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Structure and Properties of High-Entropy Polymetallic Films Synthesized by Ion-Plasma Method

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Abstract. High-entropy alloys (HEAs) are a new class of metal materials, which have a unique combination of mechanical, tribological, physical, chemical and other properties. The purpose of the present work is to obtain new knowledge about the structure and properties of high-entropy alloys synthesized in the form of thin films on the surface of metals and alloys by the electron-ion-plasma method. The films of following composition (at%): Ti (25.7), Al (17.0), Nb (21.9), Zr (22.3), Cu (13.1), were synthesized and investigated. It has been shown that the films are laminated and have an amorphous-crystal structure. Microhardness of HEAs films varies from 10.7 to 17.5 GPa.

INTRODUCTION

High-entropy alloys consisting of five or more basic elements are a new class of metal materials [1]. The beginning of their study can be dated to the 2004 year with the publications of several scientific groups [2, 3]. HEAs have a unique combination of mechanical, tribological, physical, chemical and other properties. They are single-phase thermodynamically stable solid substitution solutions in most cases, mainly based on the bcc- or fcc-crystal lattice. It is supposed that solid solution stabilization during the crystallization of the HEAs is provided by high entropy of mixing of the alloy components in a liquid state. Numerous studies have shown that HEAs can have a nanoscale structure or even be in an amorphous state, which is due to the low diffusion rate of elements and the low growth rate of crystallites. A number of works [4–7] show that high-entropy alloys can include multi-component alloys of non-equiatomic composition, which are also not single-phase solid solutions. To date, a large number of methods for the formation of HEAs have been proposed. In [8] it have been shown that multiple processing methods such as mechanical alloying, arc melting, plasma deposition technique and laser surfacing are successfully used for HEAs production. In [9, 10] the issues of HEAs formation by methods of additive technologies are considered.

The purpose of the present work is to obtain new knowledge about the structure and properties of high-entropy alloys synthesized as thin films on the surface of a solid body by an electron ion-plasma method.

MATERIAL AND METHODS

The experiments on the deposition of multi-element metal films were carried out on the QUINTA ion-plasma setup, developed in the laboratory of plasma emission electronics of the IHCE SB RAS. The formation of HEAs films up to 5 μm thick was carried out by deposition from the multi-element metal plasma generated by electric arc simultaneous independent evaporation of cathodes with selected composition with plasma assistance on metal and metal-ceramic substrates. Ti, Al, Cu, Zr and Nb were used as chemical elements forming HEAs.

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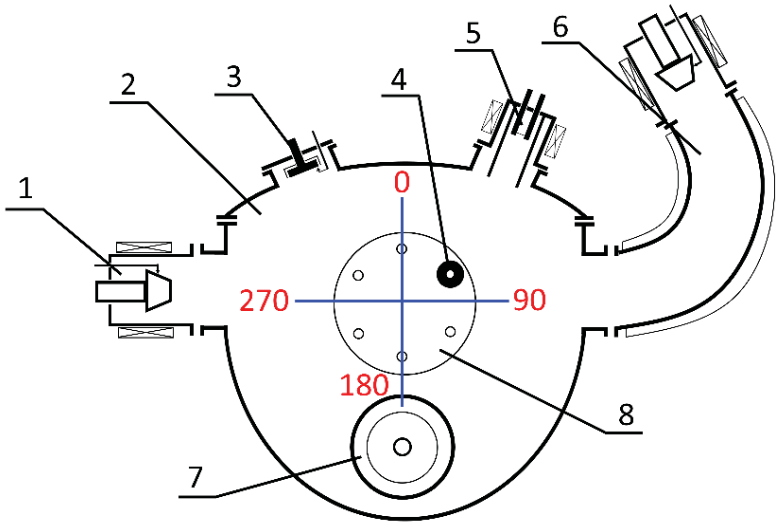


FIGURE 1. Scheme of experiment on the deposition of multi-element coatings. Top view. *1*—DI100 arc evaporator (Nb); *2*—vacuum chamber; *3*—DP400 extended arc evaporator (TiAl); *4*—ion collector; *5*—PINK-P gas plasma generator; *6*—microdroplet fraction filter + DI100 arc evaporator (Cu); *7*—DI80 arc evaporator (Zr); *8*—substrate holder.

