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Study of the short-range order of Co-W alloys electrodeposited using pulse current

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Pulsed electrodeposition modes allowed to obtain amorphous Co-W alloys. Using X-ray phase and spectral analysis methods, it was established that the deposition modes and the concentration of the amorphizing component (sodium tungstate salts) in an aqueous electrolyte solution affect the amorphization of alloys. The short-range atomic order was studied by X-ray diffraction analysis and the sizes of the regions of ordered arrangement of atoms were determined in X-ray amorphous Co-W alloys obtained by pulsed electrodeposition. The radial distribution function of atoms was analysed. The assumption is made that cobalt and tungsten atoms combine into configurations that are irregular polyhedrons.

Keywords: X-ray amorphous state, radial distribution function of atoms, regions of ordered arrangement of atoms, coordination number, short-range order.

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Introduction

X-ray amorphous metal alloys belong to the class of materials of great theoretical and practical interest [1–3]. They are characterized by short-range atomic ordering and, unlike crystals, by the absence of translational symmetry in the arrangement of atoms. The parameters characterising the short-range order are the values of the closest distances - the first, second, and third distances defining the coordination spheres, and the number of atoms around the atom chosen as the initial atom in the first, second, and third coordination spheres, i.e. the coordination number. The study of the short-range atomic order is an important and urgent task necessary for a deeper understanding of the physical processes and properties that occur at the initial stages of the formation of a solid phase under conditions far from equilibrium [4–7].

This work is devoted to the study of the phase composition of Co-W films electrodeposited using a pulse current, as well as to the determination of the short-range order of X-ray amorphous Co-W alloys based on X-ray research methods.

I. Materials and methods

Co-W alloy films were obtained by electrodeposition from ammonia electrolytes of the following composition (g/l): $CoSO_4$ – 10, $C_6H_8O_7$ – 60, Na_2WO_4 – 6÷16. The pH=11 was achieved by adding aqueous ammonia. The electrolyte temperature was maintained constant and equal to 333 K.

Plates of pure cobalt were used as an anode for electrodeposition. This allowed to keep constant the concentration of crystallising metal ions, which positively influenced the repeatability of experiments. Copper foil was used as a substrate during electrodeposition. The foil for the substrates was prepared as follows. First, the substrates were mechanically and chemically polished. The solution for chemical polishing was 5% nitric acid solution. Chemical polishing reduced the roughness and removed the work hardening formed after mechanical polishing. Then the substrates were degreased in the Vienna lime solution and washed in distilled water.

Electrodeposition was carried out with rectangular current pulses with a current pulse repetition frequency of

20 Hz and a pulse duty cycle of 2. The average current density remained constant and was equal to 6 A/dm^2. The average pulse current density was chosen so that the forming film had a qualitative appearance.

Studies of the phase composition of Co-W films were carried out on an X-ray diffractometer DRON-2 using a scintillation registration of X-rays. Imaging for the phase composition of the films was carried out in monochromatized Co-K_α radiation. The elemental composition was determined on X-ray spectrometers VRA 20, VRA 30 by measuring the intensity of analytical K_α lines for iron elements (35 kV, W - anode), and for phosphorus (35 kV, Rh - anode).

An automated experimental complex DRON-3.0-IBM was used to take diffractograms for the construction of RDF of atoms. Imaging was carried out in monochromatised Mo-K radiation (with a curved LiF monochromator) point by point with an interval of 0.1 degrees at least 100 seconds of exposure per point and averaging over five scattering intensity curves. The radial distribution function (RDF) of atoms was used to describe the structure of the X-ray amorphous systems. To obtain the RDF of atoms, a Fourier analysis of the experimental intensity curve was performed by X-ray diffraction.

II. Results and discussion

The study of the phase composition of Co-W alloys obtained by electrodeposition at direct and pulse currents showed that, depending on the concentration of sodium tungstate salts (Na_2WO_4) in the aqueous electrolyte solution, the alloys have an amorphous, amorphous-crystalline or crystalline structure (Fig. 1).

