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Multilayer amorphous-crystalline high-entropy metal films

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Abstract. High-entropy alloys (HEA) are multi-element materials and contain at least five elements of similar concentration. HEA are, as a rule, single-phase thermodynamically stable substitutional solid solutions, mainly based on a body-centered cubic and face-centered cubic crystal lattice. Solid solution stabilization during the crystallization of a high-entropy alloy is provided by the interaction of a number of factors, namely, a high mixing entropy and low diffusion rate of components, and a low growth rate of crystallites from the melt. The purpose of this work was to obtain new knowledge about the structure and properties of high-entropy films synthesized on a metal substrate during deposition of a multi-element metal plasma in argon atmosphere. The plasma was formed as a result of independent plasma-assisted electric arc cathodes of the following metals: Ti, Al, Cu, Nb, Zr sputtering. As a result of the performed studies, the deposition mode was revealed, which allows the formation of films of various thicknesses of close to equiatomic composition. Transmission electron microscopy methods have established that the films are multilayer formations and have nanoscale amorphous-crystalline structure. Microhardness of the films significantly depends on the ratio of number of the forming elements and varies from 12 to 14 GPa, Young's modulus – from 230 to 310 GPa. Crystallization of the films was carried out by irradiation with a pulsed electron beam. As a result of processing, a two-phase state is formed. The main phase is α-NbZrTiAl with a volume-centered cubic crystal lattice with a parameter of 0.32344 nm; the second phase of CuZr composition has a simple cubic lattice.

Keywords: high-entropy alloy, substrate film, multi-element plasma, pulsed electron beam, structure, hardness, wear resistance, friction coefficient

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Многослойные аморфно-кристаллические высокоэнтропийные металлические пленки

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Аннотация. Высокоэнтропийные сплавы являются многоэлементными материалами и содержат не менее пяти элементов близкой концентрации. Высокоэнтропийные сплавы являются, как правило, однофазными термодинамически стабильными твердыми растворами замещения, преимущественно на основе объемноцентрированной кубической и гранецентрированной кубической кристаллической решеток. Стабилизация твердого раствора при кристаллизации высокоэнтропийного сплава обеспечивается взаимодействием ряда факторов, а именно, высокой энтропией смешения, низкой скоростью диффузии компонентов, малой скоростью роста кристаллитов из расплава. Целью настоящей работы являлось получение новых знаний о структуре и свойствах высокоэнтропийных пленок, синтезированных на металлической подложке при осаждении многоэлементной металлической плазмы в среде аргона. Плазма была сформирована в результате электродугового с плазменным ассистированием независимого распыления катодов титана, алюминия, меди, ниобия, циркония. В результате выполненных исследований выявлен режим осаждения, который позволяет формировать пленки различной толщины близкого к эквиатомному состава. Методами просвечивающей электронной микроскопии установлено, что пленки являются

многослойными образованиями, имеют наноразмерную аморфно-кристаллическую структуру. Микротвердость пленок существенным образом зависит от соотношения количества образующих элементов и изменяется в пределах от 12 до 14 ГПа, модуль Юнга – от 230 до 310 ГПа. Кристаллизацию пленок осуществляли путем облучения импульсным электронным пучком. В результате обработки формируется двухфазное состояние. Основной фазой является α-NbZrTiAl с объемноцентрированной кубической кристаллической решеткой с параметром 0,32344 нм; вторая фаза состава CuZr имеет простую кубическую решетку.

Ключевые слова: высокоэнтропийный сплав, пленка-подложка, многоэлементная плазма, импульсный электронный пучок, структура, твердость, износостойкость, коэффициент трения

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Introduction

High-entropy alloys are composed of multiple main elements, typically five or more, with similar concentrations, as opposed to conventional alloys consisting of one or, at most, two main elements and several dopants. The development of these alloys indicates a new paradigm in the design of modern materials [1 – 3]. Generally, high-entropy alloys (HEAs) exhibit a unique combination of mechanical, tribological, physical, chemical, and other properties. In most cases, HEAs are single phase, thermodynamically stable, substitutional solid solutions, mainly based on a body-centered cubic (BCC) or face-centered cubic (FCC) crystalline lattice [4].