The setup was equipped with a DP400 extended arc evaporator with a cathode of the Ti-Al (50/50 wt%) composition, a magnetic separator of the microdroplet fraction with a rotation angle of 120° with a cathode of M3 copper, a DI80 arc evaporator with a zirconium (E110) cathode, a DI100 arc evaporator with a niobium (Hb1) cathode, as well as a PINK-P extended source of gas plasma. The scheme of the experimental setup is shown in Fig. 1.

The phase and elemental composition, defective substructure of the modified steel layer were examined by transmission diffraction electron microscopy (JEM-2100F) using microspectral analysis, dark-field analysis and microelectronogram indication techniques. Test objects (foils with 150–200 nm thick) for the transmission electron microscope were created using a portable Isomet Low Sped Saw unit (cut plates with 150–200 μm thick, located in the cross section of the sample) and Ion Slicer unit (EM-09100IS) (thinning of the plate by ion etching, the foil is created by sputtering the surface of the preform with ions and neutral argon atoms). The study of the phase composition and state of the crystal lattice of the HEAs samples was carried out on a XRD-6000 diffractometer with CuK_{α} radiation. Phase composition analysis was performed using PDF 4 + databases, as well as POWDER CELL 2.4 full-profile analysis program. The properties of the modified layer were characterized by determining microhardness (PMT-3 device, indenter load of 0.5 N).

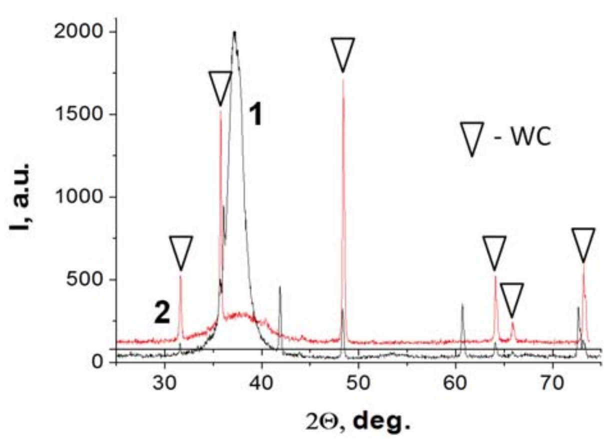


FIGURE 2. Fragments of X-ray pattern obtained from HEAs films deposited on WC–8% Co hard alloy; *1*—composition without copper; *2*—composition with copper.