Co-W alloys obtained using pulse current at a low W content (less than 12 at.%) were a mixture of X-ray amorphous and crystalline phases (Fig. 1b). The comparison of the diffractograms of pure Co (Fig. 1*a*) and $Co_{90}W_{10}$ alloy (Fig. *1b)* shows that the lines of the crystalline phase in Fig. 1(*b*) correspond to α-Co lines, from which we can conclude that the $Co_{90}W_{10}$ alloy is a solid solution of W in α-Co. When the W content in the alloy increases (more than 12 at.%), the alloy is formed in the X-ray amorphous state, i.e. the diffraction maxima corresponding to the α-Co-based crystalline phase are absent on the diffraction pattern of this alloy, and only a diffuse halo is observed (Fig. 1(c)). Thus, W is an amorphizing agent. With increasing its content in the alloy, the amount of X-ray amorphous phase increases and the amount of crystalline phase decreases. When the W content in the alloy reaches 12 at.%, the lines from the crystalline phase disappear in the diffraction patterns, i.e., the alloy is formed in the X-ray amorphous state.

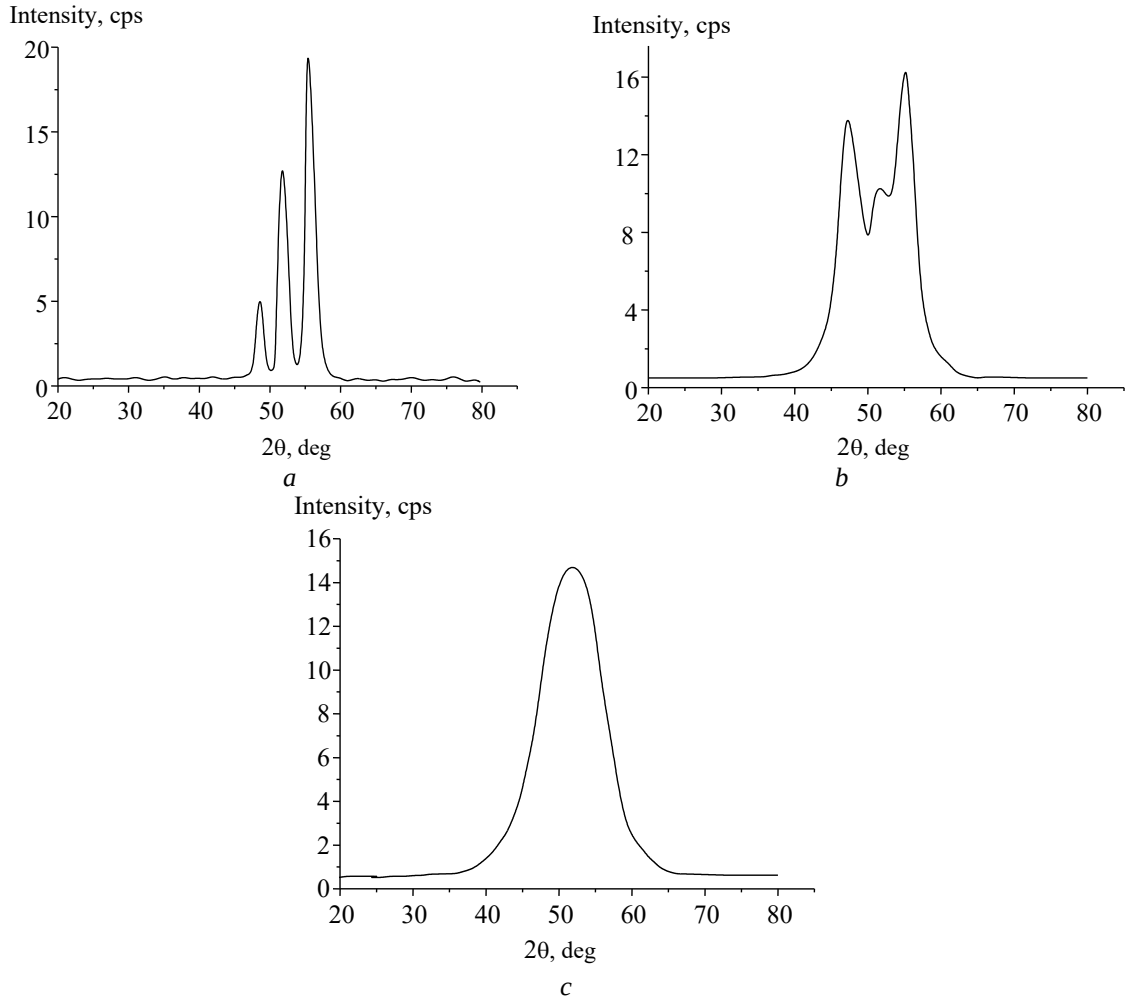

Fig. 1. Intensity of scattering by substances: (*a*) Co; (*b*) $Co_{90}W_{10}$; (*c*) $Co_{84}W_{16}$.

The sizes of regions of ordered arrangement of atoms (ROAA) of X-ray amorphous alloys were estimated by their dependence on the width of the diffraction maximum [8]

$$L \approx \lambda/(\Delta 2\Theta \cdot \cos\Theta),$$

where λ – wavelength; Θ – diffraction angle; $\Delta 2\Theta$ – width of the diffraction maximum.