It is assumed that the stabilization of solid solution during the crystallization of high entropy alloys (HEAs) is achieved through the high mixing entropy of the alloy components in the liquid state, lattice distortion, atom diffusion retardation, and the so-called "cocktail effect" [5]. Numerous studies have shown that HEAs can have a nanosized structure or even exist in an amorphous state due to the low diffusion rate of the constituent elements and low crystallites growth rate [6; 7].

It was demonstrated in [8] that HEAs have the potential to replace nickel-based heat-resistant alloys and be used as high-temperature material for the next generation. The researchers also suggested that due to their unique properties, HEAs have promising potential as coating material for high-temperature applications. This was illustrated by investigating a HEA coating with the composition of $NiCo_{0.6}Fe_{0.2}Cr_{1.5}SiAlTi_{0.2}$ processed by spark plasma sintering (SPS) and atmospheric plasma spraying (APS) and comparing the results with those of a cast MCrAlY alloy. The researchers [8] concluded that the HEA coatings processed by SPS and APS can replace conventional MCrAlY alloys as facing material for high-temperature application due to their significant high temperature hardness, good resistance to oxidation, and low heat conductivity and low-temperature expansion.

The authors [5] argue that the primary focus of research on HEAs should shift from attempts to obtain single-phase equiatomic composition to developing alloys that possess a correct balance of strengthening mechanisms and mechanical properties. Supporting this perspective, several studies [9 – 12] have demonstrated that HEAs can consist of multicomponent alloys of non-equiatomic composition, which are not single phase solid solutions. However, as shown in previous research [13 – 15], HEAs composed of refractory elements may exhibit high density (high specific weight) and brittleness. Despite the increasing number of publications dedicated to HEAs each year, as observed through Scopus analysis [16; 17], there is no consensus on the nature of the remarkable properties exhibit by these materials.

The objective of this study is to gain new insights into structure and properties of HEAs synthesized in thin (up to 5 μm) films through an ion plasma method. The method involves the deposition of a multielement metallic plasma produced by electric arc plasma-assisted simultaneous independent spraying of cathodes of selected elements.

Experimental

Titanium, aluminum, copper, zirconium, and niobium were used as the HEA forming elements in this study. The substrates upon which HEA films were sputtered, included polished samples of AISI 321 stainless steel, commercially pure Ti-Grade2 titanium, and WC – 8 % Co hard alloy. HEA films, up to 5 μm in thickness, were formed using the QUINTA ion plasma facility developed in the laboratory of Plasma Emission Electronics at the Institute of High Current Electronics, Siberian Branch, Russian Academy of Sciences. This facility is part of UNIKUUM complex and is listed among the unique electrophysical facilities of Russia (https://ckp-rf.ru/usu/434216/) [18]. A portion of the HEA films was irradiated by pulse electron beam from the SOLO facility [19], with the following parameters: electron beam duration of 50 μs; energy

density of electron beam of 20 J/cm^2; and three acting pulses at the pulse frequency of 0.3 s^{-1}. The impact of the pulsed electron beam enabled the formation of an ultrafine (up to amorphous state) structure due to the superhigh cooling rate of the material, up to 10^6 K/s, resulting from heat removal to the integral cold substrate [20].

The structure, phase and elemental compositions of the HEA films were analyzed using scanning and transmission diffraction electron microscopy. The state of the crystalline lattice was investigated by *X*-ray structure analysis. The mechanical properties of the films were determined using microhardness measurements.

