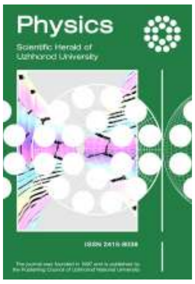
Scientific Herald of Uzhhorod University
Series “Physics”
Journal homepage: https://physics.uz.ua/en
Issue 49, 61-65
Received: 05.02.2021. Revised: 20.04.2021. Accepted: 30.05.2021



УДК 539.8
PACS 81.15.Cd 87.80. 81.05.Zx Ek 81.40.Lm
DOI: 10.24144/2415-8038.2021.49.61-65

Influence of the Lattice Parameter on Physical Properties of High-Entropy Coatings

Victor F. Gorban[1*], Anatolii O. Andreev[2], Viacheslav O. Stolbovyi[2],
Serhii O. Firstov[1], Myroslav V. Karpets[1]

[1]Institute for Problems of Material Sciences National Academy of Sciences of Ukraine
03142, 3 Krzhizhanovsky Str., Kyiv, Ukraine

[2]National Science Center “Kharkiv Institute of Physics and Technology”
61108, 1 Academichna Str., Kharkiv, Ukraine

Abstract

Relevance. The appearance of high-entropy alloys with increased values of hardness and thermal stability led to the study of their properties in coatings. High-entropy metal coatings are described by high hardness values in the range from 7 to 19 GPa.

Purpose. Study of the general regularities of the influence of various parameters on physical properties of high-entropy metal coatings.

Methods. To obtain high-entropy alloys based on solid solutions with a body-centred cubic and face-centred cubic lattice, the metals Al, Ti, Cr, V, Nb, Mo, Zr, Hf, Ta, Mn, Fe, Co, Ni of groups 3-8 of the periodic table were used. Cast alloys were obtained by vacuum arc melting. Coatings – by methods of vacuum arc sputtering and ion sputtering in the plasma of a compressed vacuum arc discharge. The thickness of the coatings varied from 4 to 6 microns. The coatings were studied using X-ray phase analysis and instrumental indentation.

Results. The study of the initial materials and metal coatings made of them allowed determining the phase composition, hardness, modulus of elasticity and normalised hardness. In the studied alloys, the phase composition of the cast high-entropy alloy and coatings did not change. However, in most cases, the lattice parameter in the coatings was less than in the cast state, and the modulus of elasticity of the coatings was slightly higher than in the cast material. Due to the substantial reduction of the structure in the coatings, their hardness is more than twice the hardness of the cast material.

Conclusions. Based on the results obtained, the influence of the lattice parameter on the hardness and modulus of elasticity in high-entropy coatings based on body-centred cubic and face-centred cubic lattices is revealed. A decrease in the lattice parameter of a high-entropy coating by 10% causes a twofold increase in hardness, which is also typical for cast high-entropy alloys

Keywords: metal coatings, phase composition, BCC lattice, FCC lattice, modulus of elasticity and normalised hardness

Introduction

A new class of materials – high-entropy alloys (HEA) in the state of a single-phase solid substitution solution, by their nature are more thermodynamically stable and high-strength compared to conventional solid-soluble alloys [1-3]. The presence of atoms with different electron concentrations, radius size, and modulus of elasticity

Suggested Citation:
Gorban VF, Andreev AO, Stolbovyi VO, Firstov SO, Karpets MV. Influence of the lattice parameter on physical properties of high-entropy coatings. *Scientific Herald of Uzhhorod University. Series “Physics”*. 2021;(49):61-65.

*Corresponding author

affect the development of both the phase composition and the physical features of solid-soluble HEA.

