence of σ -phase particles in the coating structure.

Keywords: High-entropy alloy; Electron-beam cladding; Coating; Structure; Phase composition; Mechanical properties

1 Introduction

In many situations, only the contact surface properties are important in determining the performance of the component in practical applications. To increase the life of mechanical parts, their surface is treated to increase hardness and wear resistance. Therefore, the use of a coating from new materials with high physical and mechanical characteristics, such as high-entropy alloys (HEA) (Gao et al. 2015; Murty et al. 2014), has several attractive advantages. HEAs have been found to have novel microstructures and unique properties.

As a new focus on materials research and a novel alloy design concept (Yeh et al. 2007), high entropy alloys (HEAs) have been achieved successfully by changing or designing the component elements of metallic material (Gao et al. 2015; Murty et al. 2014). HEAs are new class alloys and are quite different from traditional alloys, which are based on one or two elements. HEAs are typically defined as multicomponent alloys whose principal elements are at least five in equiatomic or near equiatomic ratio, and the concentration of each constituent element is between 5 and 35 at.% (Gao et al. 2015; Murty et al. 2014; Yeh et al. 2007).

HEAs have been studied extensively in recent years, and they are expected to be abundant in academic research and industrial applications. Some core effects in HEAs would be more pronounced than those in conventional alloys (Gao et al. 2015; Miracle and Senkov 2017; Murty et al. 2014; Tsai and Yeh 2014; Ye et al. 2016): high entropy – it enhances the formation of simple solid solution phases, such as bcc and/or fcc structures, and thus simplifies the microstructures; severe lattice distortion – it arises from the atomic size difference among different elements in solid solution phases and might markedly influence mechanical, physical and chemical properties; sluggish diffusion – it is due to the inefficient cooperative diffusion of various species and thus slow down phase transformations; and cocktail – it comes from the ideal mixing and inevitably excess interactions among the multi-principal elements in solid solution phases, and thus is a composite effect on properties.

HEAs have more excellent properties than conventional alloys and exhibit promising future for engineering applications due to their good thermal stability, high hardness and high strength, excellent wear resistance, superior oxidization, and corrosion resistance, as well as many other outstanding properties (Gao et al. 2015; Murty et al. 2014). The promising properties of HEAs offer the potential to be used in many applications, such as tools, molds, dies, mechanical parts and furnace parts which require high strength, thermal stability, and wear and oxidation resistance. These alloys can be used for various applications that demand high-temperature strength, oxidation, corrosion and wear resistance (Gao et al. 2015; Murty et al. 2014; Ye et al. 2016; Yeh et al. 2007).

The main method of manufacturing HEAs is vacuum arc remelting for bulk cast ingot, and surface coating is also possible (Gao et al. 2015; Murty et al. 2014). Electron-beam cladding materials processing is a promising route, where a

high-power electron beam is used as a source of heat for processing of materials. Faster processing speed, refinement, and homogenization of microstructure, and heat-affected zone are the notable advantages associated with electron-beam heating materials processing. Thanks to the rapid heating, only a thin surface layer of the material is heated. Electron-beam surface cladding involves the melting of clad material coating using electron beam and applying it on the surface with a minimum dilution at the interface. In the electron beam cladding process, the cooling rate can reach 103-106 K/s and this process is in situ synthesis. More importantly, electron beam cladding process has the capability of achieving metallurgical bonding between the coating and the substrate, small thermal deformation, and non-equilibrium reaction.

Until now this novel method for preparing high-entropy (HE) coatings has not just been reported by any organizations and the main properties of electron-beam cladding made HE coatings are still blank in the scientific research. Taking into account HEA's tendency to form simple structures and nano-crystallines, fabricating high-entropy coatings by electron-beam cladding is of great significance and potential for extensive use. In this study, a novel Al-Co-Ni-Fe-Cr-Ti-V_x high-entropy coating system was manufactured as the coating of the steel substrate by electron-beam cladding; also structure, phase and chemical composition, the hardness of the AlCoNiFeCrTiV_x high-entropy coatings were tested under the different ratio of V element. References (Chen et al. 2006; Dong et al. 2014; Stepanov et al. 2015) have reported that the V has great influence on the structure and properties of HEAs.