Results and discussion

During this study, experiments were conducted on the deposition of multielement metal films. The modes of gas metallic plasma generation were also investigated, along with the radial distribution of ion current density for both the metallic and gas plasma sources. The deposition rates of films for individual components were measured, and the elemental composition of the films was determined using *X*-ray structure microanalysis methods. The optimum mode of deposition for HEA films was identified. The experiments involved the deposition of multielement metal films, studying the modes of generation of gas metallic plasma, and measuring the deposition rates of films of individual components. The elemental composition of the films was determined using X-ray structure microanalysis, and the optimum mode of deposition of HEA films was identified. The structure, phase and elemental compositions of both the HEA films and those irradiated by pulsed electron beam were analyzed using scanning and transmission electron microscopy, *X*-ray structure analysis, and other techniques. The HEA films were found to be a multilayer *X*-ray amorphous material (Fig. 1), with a thickness range of 12 to 23 nm and crystallite size of 2 – 3 nm. The hardness of HEA films ranged from 12 – 14 GPa, and the Young's modulus ranged from 230 – 310 GPa.

Irradiation of the HEA film by pulsed electron beam (20 J/cm^2, 50 μs, 3 pulses) led to high-speed crystallization with formation of cellular structure (Fig. 2).

The cell size ranged from 300 to 600 nm. The cells were surrounded by interlayers of the second phase, with a thickness range of 20 – 110 nm. The cell volume was formed by the α-NbZrTiAl phase of BCC crystalline lattice with the constant of 0.32344 nm; while the interlayers of the second CuZr phase were located along the cell boundaries with a simple cubic lattice.

The hardness of films measured at the load on indenter of 30 mN ranged from 6.9 to 8.8 GPa and decreased with an increase in the energy density of the electron beam. The high hardness of the material was found to be due to substructural mechanisms (strengthening by subgrain boundaries, cells of high speed crystallization), dispersion mechanisms (strengthening by particles of the second phase located along the boundaries of crystallization cells), solid solution mechanisms (strengthening as a consequence of distortion of crystalline lattice by atoms of elements forming the alloy), and strengthening by internal stress fields formed as a consequence of the presence of phases with various coefficients of thermal expansion.

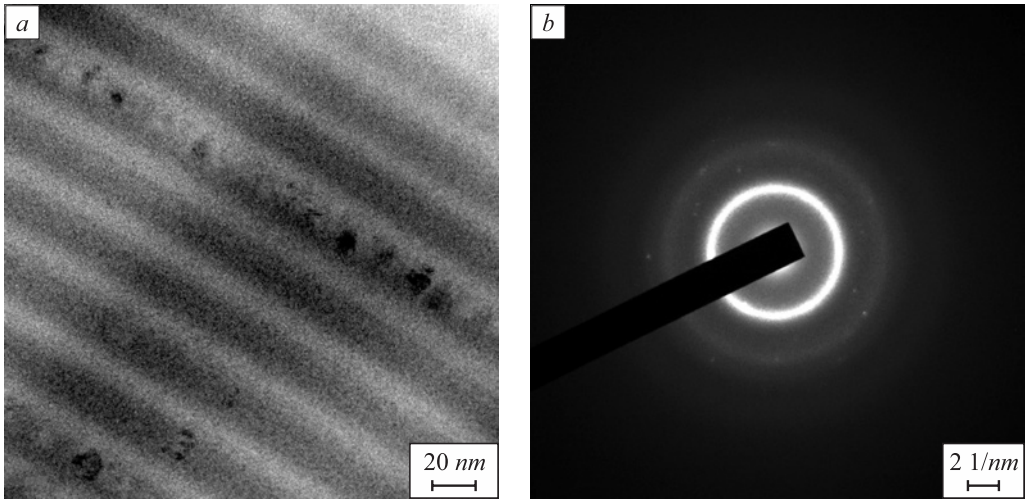

Fig. 1. Electron microscopic image of HEA multilayer film formed as a result of multi-element plasma deposition on a substrate:
a – bright field; *b* – microelectron diffraction pattern

Рис. 1. Электронно-микроскопическое изображение многослойной пленки ВЭС, сформированной в результате осаждения на подложку многоэлементной плазмы:
a – светлое поле; *b* – микроэлектронограмма

