

UDC 669.018

O. I. Kushnerov¹, V. F. Bashev¹, V. V. Burkhovetskiy²

¹Oles Honchar Dnipropetrovsk National University, Dnipropetrovsk, Ukraine

²A. A. Galkin Physical and Technical Institute of NASU, Donetsk, Ukraine

PHASE COMPOSITION AND MECHANICAL PROPERTIES OF $Al_xCoCrFe_xNiV$ HIGH-ENTROPY ALLOYS

The multicomponent high-entropy alloys $Al_xCoCrFe_xNiV$ ($x=1;2$) were investigated. The criteria to assess the possibility of formation of solid solutions, intermetallic compounds and amorphous phases in the structure of high-entropy alloys were considered. Effect of the concentration of valence electrons in the alloy to form a solid solution structure was examined. Investigated alloys were found to have a structure with the mixture of BCC and B2 phases (the ordered version of BCC). The value of lattice parameters of the investigated alloys indicates that the solid solutions are formed on the base of Cr lattice, in view of its higher melting temperature. All the alloys display a typical cast dendritic structure with various configurations and volumes of the interdendritic space. The positive influence of microstrains level and dislocation density on the microhardness values of multicomponent $Al_xCoCrFe_xNiV$ alloys is established. Improved mechanical characteristics are ensured by the strong distortion of the crystal lattice due to the differences in atomic radii of the elements.

Keywords: multicomponent high-entropy alloy, structure, microhardness.

Досліджено багатокомпонентні високоентропійні сплави системи $Al_xCoCrFe_xNiV$ ($x=1;2$). Розглянуто критерії, які дозволяють оцінити можливість формування твердих розчинів, інтерметалічних з'єднань та аморфних фаз у структурі високоентропійних сплавів. Розглянуто вплив концентрації валентних електронів у сплаві на структуру твердого розчину, що утворюється в них. Установлено, що в структурі досліджених сплавів присутні неупорядковані тверді розчини, які мають решітку типу ОЦК, та впорядковані тверді розчини, що належать до структурного типу В2. Значення параметрів решітки вказують на те, що в якості основи для формування твердих розчинів слід розглядати решітку Cr як елемента з найбільшою температурою плавлення. Встановлено, що досліджені сплави мають типову дендритну структуру з різними конфігураціями й об'ємами міждендритного простору. Досліджені сплави демонструють високі значення мікротвердості. Встановлено, що збільшення рівня мікронапружень та густини дислокацій сприяють підвищенню механічних характеристик досліджених багатокомпонентних сплавів. Підвищення міцності відбувається завдяки значному викривленню кристалічної решітки внаслідок відмінності атомних радіусів елементів.

Ключові слова: високоентропійний сплав, структура, мікротвердість.

Исследованы многокомпонентные высокоэнтропийные сплавы системы $Al_xCoCrFe_xNiV$ ($x=1;2$). Рассмотрены критерии, позволяющие оценить возможность формирования твердых растворов, интерметаллических соединений и аморфных фаз в структуре высокоэнтропийных сплавов. Рассмотрено влияние концентрации валентных электронов в сплаве на структуру образующегося твердого раствора. Установлено, что в структуре изученных сплавов присутствуют неупорядоченные твердые растворы с решеткой типа ОЦК и упорядоченные твердые растворы, относящиеся к структурному типу В2. Значения параметров решетки указывают на то, что в качестве основы для формирования твердых растворов выступает решетка Cr как элемента с наибольшей температурой плавления. Установлено, что изученные сплавы имеют типичную дендритную структуру с различными конфигурациями и объемами между дендритного пространства. Исследованные сплавы демонстрируют высокие значения микротвердости. Установлено, что повышение уровня микронапряжений и плотности дислокаций способствуют повышению механических характеристик исследованных многокомпонентных сплавов. Повышенные прочностные характеристики обусловлены сильным искажением кристаллической решетки вследствие различий в атомных радиусах элементов.

Ключевые слова: высокоэнтропийный сплав, структура, микротвердость.