2 Experiment details

2.1 Materials and Processing

In order to investigate the effect of V on the microstructure and the mechanical properties of the HE coatings, the coatings with different V contents are fabricated. Al, Co, Ni, Fe, Cr, Ti and V powders with commercial purity (99.7 wt.%) and particle size of $\leq 50 \mu\text{m}$ was chosen for experimentations, prepared and well mechanically mixed as the raw materials. All the elements except V are equiatomic. Then the mixed powders were preplaced onto the surface of St3 steel substrate (C: 0.14-0.22; Ni: ≤ 0.3 ; Cr: ≤ 0.3 ; Mn: 0.4-0.65; Si: 0.15-0.3; Cu: ≤ 0.3 ; S: ≤ 0.05 ; P: ≤ 0.04 ; Fe: 97 balance in mass percentage) to form powder bed with the thickness of 1.7–2.0 mm. In order to evaluate the influence of V content in AlCoNiFeCrTiV_x coatings, the x factor was set as variable quantity and the experiments were divided into 4 groups: x=0, 0.25, 0.5, and 1.0. Powders of the raw compo-

nents were mixed in a planetary ball mill for 5 minutes. With ELA-6 electron-beam equipment, in a vacuum (10^{-2} Pa), the HEA coatings were synthesized on the surface of the steel substrate. The performance of the cladding coatings is controlled by the electron-beam power and scanning speed. The electron beam scanning speed along the surface of the powder pressing was 4 mm/s.

2.2 Structural Characterization

The effects of vanadium content on the structure and phase transformation of electron-beam coatings were investigated by means of Rigaku Ultima IV X-ray diffractometer (XRD) with Cu K α radiation and the working voltage and current were 30 kV and 20 mA, respectively. The range of scanning angle (2θ) was from 20° to 120° . The scanning step was 0.04° with an angular speed of the goniometer rotation of $2^\circ/\text{min}$. The lattice parameters of solid solutions were calculated according to the positions of the gravitation centers of the diffraction profiles by linear extrapolation method.

A scanning electron microscope (SEM) equipped with an energy dispersive spectrometer (EDS) was used to obtain basic information concerning microstructural features and measure the chemical composition of coatings. Prior to SEM observation, the specimens with coatings were sectioned perpendicular to the scanning track for preparing a slice by standard metallographic technique with polishing by diamond slurry.

2.3 Mechanical Testing

Microhardness measurements were performed using a conventional microhardness machine Digital Microhardness Tester MHV-1000 equipped by standard Vickers' pyramid. Microhardness numbers were determined under indentation loads not higher than 1.5 N and a duration time of 15 s. Each coating was tested for multi-points from the interface to the surface with an equal interval of about 0.3 mm. 10-20 measurements were made on each coating/sample for an average.

3 Results and discussion

3.1 Structure Evolution of Elemental Powders to Coatings by Electron-Beam Cladding

Fig. 1 presents the X-ray diffraction patterns of the initial Al-Co-Ni-Fe-Cr-Ti- M_x powder blend and AlCoNiFeCrTiV₀, AlCoNiFeCrTiV_{0.5}, AlCoNiFeCrTiV_{1.0}, AlCoNiFeCrTiV_{1.5} coatings, resulted from electron-beam cladding. The XRD pattern of powder blend exhibits peaks of all the pure elements in the initial powder mix. It can be seen that the phase composition of the V-free AlCoNiFeCrTiV₀ as-clad coating showed the presence of two body-centered-cubic (BCC) solid solution phases with different lattice parameters: BCC and BCC1 (β - and β_1 -phases, respectively) and the small volume fraction of σ -phase which can be identified as Co₃Ti type.

Thus Al, Co, Ni, Fe, Cr, and Ti elements are expected to distribute in two multi-element supersaturated solid solutions of BCC structure and increase