The development of the HEA phase composition is substantially influenced by the electron concentration [4; 5]. Thus, solid HEA solutions based on a body-centred cubic (BCC) lattice are developed in the electronic concentration range from 4.2 to 7.2 el/at. At an electron concentration above 7.9 el/at, solid HEA solutions are developed based on a face-centred cubic (FCC) lattice. The study [6] demonstrates that the displacement of the enthalpy characteristics towards negative values in solid solutions with BCC and FCC lattices contributes to a decrease in the lattice parameter. This process is accompanied by an increase in hardness, modulus of elasticity, and normalised hardness. The dimensional discrepancy according to data [7] makes a substantial contribution to the hardening of solid HEA solutions. Thus, the electron concentration, mixing enthalpy, dimensional mismatch, and other factors contribute to the development of the lattice parameter, on which, as shown in studies [5; 6], the physical properties of cast HEA based on the BCC lattice depend.

High-entropy coatings are given much attention because of the high hardness values compared to one or two-component coatings [8-14]. At the same time, there are no scientific papers investigating the correlation of the lattice parameter of high-entropy coatings with physical characteristics.

The purpose of this study is to investigate the influence of the lattice parameter of solid-state high-entropy coatings on their physical and mechanical properties.

Materials and Methods

Solid-soluble high-entropy alloys based on BCC and FCC lattices were chosen as the material for obtaining coatings. The alloys were chosen based on the recommendations of the studies [5; 6]. The composition of solid-soluble high-entropy alloys based on the BCC lattice included such elements as Al, Ti, Cr, V, Nb, Mo, Zr, Hf, Ta. The composition of a solid-soluble high-entropy alloy based on the FCC lattice comprised Cr, Mn, Fe, Co, and Ni in equiatomic proportions.

The sputtering targets were made by vacuum arc melting in an atmosphere of high-purity argon using a non-consumable tungsten electrode. Cathodes for vacuum arc sputtering were made with a diameter of 60 mm and a height of 50 mm. Targets with a diameter of 60 mm and a thickness of 5 mm were made for ion sputtering in a compressed vacuum-arc discharge plasma. To obtain high-entropy coatings, the study employed the methods of vacuum arc sputtering and ion sputtering in a compressed vacuum arc discharge plasma.

Polished plates made of 12X18H9T stainless steel with dimensions of 20×20×3 mm were sprayed. Vacuum arc deposition of coatings was performed upon the application of a constant negative potential (-200 V) to the substrate, at an arc current of 85 A, and a residual gas pressure of 0,0066 Pa. The coatings were obtained in the plasma of a compressed vacuum arc discharge at a gas discharge current of 25 A, a magnetic field of 3.6 mT, a potential on the target (-850 V) and a displacement potential on the substrate (-50 V), the pressure of the gas mixture during deposition was 0.3 Pa. The substrate temperature for all deposition methods depended on the application conditions and was in the range of 170-280 °C. The thickness of the coatings varied from 4 to 9 μm.

The phase composition was determined using a DRON-UM1 diffractometer in monochromatic CuKα radiation. The values of hardness (H_{IT}) and modulus of elasticity (E) were determined by the indentation method in accordance with the international standard ISO 14577:1-2015 [15]. The paper uses the H/E characteristics, which, according to [16], describes the structural state of the material.

Results and Discussion

The study of the lattice parameter and the physical and mechanical properties of the target material and coatings obtained from them by vacuum arc sputtering is presented in Table 1.

Table 1. Lattice parameter (a), hardness (H) and modulus of elasticity (E) of cast materials and coatings made of them obtained by vacuum arc spraying

Composition	Target				Coating			
	a, nm	*N*, gPa	*E*, gPa	*H/E*	a, nm	*N*, gPa	*E*, gPa	*H/E*
AlTiCrVNbMo	0,3133	6.8	178	0,038	0,3137	17.0	175	0,097
TiZrVNbMo	0,3224	-5.4	126	0,043	0,3220	12.0	135	0,088
TiZrNbTaV	0,3304	4.3	117	0,038	0,3264	10.0	125	0,080
TiZrNbTaHf	0,3338	4.0	103	0,039	0,3336	8.0	101	0,079
TiZrHfNbTaV	0,3348	-3.4	87	0,039	0,3346	7.0	96	0,073

The data presented in Table 1 suggests that high-entropy coatings have a substantially higher hardness than the target material while maintaining the phase composition and a close lattice parameter. Upon spraying, some evaporation of the elements occurs, which affects the change in the lattice parameter of the coating compared to the target. Both a slight increase in the lattice parameter and its decrease are observed. Therewith, the modulus of elasticity also changes in accordance with the change in the lattice parameter. With an increase in the lattice parameter, a decrease in the modulus of elasticity is observed (Fig. 1).