The obtained values of the dimensions of the ROAA of $Co_{88}W_{12}$ and $Co_{84}W_{16}$ alloys were 1.03 nm and 1.27 nm, respectively, which is consistent with the literature data for X-ray amorphous materials [9].

The construction and analysis of the RDF of atoms provided data on the effect of the introduction of tungsten atoms into the alloy on some short-range order parameters, i.e. the distance between the nearest neighbours and the number of the nearest neighbours. The RDF of atoms of the binary system was found by the formula [10, 11]

$$G(r) = 4\pi\rho_0(n_1c_1 + n_2c_2)^2r^2 + \frac{2r}{\pi}\int_0^{Smax}[i(s) - 1]\, se^{-\alpha s^2}\sin(sr)ds$$

where n_i – relative number of particles of the *i*-th variety, ρ_0 – average interatomic density, *S* – wave vector, *i*(*S*) – current value of the structure factor, $c_i = \left(\frac{F_i^2}{F^2}\right)_{cp}$, F_i – scattering amplitude of particles of the *i*-th variety, $F^2 = n_1F_1^2 + n_2F_2^2$, α – attenuation coefficient, which reduces false maxima and takes values from 0.01 to 0.02 [12]. The average interatomic density ρ_0 for $Co_{88}W_{12}$ and $Co_{84}W_{16}$ alloys was determined experimentally. Experimental X-ray diffraction data were used to find the structure factor. Normalisation of the scattering intensity curves was carried out according to the standard technique [13, 14].

Figure 2 shows the radial distribution functions of atoms of Co-W alloys with tungsten content of 16 at.% (Fig. 2 *a*) and 12 at.% (Fig. 2 *b*).