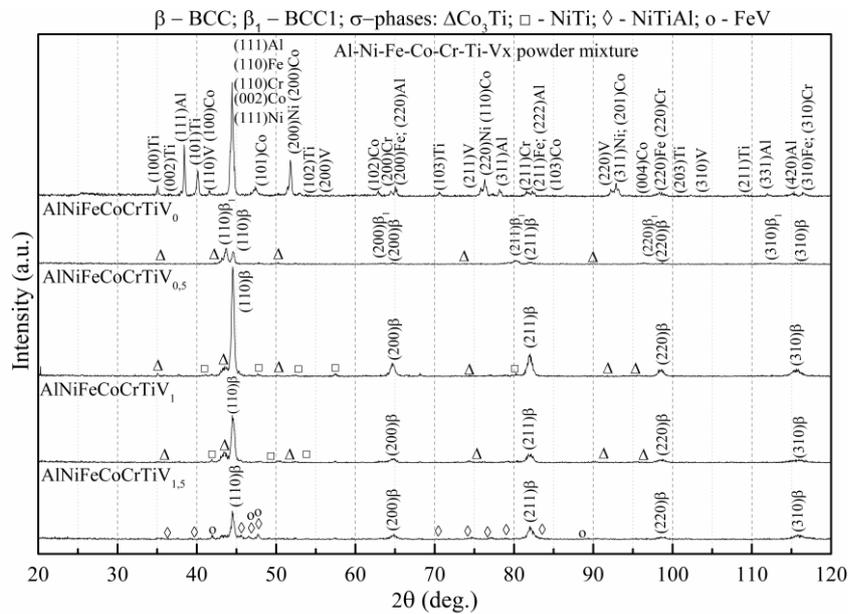


Fig. 1. XRD patterns of Al-Co-Ni-Fe-Cr-Ti-V_x powder blend and AlCoNiFeCrTi, AlCoNiFeCrTiV_{0.5}, AlCoNiFeCrTiV_{1.0}, and AlCoNiFeCrTiV_{1.5} coatings, resulted from electron-beam cladding.

the distortion of the crystal lattices. It is apparent that one BCC1 solid solution is with larger lattice parameter of 0.2931 nm and the other BCC with smaller one of 0.2877 nm from the strongest (110) peak as marked by β_1 -phase and β -phase in Fig. 1, respectively, the larger BCC1 (β_1 -phase) has a higher volume percent.

Peak broadening and their small intensity can be observed and a lot of peaks become nearly invisible. The intensity decrement and peak broadening in the diffraction can be attributed to the formation of high lattice strain, different atomic diffraction factor proportional to the atomic number, crystallinity decrement, and formation of solid solutions.

For the XRD peak intensity, the distorted atomic planes increase X-ray diffuse scattering effect and give smaller peak intensity (Yeh et al. 2007). Moreover, the size mismatch effect between the constituents and increasing dislocation density leads to the increment of lattice strain (Yeh et al. 2007).

According to the XRD analysis, it may be reasonable to consider that the addition of V significantly influences the structure of HE coatings. Really, the addition of V element to the HE coatings composition promotes the transition of two BCC1 and BCC solid solutions and one type Co_3Ti of σ -phase to a single solid solution of BCC structure and intermetallic σ -phases of different types as it can be seen in Fig. 1. Furthermore, the relative intensity of the σ -phase reflections is evidently lower than that of the BCC solid solution phase, revealing that the main phase still is the latter in this coating system. This may be ascribed to the high-entropy effect that greatly lowers the Gibbs free energy of the system, which more easily yields the formation of solid solutions during solidification, rather than ordered compounds especially at the high temperature and leads to the total number of phases well below the maximum equilibrium number allowed by the Gibbs phase rule (Gao et al. 2015; Miracle and Senkov 2017; Murty et al. 2014; Tsai and Yeh 2007).

Intermetallic σ -phases of different composition are formed, probably because of the decomposition of the BCC solid solution under V addition. The as-cladded $\text{AlCoNiFeCrTiV}_{0.5-1.0}$ HE coatings are composed of BCC solid solutions with the lattice parameters of 0.2878 nm and 0.2874 nm, respectively, and intermetallic compounds Co_3Ti and NiTi (σ -phase), while the increase of V content to $x=1.5$ induces changes in phase composition and $\text{AlCoNiFeCrTiV}_{1.5}$ coatings are composed of BCC solid solution, which lattice parameter is calculated to be 0.2871 nm, and another intermetallic compounds (σ -phase): NiTiAl and FeV instead of Co_3Ti and NiTi . With the increase of V content, the increase of the relative amount of σ -phase is observed.

The reflection peaks of the BCC phases practically are not shifted with the increase of V content from 0.5 to 1.5 mol. due to an insignificant solid solution effect as can be seen in Fig. 2a.