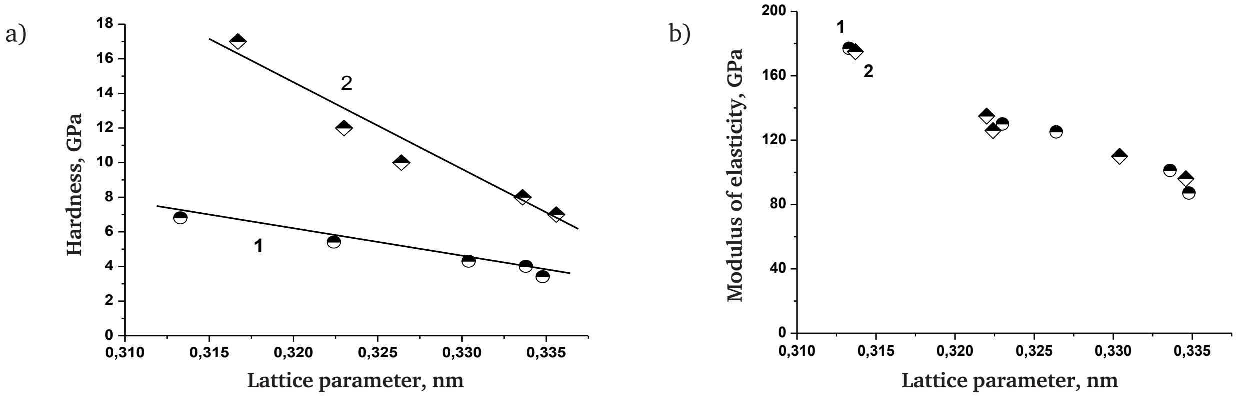


Figure 1. Influence of the lattice parameter of solid-soluble alloys on the hardness (a) and modulus of elasticity (b) for the cast state (1) and coating (2)

Evidently, the hardness in the coating exceeds the hardness of the target by two or more times. This increase in the hardness of the coatings is explained by a change in the structural state (Fig. 2). If the grain size in the cast state is in the range of 20-50 microns (Fig. 2a), then for coatings it is reduced to 20-200 nm (Fig. 2b).

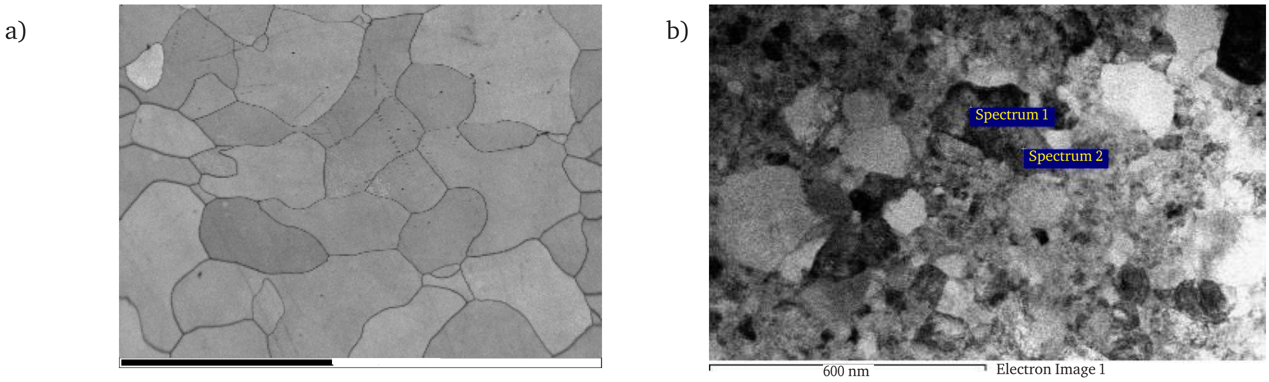


Figure 2. The structure of the target (a) and the coating (b) made of a high-entropy alloy of the AlTiCrVNbMo system