1. Introduction

Conventionally, the alloy design and alloy production are almost confined by one- or two-element concept. This alloy concept seriously limits the degree of freedom in alloy's composition and thus limits the development of special microstructure and properties. The main reason for limiting the number of basic elements is the expected formation of a large number of brittle intermetallic compounds and complex microstructures in the structure of alloys. However, in the last time increasing industrial demands for various structural and functional metallic materials have stimulated the advent of new technologies and the development of multicomponent alloys. The range of alloying elements gradually widens and their fraction in the total mass of materials increases. Recently some studies have developed a new thermodynamic approach to design alloys with multiprincipal metallic elements [1]. As a result, a new class of materials known in the literature as multicomponent high-entropy alloys (HEA) was obtained. High-entropy alloys are defined as solid solution alloys that contain more than five principal elements (usually from five to thirteen) in equal or near equal atomic percent. The basic principle of HEAs is that the solution phase is stabilized by the significantly higher configurational entropy of mixing compared to conventional alloys. This stabilizing effect becomes even stronger as increasing temperature and the number of components in the system. A direct consequence of thermodynamic stabilization of the high-entropy phase is reducing the thermodynamic driving force towards oxidation and phase transformation. Due to the high mixing entropy, HEA's are observed to form solid solutions with simple crystal structures (FCC or BCC), without detectable intermetallic compounds or ordered phases. It has been reported that HEA's possess many attractive properties, such as high hardness, outstanding wear resistance, irradiation resistance, excellent high-temperature strength, good thermal stability and corrosion resistance [2-6]. Improved mechanical characteristics are ensured by the strong distortion of the crystal lattice due to the differences in atomic radii of the elements. These properties suggest great potential in a wide variety of applications. Thus, HEA's have received significant attention in recent years. In this work the effect of the value of mixing entropy and composition on the microhardness, phase composition and parameters of the fine structure of $\text{Al}_x\text{CoCrFe}_x\text{NiV}$ ($x = 1; 2$) high-entropy alloys is investigated.

2. Experimental details

The as-cast (cooling rate of $\sim 10^2 \text{ K}\cdot\text{s}^{-1}$) ingots of $\text{Al}_x\text{CoCrFe}_x\text{NiV}$ high-entropy alloys were polished and electrochemically etched for observation. The microstructures of the as-cast samples were studied using an optical microscope Neophot-21. The XRD studies were carried out using a DRON-2.0 X-ray diffractometer in $\text{Cu } K\alpha$ monochromatized radiation. The microhardness was measured on a PMT-3 microhardness-meter at a load of 200g.

3. Solid solution formation criteria in $\text{Al}_x\text{CoCrFe}_x\text{NiV}$ high entropy alloys

In accordance with the Gibbs equation,

$$\Delta G_{mix} = \Delta H_{mix} - T \Delta S_{mix}. \quad (1)$$

Here ΔG_{mix} - the Gibbs potential, ΔH_{mix} - the enthalpy and ΔS_{mix} - entropy of mixing, which is determined from the equation

$$\Delta S_{mix} = -R \sum_{i=1}^n c_i \ln c_i, \quad (2)$$

c_i - atomic fraction of the i -th component, R - universal gas constant. Increasing of mixing entropy in accordance with Eq. (1) reduces the Gibbs free energy of the alloy and improves the stability of the solid solution. For the alloy where n is the number of components, the maximum mixing entropy is in the case when they are mixed in equal atomic fractions. Usually in HEA's ΔS_{mix} value is in the range of 12-19 J/(mol·K). But to avoid the appearance of brittle intermetallic compounds, complex microstructures and amorphous phases in the structure of alloys, some phase formation criteria are required to be completed. According to [7, 8], the Ω parameter can be used to estimate the phase composition of HEA.

$$\Omega = \frac{T_m \Delta S_{mix}}{|\Delta H_{mix}|}, \quad (3)$$

where T_m is the average melting temperature of n -elements alloy.

$$T_m = \sum_{i=1}^n c_i (T_m)_i, \quad (4)$$

$$\Delta H_{mix} = \sum_{i=1, i \neq j}^n \Omega_{ij} c_i c_j, \quad (5)$$

where the regular melt-interaction parameter between i -th and j -th elements $\Omega_{ij} = 4\Delta H_{mix}^{AB}$, and ΔH_{mix}^{AB} - mixing enthalpy of binary liquid AB alloy.