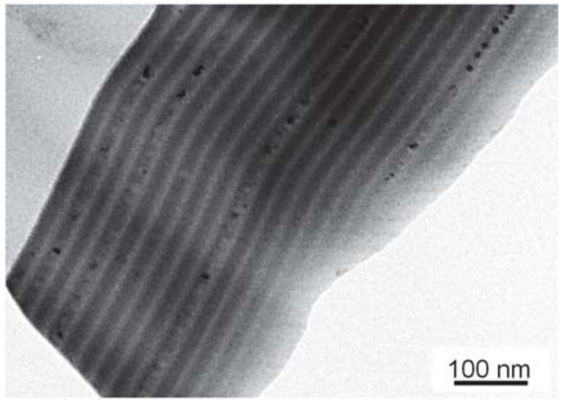


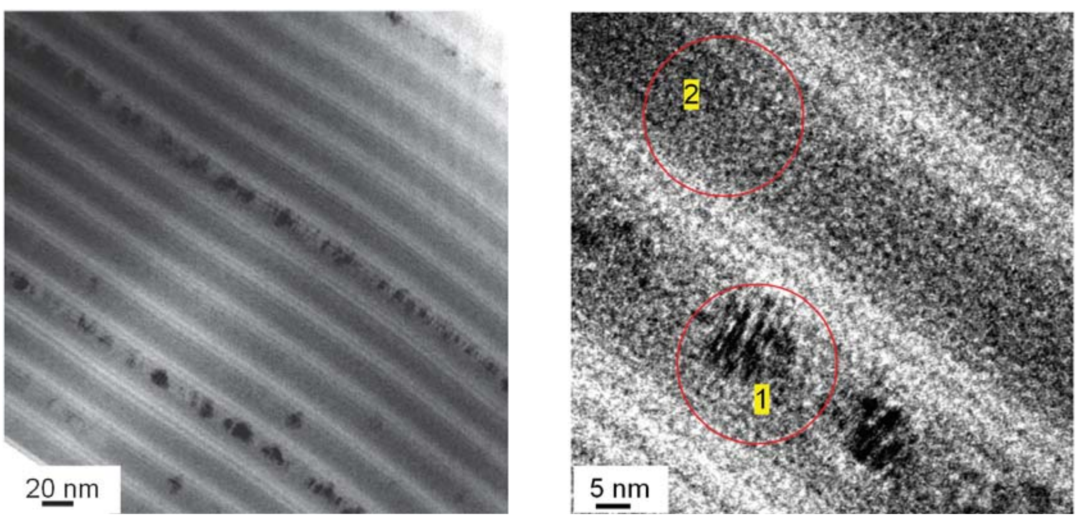
FIGURE 3. STEM-image of a HEAs film deposited from a multi-element metal plasma created by electric arc evaporation with plasma assistance in an argon atmosphere.

RESULTS AND DISCUSSION

Changing the experiment parameters, the films were synthesized where the concentration of chemical elements varied near the equiatomic composition. Microspectral analysis methods showed that the films closest to the equiatomic composition have the following chemical element composition (at %): Ti (25.7), Al (17.0), Nb (21.9), Zr (22.3), Cu (13.1). By X-ray phase analysis it was found that four-element films (films without copper) are two-phase (Fig. 2, X-ray diffraction pattern 1). The presence of niobium-based solid solution lines and $Zr_{0.504}Ti_{0.496}$-based solid solution lines was revealed by X-ray analysis. Addition of copper ions and atoms to the plasma leads to the formation of a metal film. Its X-ray diffraction pattern is a superposition of diffraction maxima and diffraction halo. Analysis of the X-ray diffraction pattern suggests that the diffraction maxima belong to the tungsten carbide crystal lattice WC (substrate), the halo is obviously formed by scattering X-rays on the HEAs film. Thus, the formed HEAs film of chemical TiAlZrNbCu composition is an X-ray amorphous material.

The synthesized films are laminates (Fig. 3).

The film layers differ in thickness, contrast, and substructure. This allows suggesting that the identified layers have different element and phase composition. Electron diffraction microscopy shows that the layers forming the film have different thicknesses (Fig. 4a).



(a) (b)

FIGURE 4. Electron microscopic images of the structure of the HEAs film formed on samples of VT1-0 alloy; on the (b) indicating areas of microdiffraction analysis of the foil is shown.

Namely, the thickness of the dark contrast layers is 23 nm; that of light contrast—12 nm. In turn, light layers are also divided into sublayers of different contrast with a thickness of 2–3 nm. In layers of dark contrast, the islands of the columnar structure are detected (Fig. 4b). Longitudinal axis of columns is oriented perpendicular to layers, i.e. perpendicular to surface of coating. By microdifraction analysis methods the electrograms from a layer having a columnar structure and a layer having no columnar structure were produced. The microelectronogram obtained from the columnar structure (Fig. 4b, area 1) is dotted and contains reflections from the bulk-centered cubic crystal lattice formed by a solid solution of the β (Ti, Zr, Nb, Al) composition. In the second case (Fig. 4b, area 2) a blurred halo containing weakly expressed point reflexes is detected on the microelectronogram.

It has been shown that the microhardness of the HEAs films deposited on the WC–8% Co at a load on the indenter of 0.5 N is 13.5 GPa and varies from 10.7 to 17.5 GPa.

CONCLUSION

By simultaneous independent electric arc evaporation of cathodes with plasma assistance, the synthesis of HEAs films with thickness of up to 5 μm on hard substrate. Elemental composition of films is following (at %): Ti (25.7), Al (17.0), Nb (21.9), Zr (22.3), Cu (13.1). The HEAs films are laminate with an amorphous crystal structure. Crystallites are formed by solid solution with β (Ti, Zr, Nb, Al) composition. The microhardness of the HEAs films deposited on the WC–8% Co is 13.5 GPa within the range from 10.7 to 17.5 GPa.

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