A sharp increase in hardness with minor changes in the values of the modulus of elasticity leads to a substantial increase in the ratio of normalised hardness, which reaches values close to 0.1. Values above 0.1 are typical only for amorphous metals and alloys [17]. The results obtained show that in solid-soluble high-entropy coatings based on the BCC lattice, the regularities inherent in cast high-entropy BCC alloys are preserved. The lattice parameter determines the hardness and modulus of elasticity of the coatings, despite the substantial difference in the chemical composition of the initial alloys (Table 1). A similar pattern of the influence of the lattice parameter on the physical properties was also found for a high-entropy coating based on the FCC lattice. Coatings made of a high-entropy CrFeCoNiMn alloy were obtained by ion sputtering in a compressed vacuum arc discharge plasma under various deposition modes (Table 2).

Table 2. Phase composition lattice parameter and physical characteristics of the target and coatings from the CrFeCoNiMn weight composition depending on the technological deposition modes

Seq. No.	U_s, V	U_t, kV	H_{IT}, GPa	E, GPa	H/E	a, nm
Target			2.2	150	0.015	3605
Coatings						
1	50	0.8	5.5	170	0,032	0,3608
2	50	1.2	9.0	200	0,045	0,3597
3	100	1.0	10.0	205	0,049	0,3587
4	100	1.0	10.5	205	0,056	0,3580
5	150	1.2	11.0	210	0,056	0,3577

Notes: U_s – voltage on the substrate; U_t – voltage on the target

X-ray phase analysis confirmed that the coatings, like the target, are an FCC solid solution. The data presented in Table 2 demonstrate that a high-entropy alloy of the CrFeCoNiMn composition has a low hardness, modulus of elasticity, and H/E ratio. This is explained by the small values of the dimensional discrepancy and the low level of hardening of this alloy [18]. At the same time, with almost equal parameters of the cast alloy lattice (0,3605) and the coating (0,3608), the hardness in-creased from 2.2 to 5.5 GPa, which is typical for grain grinding.

As in the case of solid-soluble high-entropy BCC coatings, the lattice parameter in a high-entropy coating based on an FCC lattice affects the hardness and modulus of elasticity. A decrease in the lattice parameter of a high-entropy coating of the CrFeCoNiMn composition from 0,3608 to 0,3577 nm is accompanied by an increase in the modulus of elasticity from 165 to 210 gPa, and the hardness from 5.5 to 11 gPa. The results obtained show that HEA are a new class of materials, which are described by their unique features. Most importantly, these include the influence of the lattice parame-ter of solid-soluble materials on the modulus of elasticity and hardness. As the lattice parameter in HEA decreases, the binding forces between the atoms increase, which leads to an increase in the modulus of elasticity. In addition, when the lattice parameter decreases, the voltage required for the "non-conservative" elastic displacement of dislocation sites increases. This process contributes to increasing the hardness of the HEA.

Conclusions

High-entropy solid-soluble alloys based on BCC and FCC lattices were smelted and studied. It is shown that high values of normalised hardness are inherent in cast solid-solution alloys based on the BCC lattice, which are characteristic of metals only in the nanostructured state. The coatings obtained by vacuum arc sputtering from high-entropy solid-soluble alloys based on BCC lattices have a high hardness from 7 to 17 gPa, which is more than twice the hardness of the cast metal.