Alloy components should not have large atomic-size difference, which is described by the parameter

$$\delta = 100 \sqrt{\sum_{i=1}^n c_i \left(1 - \frac{r_i}{\bar{r}}\right)^2} \quad (6)$$

where $\bar{r} = \sum_{i=1}^n c_i r_i$, r_i - the atomic radius of the i -th element.

According to [8] the HEA alloys for which $\Omega \geq 11$ and $\delta \leq 6.6$ can form the solid solutions without intermetallic compounds and amorphous phases. However, simple (not ordered) solid solutions form if $-5 \text{ kJ/mol} < \Delta H_{mix} < 5 \text{ kJ/mol}$ and $\delta \leq 4.6$.

The other useful parameter is the valence electron concentration, VEC , which has been proven to be useful in determining the phase stability of high-entropy alloys [9, 10]. VEC is defined by

$$VEC = \sum_{i=1}^n c_i (VEC)_i \quad (8)$$

where $(VEC)_i$ is the valence electron concentration (including the d -electrons) of the i -th element. As pointed in [10], at $VEC \geq 8.0$, sole FCC phase exists in alloy; at $6.87 \leq VEC < 8.0$, mixed FCC and BCC phases will co-exist, and sole BCC phase exists at $VEC < 6.87$.

The data required for calculation are in Tab.1 and 2; calculated values are in Tab. 3.

4. Results and discussion

The phase composition of the investigated Al_xCoCrFe_xNiV alloys, crystal lattice parameters and the fine structure parameters (coherent scattering areas and microstrains) were determined from the XRD patterns (Fig.1). The dislocation density (ρ) was obtained from the profile of the first diffraction peak (Tab.4).

Table 1

Atomic radii of elements, valence electron concentrations [11] and nominal chemical compositions of $Al_xCoCrFe_xNiV$ alloys

	Al	Co	Cr	Fe	Ni	V
Atomic radii, nm.	0.143	0.125	0.129	0.126	0.125	0.135
VEC	3	9	6	8	10	5
Composition of $AlCoCrFeNiV$, at.%	16.67	16.67	16.67	16.67	16.67	16.67
Composition of $AlCoCrFe_2NiV$, at.%	14.28	14.28	14.28	28.57	14.28	14.28
Composition of $Al_2CoCrFeNiV$, at.%	28.57	14.28	14.28	14.28	14.28	14.28
Composition of $Al_2CoCrFe_2NiV$, at.%	25	12.5	12.5	25	12.5	12.5

Table 2

Values of ΔH_{mix}^{AB} (kJ/mol), calculated by Miedema's model [12]

Element	Co	Cr	Fe	Ni	V
Al	-19	-10	-11	-22	-16
Co		-4	-1	0	-14
Cr			-1	-7	-2
Fe				-2	-7
Ni					-18

Table 3

Values of ΔH_{mix} , ΔS_{mix} , δ , VEC and Ω for $Al_xCoCrFe_xNiV$ high-entropy alloys

Alloy	ΔH_{mix} , kJ/mol	ΔS_{mix} , J/(mol·K)	δ	VEC	Ω
$AlCoCrFeNiV$	-14.89	14.89	5.04	6.83	1.76
$AlCoCrFe_2NiV$	-12.72	14.52	4.84	6.99	2.02
$Al_2CoCrFeNiV$	-17.29	14.52	5.67	6.28	1.38
$Al_2CoCrFe_2NiV$	-15.31	14.4	5.56	6.5	1.57