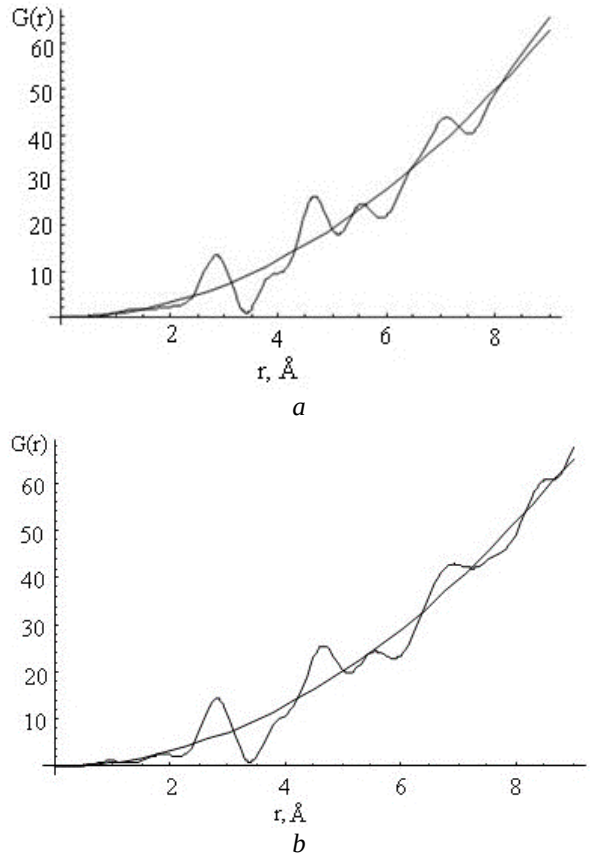

Fig. 2. RDF of atoms for alloys: (*a*) $Co_{84}W_{16}$; (*b*) $Co_{88}W_{12}$.

The data of the RDF analysis, as well as some short-range order parameters of amorphous and crystalline cobalt, are given in the table (where *r* is the distance between the nearest neighbors, *Z* is the coordination number). The coordination number was determined by the "symmetric RDF of atoms" method [15].

Table

Short-range order parameters for Co and Co-W alloys

Substance	State	*r*, nm	*Z*
$Co_{84}W_{16}$	X-ray amorphous	0.2857	14.61
$Co_{88}W_{12}$	X-ray amorphous	0.281	14.0
Co	amorphous	0.251	11.0
Co	crystalline	0.25	12.0

From the analysis of the obtained results (Table), it follows that with increasing tungsten content in the alloy, an increase in the distance between the nearest neighbours is observed. This is obviously due to the fact that the radius of the tungsten atom (0,37 nm) exceeds the radius of the cobalt atom (0,125 nm). When tungsten atoms are introduced into clusters consisting of cobalt atoms, their "swelling" occurs. The increase in the coordination number with increasing tungsten content in the alloy is, in turn, associated with an increase in the distance between the nearest neighbours.

Attention should be paid to the fact that although in the closest atomic packings the number of the nearest neighbours should not exceed 12, the coordination number of X-ray amorphous Co-W alloys is greater than 12. This is probably due to the fact that tungsten and cobalt atoms combine into irregular polyhedra, the structure of which represents regions of space divided into irregular polyhedrons. Such structures have an increased density.

Conclusion

Based on the analysis of the RDF of atoms, it is found that an increase in the tungsten content in the Co-W alloy leads to an increase in the coordination number and the distance between the nearest neighbours. It is suggested that tungsten and cobalt atoms combine to form irregular polyhedra. The ROAA dimensions of the X-ray amorphous alloys $Co_{88}W_{12}$ and $Co_{84}W_{16}$ are estimated, the values of which are 1.03 nm and 1.27 nm, respectively.

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Вивчення ближнього порядку сплавів Co-W, електроосаджених за допомогою імпульсного струму

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За допомогою імпульсного режиму електроосадження отримані аморфні сплави Co-W. Методами рентгенофазового та спектрального аналізів встановлено, що на аморфізацію сплавів впливають режими осадження та концентрація компонента, що аморфізує (солей вольфрамату натрію) у водному розчині електроліту. При збільшенні вмісту W у сплаві (більше 12 ат.%), сплав формується у рентгеноаморфному стані. Методом рентгеноструктурного аналізу вивчено ближній атомний порядок та визначено розміри областей упорядкованого розташування атомів рентгеноаморфних сплавів Co-W, отриманих методом імпульсного електроосадження. Проведено аналіз радіальної функції розподілу атомів. Зроблено припущення, що атоми кобальту і вольфраму об'єднуються у конфігурації, є неправильними багатогранниками.

Ключові слова: рентгеноаморфний стан, радіальна функція розподілу атомів, області впорядкованого розташування атомів, координаційне число, ближній порядок.