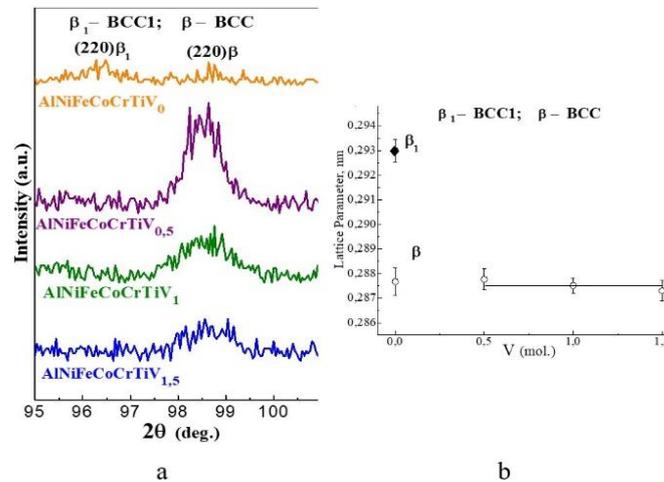


Fig. 2. The shift of the XRD (220)β peaks in the XRD of AlCoNiFeCrTiV_x coatings with different V content (a); and Lattice constant of AlCoNiFeCrTiV_x coatings as functions of V content (b).

In this connection, the lattice parameter of BCC structure is around a constant and varies only within the measurement error. Fig. 2b shows the BCC solid solution (β-phase) lattice parameter changes as a function of V content.

V addition has an evident effect on the BCC solid solution reflection peaks intensity. The addition of 0.5 mol. of V to the V-free equiatomic AlCoNiFeCrTi composition increases the relative intensity of BCC phase peaks owing to the decreasing the crystal lattice distortion because of decreasing the atomic size difference from $\delta=7.2$ to $\delta=6.94$. However, the further V increasing to 1 and 1.5 mol in spite of decreasing in δ parameter to $\delta=6.46$ effects in the decreasing of the BCC reflection peaks intensity through increment of σ -phase volume fraction in coating composition.

3.2 Microstructure Characterization of AlCoNiFeCrTiV_x High-Entropy Coatings Resulted from Electron-Beam Cladding

Fig. 3 shows the microstructure of the as-cladded AlCoNiFeCrTiV_x HE coatings. A dendrite structure was observed in the solidified AlCoNiFeCrTiV_x coatings.

The chemical compositions of the dendrite area and the interdendritic area in Fig. 3 characterized by EDS. It is shown that the dendrite area is rich in Ni, Fe, Co, V, and interdendritic area is rich in Ni. Al and Ti elements are slightly rich in dendrite area.

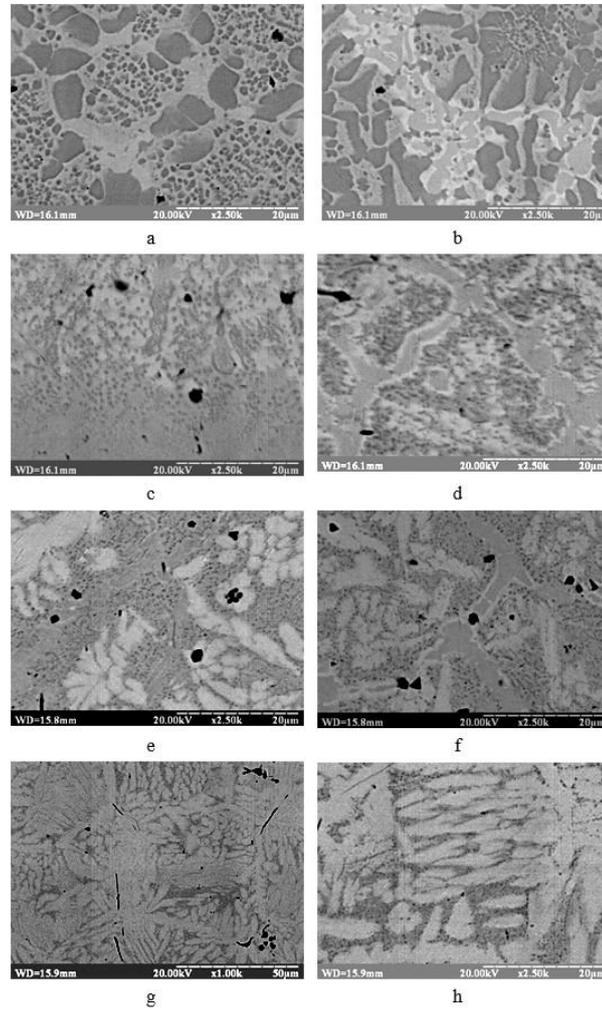


Fig. 3. SEM images of the AlCoNiFeCrTiV_x coatings, $x=0, 0.5, 1.0,$ and 1.5 corresponding to (a,b), (c,d), (e,f) and (g,h), respectively; (a,c,e,g) near the substrate and (b,d,f, h) near the surface.