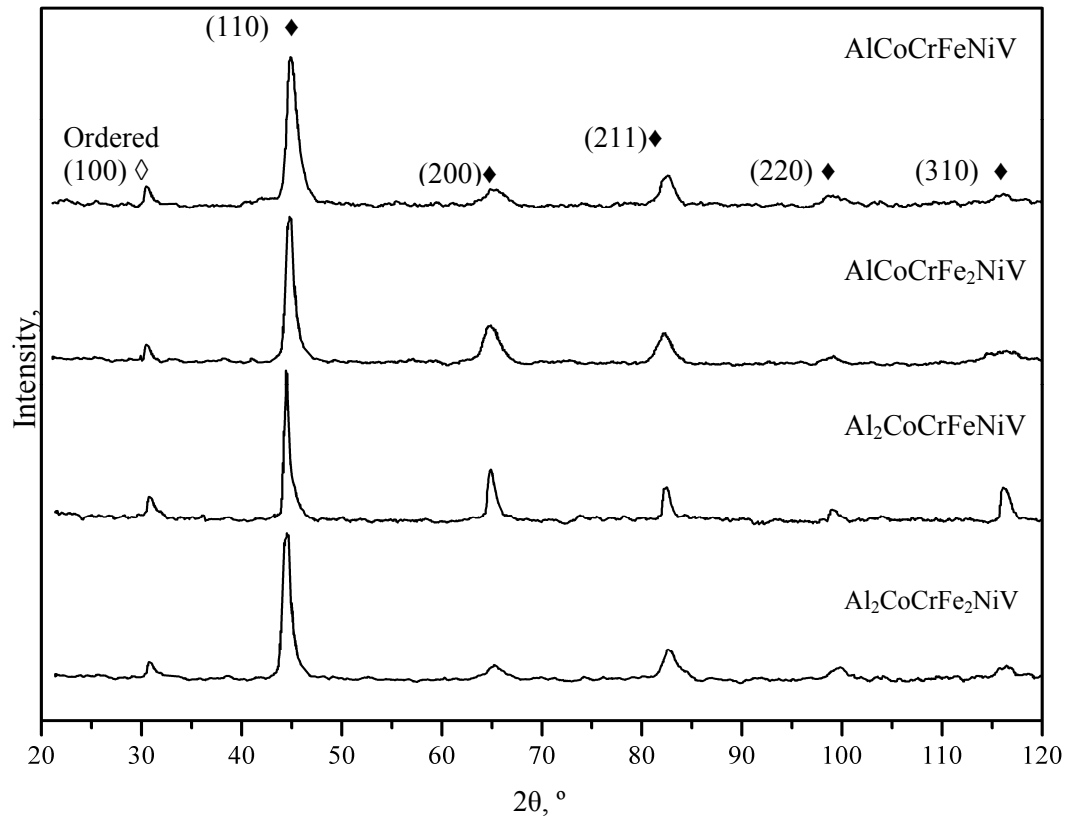


Fig.1. XRD patterns of $Al_xCoCrFe_xNiV$ high-entropy alloys: \diamond -B2, \blacklozenge -BCC.

Table 4

Phase composition, coherent scattering areas (L), the degree of distortion of the crystal lattice ($\Delta a/a$), microhardness (H_u) and the dislocation density (ρ) of the investigated alloys

Alloy	Phase composition	L , nm	$\Delta a/a$	H_u , MPa	ρ , cm^{-2}
AlCoCrFeNiV	BCC + B2 ($a=0.2889$ nm)	19 ± 2	$3.2\cdot 10^{-3}$	6900 ± 300	$1.55\cdot 10^{12}$
$\text{AlCoCrFe}_2\text{NiV}$	BCC + B2 ($a=0.2883$ nm)	30 ± 2	$2.5\cdot 10^{-3}$	4700 ± 200	$6.3\cdot 10^{11}$
$\text{Al}_2\text{CoCrFeNiV}$	BCC + B2 ($a=0.2889$ nm)	35 ± 2	$1.6\cdot 10^{-3}$	6400 ± 300	$4.6\cdot 10^{11}$
$\text{Al}_2\text{CoCrFe}_2\text{NiV}$	BCC + B2 ($a=0.2887$ nm)	36 ± 2	$1.5\cdot 10^{-3}$	4500 ± 200	$4.52\cdot 10^{12}$

XRD analysis allowed us to establish that $\text{Al}_x\text{CoCrFe}_x\text{NiV}$ alloys have two-phase BCC + B2 (CsCl) structure. Indeed, from the analysis of Tab. 3 it is seen that ΔH_{mix} has a large negative value favoring the formation of a compound. The low value of VEC favors the formation of a BCC phase. These factors put together lead to the formation of a mixture of BCC and B2 phases (the ordered version of BCC). Exception is the $\text{AlCoCrFe}_2\text{NiV}$ alloy, for which the value of VEC lies in the range, where a FCC + BCC mixture is favored. But, as pointed in [13, 14], if the value of VEC is close to the boundary values, predictions of the phase compositions sometimes do not work. The values of lattice parameters of the investigated alloys suggests that the solid solutions are formed on the base of Cr lattice ($a = 0.2884$), in view of its higher melting temperature.