The values of the normalised hardness in coatings made of high-entropy solid-soluble alloys based on the BCC lattice reach values of 0,097 and approach the values inherent in amorphous alloys. The obtained results suggest that in high-entropy coatings, in the state of a single-phase solid substitution solution, the modulus of elasticity and hardness are proportional to the lattice parameter.

The reduction of the lattice parameter in solid-soluble high-entropy alloys based on the BCC lattice from 0,3356 to 0,3133 nm contributes to an increase in hardness and modulus of elasticity almost twice, both for the cast state and for coatings. For a high-entropy coating of the CrFeCoNiMn composition, a decrease in the lattice parameter from 0,3608 to 0,3577 nm is accompanied by an increase in the modulus of elasticity from 165 to 210 GPa, and the hardness from 5.5 to 11 gPa.

References

[1] Yeh JW, Chen SK, Lin SJ, Gan JY, Chin TS, Shun TT, et al. Nanostructured high entropy alloys with multiple principal elements: Novel alloy design concepts and outcomes. *Adv. Eng. Mater.* 2004;6(5):299-303.

[2] Murty BS, Yeh JW, Ranganathan S, Bhattacharjee PP. High entropy alloys. Oxford: Butterworth-Heinemann Ltd; 2014. 204 p.

[3] Cantor B. Multicomponent and high entropy alloys. *Entropy.* 2014;(16):4749-68. https://doi.org/10.3390/e16094749.

[4] Zhang Y, Zhou YJ. Solid solution formation criteria for high entropy alloys. *Mater. Sci. Forum.* 2007;(561-565):1337-39.

[5] Firstov SA, Gorban VF, Krapivka NA, Karpets MV, Pechkovskii ÉP. Structural materials research: Effect of electron density on phase composition of high-entropy equiatomic alloys. *Powder Metall. Met. Ceram.* 2016;54(9):607-13.

[6] Gorban VF, Krapivka NA, Firstov SA, Kurilenko DV. Role of various parameters in the formation of the physicomechanical properties of high-entropy alloys with BCC lattices. *Phys. Met. Metallogr.* 2018;119(5):477-81.

[7] Senkov ON, Wilks GB, Miracl DB, Chuang CP, Liaw PK. Refractory high-entropy alloys. *Intermetallics.* 2010;18(9):1758-65.

[8] Lai Ch-H, Lin S-J, Yen L-W, Chang Sh-Y. Preparetion and characterization of AlCrTaTiZr multi-elemant nitride coatings. *Surf. Coat. Technol.* 2006;(201):3275-80.

[9] Gorban VF, Andreev AA, Chikryzhov AM, Kanzir AV, Samelyuk AV. The phase composition and mechanical properties of vacuum coatings produced from equiatomic CrFeCoNiMn alloy. *Powder Metall. Met. Ceram.* 2019;58(1-2):58-63.

[10] Chen TK, Shun TT, Yeh JW, Wong MS. Nanostructured nitride films of multi-element high-entropy alloys by reactive DC sputtering. *Surf. Coat. Technol.* 2004;(188-189):193-200.

[11] Feng X, Tang G, Sun M, Ma X, Wang L, Yukimura K. Structure and properties of multi-targets magnetron sputtered ZrNbTaTiW multi-elements alloy thin films. *Surface Coat. Technol.* 2013;(228):424-27.

[12] Feng XB, Fu W, Zhang JY, Zhao JT, Li J, Wu K, et al. Effects of nanotwins on the mechanical properties of AlxCoCrFeNi high entropy alloy thin films. *Scr. Mater.* 2017;(139):71-6. https://doi.org/10.1016/j.scriptamat.2017.06.009.

[13] Chang Sh-Y, Lin Sh-Y, Huang Y-Ch, Wu Ch-L. Mechanical properties, deformation behaviors and interface adhesion of (AlCrTaTiZr)Nx multi-component coatings. *Surf. Coat. Technol.* 2010;204(20):3307-14.