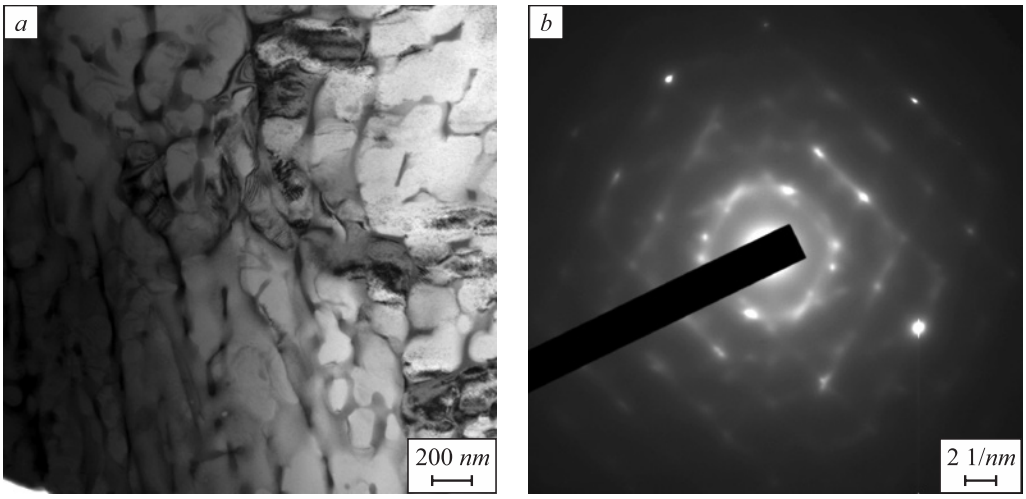

Fig. 2. Electron-microscopic image of HEA multilayer film formed as a result of multi-element plasma deposition on a substrate and additionally irradiated with a pulsed electron beam:
a – bright field; *b* – microelectron diffraction pattern

Рис. 2. Электронно-микроскопическое изображение многослойной пленки ВЭС, сформированной в результате осаждения на подложку многоэлементной плазмы и дополнительно облученной импульсным электронным пучком:
a – светлое поле; *b* – микроэлектронограмма

Conclusions

The present study determined the optimal deposition conditions for the formation of high-entropy alloy (HEA) films with an elemental composition close to equiatomic and characterized by high strength properties, while minimizing energy consumption. The resulting multilayer films were found to be amorphous crystalline and composed of 25.7Ti–17.0Al–21.9Nb–22.3Zr–13.6Cu. Additionally, the films were subjected to irradiation by pulsed electron beam under conditions of high-speed cooling, resulting in the formation of a cellular crystallization structure with submicron-sized cells. The α-NbZrTiAl phase of BCC crystalline lattice with a constant of 0.32344 nm formed the volume, and interlayers of the second CuZr phase located along the cell boundaries (simple cubic lattice).

The obtained results suggest that an environmentally-friendly fully-automated electron ion plasma method for formation of HEAs can be recommended to improve the service properties of various parts and items scientific and engineering applications.

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Contribution of the Authors

Yu. F. Ivanov – formulation of the work concept, writing the text, conducting electron microscopic studies, analysis and discussion of the results.
N. A. Prokopenko – applying HEA coatings, identification of the optimal spraying modes.
V. V. Shugurov – preparation of the samples and equipment for applying HEA coatings, discussion of modes, analysis of the results.
E. A. Petrikova – conducting mechanical tests of the obtained coatings, conducting studies of the samples surface by scanning electron microscopy, discussion of the results.

A. D. Teresov – selection of optimal modes of the samples electron beam processing, conducting irradiation, discussion of the results.

Вклад авторов

Ю. Ф. Иванов – формулирование концепции работы, написание текста статьи, проведение электронно-микроскопических исследований, анализ и обсуждение результатов.
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