High microhardness values of $\text{Al}_x\text{CoCrFe}_x\text{NiV}$ alloys can be explained by the presence of the dissimilar atoms of elements with different size, electronic structure and thermodynamic properties in the crystal lattice. This leads to significant distortion ($\Delta a/a$) of the crystal lattice. Consequently the hardness of the alloys increases.

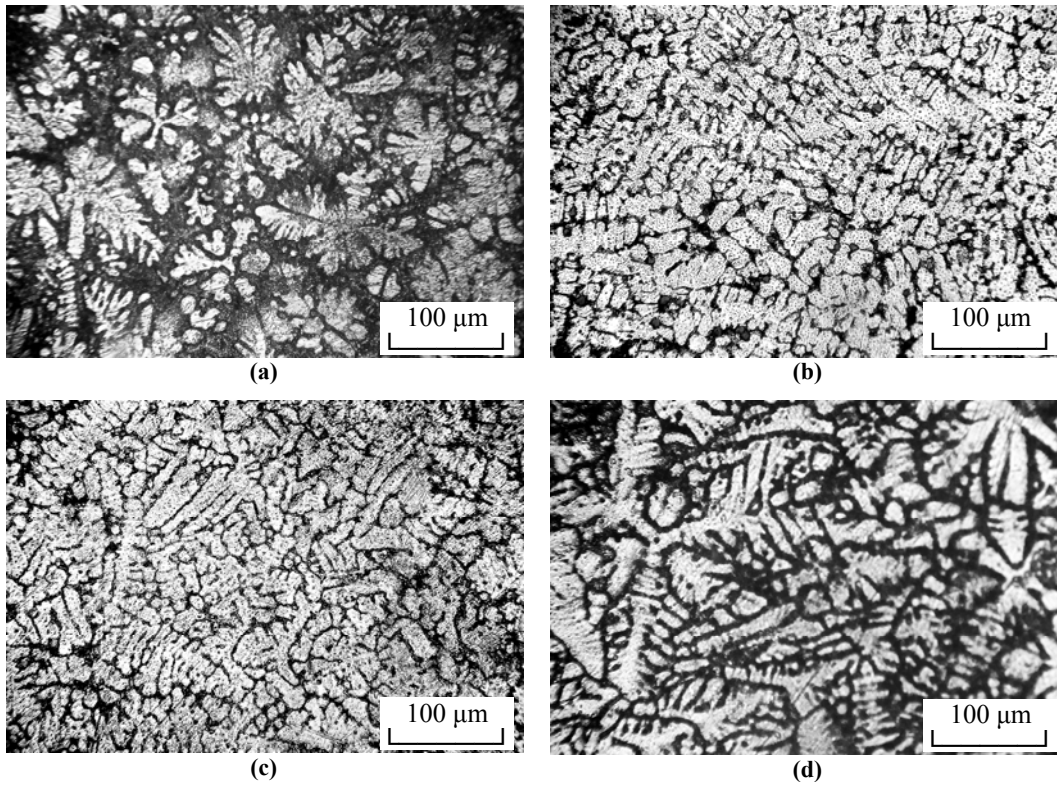


Fig.2. Microstructure of the $\text{Al}_x\text{CoCrFe}_x\text{NiV}$ alloy specimens: (a) - $\text{Al}_x\text{CoCrFe}_x\text{NiV}$, (b) - $\text{Al}_x\text{CoCrFe}_x\text{NiV}$, (c) - $\text{Al}_x\text{CoCrFe}_x\text{NiV}$, (d) - $\text{Al}_x\text{CoCrFe}_x\text{NiV}$

Fig. 2 is an optical micrograph of the as-cast $\text{Al}_x\text{CoCrFe}_x\text{NiV}$ alloys subjected to electrochemical etching. All of the alloys display a typical cast dendritic structure with various configurations and volumes of the interdendritic space.

