Formation of high-entropy alloy by methods of ion-plasma technologies

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Abstract. Multi-element equiatomic single-phase thermodynamically stable substitutional solid solutions (high-entropy alloys) have a unique combination of mechanical, tribological, physical and other properties. The purpose of this research is to develop an ion-plasma method for the formation of high-entropy alloys. A method for the formation of high-entropy alloys has been developed, which consists in the deposition of a multi-element metal plasma on a substrate in a vacuum. Plasma is formed by vacuum-arc plasma-assisted simultaneous independent sputtering of the cathodes of the selected elements. The modes allowing synthesizing thin Ti-Al-Nb-Zr films with a composition close to equiatomic were revealed. The presence of droplet fraction particles of various elemental composition in the films was found. It is shown that the phase composition of the films depends on the concentration of elements in the plasma.

1. Introduction
High-entropy alloys (HEAs) are multi-element equiatomic single-phase thermodynamically stable substitutional solid solutions based mainly on BCC or FCC crystal lattice, possessing a unique combination of mechanical, tribological, physical and other properties, which makes it possible to recommend their use under extreme conditions in various industries [1-3]. The disadvantages of HEAs include the results presented in [4], which shows that HEAs made of refractory elements have high density (high specific weight) and fragility. The existing high-temperature HEAs with low density do not have high strength at high temperatures, with the exception of the NbMoCrTiAl compound, which demonstrated a yield strength of 600 MPa at 1000 °C, but this alloy turned out to be very brittle at room temperature [5]. One of the promising ways to improve the plastic properties of heat-resistant HEAs without losing their strength is, as shown in [6, 7], the nanostructuring of the material. Alloy compositions with high entropy are currently obtained mainly by vacuum arc melting and mechanical alloying. For the creation of heat-resistant alloys from refractory elements, the methods of powder metallurgy seem to be practically significant [4].

The aim of this research is to develop an ion-plasma method for the formation of HEAs synthesized in the form of thin films, which consists in the deposition in a vacuum of a multi-element metal plasma created by an electric arc plasma-assisted simultaneous independent sputtering of the cathodes of the selected elements.

2. Material and methods
The HEA film is deposited using the plasma-assisted arc deposition method on the QUINTA installation (is
part of the UNIKUUM complex, in the catalog of unique scientific installations, http://ckp-rf.ru/usu/434216/). The experimental scheme is shown in figure 1.

![Figure 1](https://example.com/image1.png)

**Figure 1.** The scheme of the experiment for obtaining WPP:

1 – arc evaporator DI100 with Nb cathode, 2 – arc evaporator DI80 with Cu cathode, 3 – arc evaporator DI80 with Zr cathode, 4 – Y-shaped magnetic filter, 5 – vacuum chamber, 6 – samples, 7 – substrate holder, 8 – electromagnetic filter with a deflection angle of 120 degrees, 9 – heated cathodes, 10 – gas plasma generator PINK-P, 11 – arc evaporator DI100 with Ti-Al or Ti-Al-Si cathode.

For depositing, cathodes of copper M3, zirconium, niobium are used, as well as a composite cathode of composition (Ti-Al 50/50) or (Ti-Al-Si 45/45/10). Zirconium and copper cathodes are installed on a Y-shaped filter with two separate cathode units, a niobium cathode - on an arc evaporator DI100, and a composite Ti-Al or Ti-Al-Si cathode is installed on a magnetic filter with a plasma flow angle of 120 degrees. Deposition is carried out on substrates made of VK8 hard alloy.

After installing the samples (substrate) on the substrate holder, the vacuum chamber is pumped out to a pressure of $6.6 \cdot 10^{-3}$ Pa. Then argon is puffed up to a pressure of 0.3 Pa, the PINK-P gas plasma generator is switched on, and ion-plasma cleaning of the sample surface occurs. After cleaning, the metal plasma generators are started and starts the deposition of coating. After the end of deposition, the samples are cooled in a vacuum chamber to a temperature below 373 K.

The indisputable advantage of this method is the ecological cleanliness of the process, the possibility of complete automation of the ion-plasma deposition process and the formation of HEAs with a predetermined elemental composition, as well as the admissibility of the stage-by-stage formation of coatings with a strictly controlled elemental composition. This work presents the results of studying the structure and phase composition of four-elemental metal films, the thickness of which is 5 μm.

Films were sprayed onto WC-Co hard alloy. Investigations of the elemental and phase composition, the state of the defective substructure were carried out by scanning electron microscopy (Philips SEM-515 instrument with an EDAX ECON IV microanalyzer) and X-ray diffraction analysis (Shimadzu XRD 6000 diffractometer).

3. **Results and discussion**

Micro-X-ray spectral analysis was used to study the formed multi-element metal films. The results of
the study, given in Table 1, indicate that the elemental composition of the obtained films can be controlled by changing the operating modes of the power supplies of the evaporated cathodes.

Table 1. Elemental composition of metal films.

| Experiment | Ti   | Al  | Nb  | Zr  |
|------------|------|-----|-----|-----|
| 1          | 13.8 | 9.9 | 47.9| 28.4|
| 2          | 14.7 | 13.2| 45.5| 26.6|
| 3          | 14.5 | 9.3 | 40.5| 35.7|
| 4          | 19.5 | 27.3| 26.4| 26.8|
| 5          | 20.5 | 25.1| 25.1| 29.3|

The surface structure of the deposited metal films has been studied by scanning electron microscopy (figure 2).

Figure 2. SEM image of the structure of films of the composition Ti-Al-Nb-Zr (a); (b) shows the energy spectra obtained from section (a) and the elemental composition of this section (table).

It was found that during the formation of films, irrespective of the concentration of the elements forming the film, particles of the microdroplet fraction are observed (figure 3). Particle sizes range from hundreds of nanometers to micrometer units.

Figure 3. SEM image of the structure of films of the composition Ti-Al-Nb-Zr (a); numbers indicate drops, the elemental composition of which is given in table 2.
The elemental composition of the particles of the droplet fraction, indicated by numbers in figure 3, is shown in Table 2. It can be seen that the droplets can be enriched with atoms of different elements that form the film.

**Table 2.** Elemental composition of particles of micro-droplet fraction indicated in figure 3.

| Area | Elemental composition, at. % |
|------|-----------------------------|
|      | **Ti** | **Al** | **Nb** | **Zr** |
| 1    | 21.6   | 37.6   | 22.1   | 18.7   |
| 2    | 59.6   | 16.5   | 12.2   | 11.7   |
| 3    | 7.8    | 15.8   | 66.5   | 9.9    |

The phase composition of the films was studied by X-ray structural analysis. It was found that the main phase forming the films is a solid solution based on Zr,Ti.

**4. Conclusions**

A method for the formation of high-entropy films has been developed, which consists in the deposition on a substrate in a vacuum of a multi-element metal plasma created by an electric arc plasma-assisted simultaneous independent evaporating of the cathodes of the selected elements. The possibility of controlling the elemental composition of the film by varying the operating mode of the arc discharge power supply sources is demonstrated. The modes are revealed that allow synthesizing thin Ti-Al-Nb-Zr films with a composition close to equiatomic. It is shown that the formed films contain droplet particles. It was found that the particles present in the films have different elemental compositions. It is shown that the phase composition of the films is a controllable characteristic and depends on the concentration of elements in the plasma, i.e. on the operating parameters of the evaporation system of the installation.

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