[14] Tsai D-Ch, Shieu F-Sh, Chang Sh-Y, Yao H-Ch, Deng M-J. Structures and characterizations of TiVCr and TiVCrZrY films deposited by magnetron sputtering under different bias powers. *J. Electrochem. Soc.* 2010;157(3):K52-K58.

[15] ISO [Internet]. 14577-1:2015: Metallic materials – Instrumented indentation test for hardness and materials parameters – Part 1: Test method; 2015 [updated 2015 July 20; cited 2021 May 10]. Available from: https://www.iso.org/ru/standard/56626.html.

[16] Firstov SA, Gorban VF, Pechkovsky EP. New methodological possibilities for determining the mechanical properties of modern materials by the method of automatic indentation. *Sci. & Innov.* 2010;6(5):7-18.

[17] Inoue A. Stabilization of metallic supercooled liquid and bulk amorphous alloys. *A. Materialia.* 2000;(48):279-306.

[18] Owen LR, Pickering EJ, Playford HY, Stone HJ, Tucker MG, Jones NG. An assessment of the lattice strain in the CrMnFeCoNi high-entropy alloy. *Acta Mater.* 2017;(122):11-18.

Вплив параметра решітки на формування фізико-механічних властивостей високоентропійних покриттів

Віктор Федорович Горбань[1], Анатолій Опанасович Андрєєв[2],
В'ячеслав Олександрович Столбовий[2], Сергій Олексійович Фірстов[1],
Мирослав Васильович Карпець[1]

[1]Інститут проблем матеріалознавства імені І.М. Францевича НАН України
03142, вул. Академіка Кржижановського, 3, м. Київ, Україна

[2]Національний науковий центр «Харківський фізико-технічний інститут»
61108, вул. Академічна, 1, м. Харків, Україна

Анотація

Актуальність. Поява високоентропійних сплавів, що володіють підвищеними значеннями твердості й термостабільності, зумовило дослідження їх властивостей у покриттях. Високоентропійним металічним покриттям властиві високі значення твердості у межах від 7 до 19 ГПа.

Мета. Вивчення загальних закономірностей впливу різних параметрів на фізико-механічні властивості високоентропійних металевих покриттів.

Методи. Для отримання високоентропійних сплавів на основі твердих розчинів із об'ємно-центрованої кубічної і гранецентрованої кубічної решіток використано метали Al, Ti, Cr, V, Nb, Mo, Zr, Hf, Ta, Mn, Fe, Co, Ni 3-8 груп таблиці Менделеєва. Литі сплави отримано методом вакуумно-дугової плавки. Покриття – методами вакуумно-дугового напилення та іонного розпилення у плазмі стисненого вакуумно-дугового розряду. Товщина покриттів варіювалася від 4 до 6 мкм. Дослідження покриттів проводили за допомогою рентгенофазового аналізу та інструментального індентування.

Результати. Проведене дослідження вихідних матеріалів і металевих покриттів з них дозволили визначити фазовий склад, значення твердості, модуля пружності й нормованої твердості. У досліджених сплавах фазовий склад вихідних високоентропійних сплавів і покриттів не зазнавав змін. Однак, параметр решітки у покриттях, здебільшого, був менше, ніж у литому стані, а модуль пружності покриття був дещо вищим, ніж у литому матеріалі. У зв'язку з істотним зменшенням структури у покриттях їх твердість більш ніж у два рази перевершує твердість литого матеріалу.

Висновки. На підставі отриманих результатів виявлено вплив параметра решітки на твердість і модуль пружності у високоентропійних покриттях на основі об’ємно-центрованої кубічної і гранецентрованої кубічної решіток. Зниження параметра решітки високоентропійного покриття на 10 % викликає зростання твердості у два рази, що характерно і для литих високоентропійних сплавів

Ключові слова: металічні покриття, фазовий склад, ОЦК решітка, ГЦК решітка, модуль пружності і нормована твердість