3.3 Mechanical Properties of AlCoNiFeCrTiV_x High-Entropy Coatings Resulted from Electron-Beam Cladding

Fig. 4 shows the Vickers microhardness distribution from the surface to the interface of the AlCoNiFeCrTiV_x HE coatings. The thickness of the coatings is about

1.5 mm. The microhardness of V-free AlCoNiFeCrTiV_0 coating is 8.4 ± 0.2 GPa. As can be seen, with V addition from 0.5 to 1.5 mol the microhardness of the AlCoNiFeCrTiV_x coatings increases significantly and reaches about 11 ± 0.3 GPa, which is much higher than most of the HEAs prepared by other methods with the hardness value of 3–6 GPa (300–600 HV) (Alaneme et al. 2016; Chen et al. 2006; Gao et al. 2015; Murty et al. 2014; Stepanov et al. 2015; Tsai and Yeh 2014; Tung et al. 2007) and is much higher than that of the similar alloys prepared by laser cladding technique with the value of 4–7.6 GPa (Zhang et al. 2010; Zhang et al. 2011) and almost four times higher than the steel substrate with the value of about 2.3 GPa. The high hardness could be attributed to the strong super-saturation hardening solid solution strengthening and the presence of σ -phase precipitations (Gao et al. 2015; Miracle and Senkov 2017; Murty et al. 2014; Tsai and Yeh 2014). The very high hardness of 10–11 GPa proves the promising future of the HE coating. These AlCoNiFeCrTiV_x HE coatings would also have good wear resistance according to the conclusion, that is, the wear resistance of materials is in general proportional to their Vickers hardness.

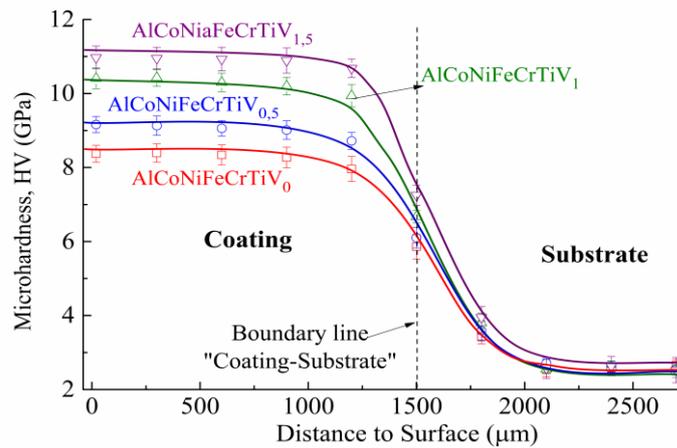


Fig. 4. Microhardness distribution of the AlCoNiFeCrTiV_0 , $\text{AlCoNiFeCrTiV}_{0.5}$, AlCoNiFeCrTiV_1 , and $\text{AlCoNiFeCrTiV}_{1.5}$ high-entropy coatings resulted from electron-beam cladding.

4 Conclusions

The evolution of multicomponent powder Al-Co-Ni-Fe-Cr-Ti-V_x (x=0; 0.5; 1.0; and 1.5) mixture from elemental components to high-entropy coatings during electron-beam cladding was shown.

The addition of V element to the V-free AlCoNiFeCrTi HE coating changes the initial phase composition from two solid solutions with BCC1 and BCC crystal structure with larger lattice parameter of 0.2931 nm and smaller one of 0.2877 nm, respectively, and a small volume fraction of intermetallic σ -phase (Co_3Ti) to single BCC solid solution in AlCoNiFeCrTiV_{0.5-1.5} coatings with increasing in the volume fraction of intermetallic σ -phases of different type (Co_3Ti , NiTi, NiTiAl, and FeV) while increasing vanadium content from $x = 0.5$ to $x = 1.5$. Moreover, the lattice parameter of AlCoNiFeCrTiV_{0.5-1.5} coatings BCC solid solutions is around a constant and varies only within the measurement error.

This research indicates that with the addition of V element the AlCoNiFeCrTiV_{0-1.5} coatings prepared by electron-beam cladding exhibit a monotonic trend of increasing microhardness. Higher vanadium coatings exhibit higher hardness. With the increase of V content from $x=0$ to $x=1.5$ the values of Vickers hardness increased from 8.4 GPa to 11 GPa because of an increase in the sigma-phase volume fraction resulted in continuous strengthening.

AlCoNiFeCrTiV_x HE coatings show a solid solution hardening effect because different-sized atoms occupying the BCC crystal lattice sites cause lattice distortion and σ -phase precipitations harden effect serve as harden mechanism too.

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