5. Conclusions

The leading role of the element with higher melting temperature as the basis for the formation of solid solution in the studied high-entropy $\text{Al}_x\text{CoCrFe}_x\text{NiV}$ alloys is confirmed. The positive influence of microstrains level and dislocation density on the microhardness values of multicomponent $\text{Al}_x\text{CoCrFe}_x\text{NiV}$ alloys is established.

References

1. **Yeh, J.W.** Nanostructured high-entropy alloys with multiple principal elements: Novel alloy design concepts and outcomes/ J.W. Yeh, S.K. Chen, S.J. Lin, J.Y. Gan, T.S. Chin, T.T. Shun, C.H. Tsau, S.Y. Chang // *Advanced Engineering Materials*. –2004. –V.6. –P.299-303.
2. **Wu, J.M.** Adhesive wear behavior of $\text{Al}_x\text{CoCrCuFeNi}$ high-entropy alloys as a function of aluminum content/ J.M. Wu, S.J. Lin, J.W. Yeh, S.K. Chen, Y.S. Huang // *Wear*. –2006. –V.261. –P.513-519.
3. **Yeh, J.W.** Alloy Design Strategies and Future Trends in High-Entropy Alloys/J.W. Yeh // *JOM*. – 2013. – V. 65. – P. 1759–1771.
4. **Egami T.** Irradiation Resistance of Multicomponent Alloys/ T. Egami, W. Guo, P.D. Rack, T. Nagase // *Metallurgical and Materials Transactions A*. – 2014, – V. 45, –P. 180–183.
5. **Tsai, M.H.** Physical Properties of High Entropy Alloys/M.H. Tsai// *Entropy*. –2013, –15, P. 5338 – 5345.
6. **Kushnerov, O.I.** Microstructure and mechanical properties of new multicomponent high-entropy alloys/O. I. Kushnerov, V.F. Bashev// *Visn. Dnipropetr. univ., Ser. Fiz. radioelectron.* – 2013. – V.21. №2. Iss.20. –P.88-93.
7. **Zhang, Y.** Solid-Solution Phase Formation Rules for Multi-component Alloys/ Y. Zhang, Y.J. Zhou, J.P.Lin, G.L. Chen, P.C. Liaw//*Advanced Engineering Materials*. –2008. –V.10, Iss. 6. –P. 534–538.
8. **Zhang, Y.** Alloy Design and Properties Optimization of High-Entropy Alloys/ Y. Zhang, X.Yang, P.K. Liaw//*JOM*. –2012. –V.64, Iss. 7. –P. 830–838.
9. **Guo, S.** Phase stability in high entropy alloys: Formation of solid-solution phase or amorphous phase/S. Guo, C.T.Liu// *Progress in Natural Science: Materials International*. –2011. –V. 21, Iss. 6, –P. 433–446.
10. **Guo, S.** Effect of valence electron concentration on stability of fcc or bcc phase in high entropy alloys /S. Guo, C. Ng, J.Lu, C.T.Liu// *Journal of Applied Physics*. –2011. –V. 109, Iss. 10, –P. 103505-1–103505-5.
11. **Li, W.K.** *Advanced Structural Inorganic Chemistry*/W.K. Li, G.D. Zhou, T.C.W. Mak. –New York: Oxford University Press, 2008. –688 p.
12. **Takeuchi, A.** Classification of Bulk Metallic Glasses by Atomic Size Difference, Heat of Mixing and Period of Constituent Elements and Its Application to Characterization of the Main Alloying Element/A. Takeuchi, A. Inoue// *Materials Transactions*. –2005. –V. 46, № 12. –P. 2817-2829.
13. **Sriharitha, R.** Phase formation in mechanically alloyed $\text{Al}_x\text{CoCrCuFeNi}$ ($x = 0.45, 1, 2.5, 5$) high entropy alloys/ R. Sriharitha, B. S. Murty, R. S. Kottada// *Intermetallics*. –2013. –V.32. –P. 119-126.
14. **Singh, A.K.** On the formation of disordered solid solutions in multi-component alloys/ A.K. Singh, A. Subramaniam// *Journal of Alloys and Compounds*. –2014. –V.587. –P. 113-119.

Received 15.03.2014.