

Influence of Pulsed Current Parameters on the Structure Formation of Amorphous Co-W Alloys and their Thermal Stability

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Abstract

The structure and thermal stability of Co-W alloys electrodeposited with direct and pulsed currents have been investigated by X-ray diffraction and differential thermal analyses. It has been established that amorphization of alloys is influenced by deposition modes and concentration of amorphizing component (sodium tungstate salts) (Na_2WO_4) in the aqueous electrolyte solution. It is shown that with increasing tungsten content in the alloy or under more non-equilibrium conditions of electrodeposition the onset of crystallisation shifts to higher temperatures.

Keywords: amorphous-crystalline structure; pulsed electrodeposition modes; differential thermal analysis; phase

Introduction

Due to the discovery of unique physical properties of cobalt-based alloys, their study is of scientific and practical interest. Usually amorphous structures are obtained by rather complicated and expensive methods, such as sputtering in ultrahigh vacuum, molecular beam epitaxy, grinding in high-energy ball mills, or relatively cheaper methods such as electrodeposition. It should be noted that DC electrodeposition is traditional and the phase composition of the resulting alloy depends on the percentage of amorphizing additive in the electrolyte.

Currently, there is a growing interest in the method of transient electrodeposition of alloys, which is due not only to its efficiency and relative simplicity, but also to the wide possibilities of controlling the crystallisation kinetics and, consequently, changing the physical and chemical properties of electrodeposited alloys [1-3]. As a rule, the amorphous state in Co films is achieved by the introduction of the second component [4-6].

The increased tendency to amorphisation found in alloys obtained by deposition of iron group metals with refractory metals such as tungsten (W) and molybdenum (Mo), which are not independently released at the cathode, is explained by the fact that during the deposition of alloys, non-metallic particles are included in the formed coating. Such particles act as modifiers of the base metal structure, preventing the normal growth of crystallites, which leads to their grinding.

During the deposition of W and Mo alloys with iron group metals [7], it was found that with increasing supersaturation at the cathode, fully reduced compounds of W and Mo are found in the coatings. An increase in the corrosion resistance of tungsten alloys with iron group metals was observed with an increase in the amorphous component in the coating.

The use of transient current [8] in comparison with direct current made it possible to obtain coatings with a lower content of impurities in the coating during deposition of W and Mo with iron group metals, as well as to reduce the percentage of W and Mo in the coating, at which it had an amorphous structure.

In [9], the coatings were deposited by current with a frequency of 50 Hz. Depending on the value of the average current density (j_{av}) and the cut-off angle (T_a) the crystalline and X-ray amorphous Co-W alloys were formed. X-ray amorphous coatings were formed at $j_{av}=14 \text{ A/dm}^2$ and $T_a=T/2$, where T is the period of current pulses. At $j_{av}=2 \text{ A/dm}^2$ and $T_a=T/4$, the alloy consisted of two phases: X-ray amorphous and supersaturated α -Co solid solution. The formation of the X-ray amorphous structure of the coatings was explained by an increase in the tungsten content in the alloy as a result of an increase in the amplitude and decrease in the duration of current pulses. The second factor contributing to the electrodeposition of amorphous alloys is the high value of overvoltage at the cathode in the process of metal reduction based on the alloy being formed. The third factor includes the concentration of components. Since the amorphous structure can be obtained in a certain range of components, during electrocrystallisation amorphous alloys are formed mainly at the content of the second component above 15 at.%.

In order to obtain an amorphous state in electrodeposited cobalt films, we applied a complex approach of introducing the required amount of tungsten as an amorphizing component into the coating and non-equilibrium electrodeposition conditions. This work provides a comparative analysis of the changes in the structure and temperature stability of Co-W alloys electrodeposited using direct and pulsed currents.

Materials and Methods

Co-W alloy films were obtained by electrodeposition from ammonia electrolytes of the following composition (g/l): $\text{CoSO}_4 - 10$, $\text{C}_6\text{H}_8\text{O}_7 - 60$, $\text{Na}_2\text{WO}_4 - 6 \div 16$. 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 by rectangular current pulses. The current pulse repetition frequency (f) varied from 20 Hz to 300 Hz. The duty cycle (Q) varied from 2 to 6. 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 3.0 using a scintillation reg-

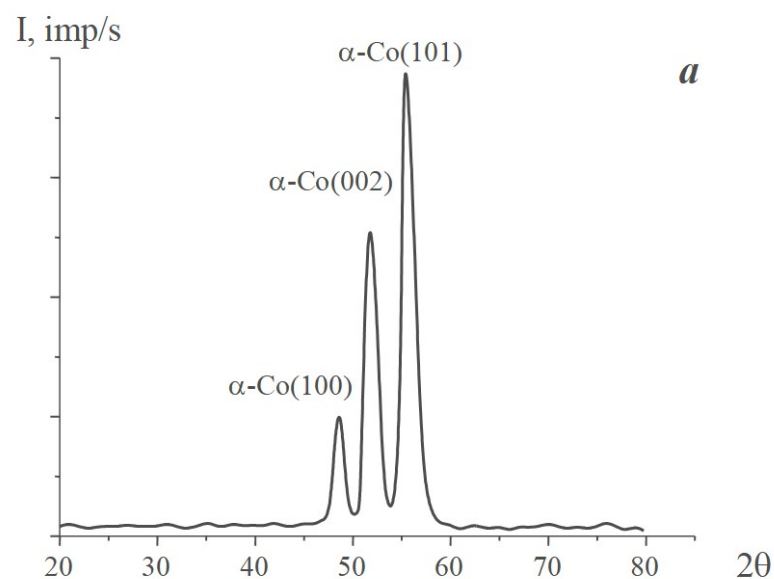
istration of X-rays. Imaging for the phase composition of the films was carried out in monochromatized Co-K_α radiation.

Differential thermal analysis (DTA) curves were obtained on a Q-1500 derivatograph in an inert argon gas environment at a heating rate of 10 deg/min. Al₂O₃ powder was used as a comparative standard of uniform heating. Isothermal annealings were carried out in a vacuum of at least 10⁻² Pa with a heating rate of 20 grad/min. The elemental composition was determined on X-ray spectrometers VRA 20, VRA 30 by measuring the intensity of analytical K_α lines for cobalt elements (35 kV, W - anode), and for tungsten (35 kV, Rh - anode).

Results and their 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 (Na₂WO₄) in the aqueous electrolyte solution, the alloys have an amorphous, amorphous-crystalline or crystalline structure (Figure 1).

Figure 1 (a) shows that Co-W alloys obtained at Na₂WO₄ concentration in the electrolyte equal to 5 g/l have a crystalline structure corresponding to α-Co. When the Na₂WO₄ concentration in the aqueous electrolyte solution is increased up to 9 g/l, the structure of the electrodeposited alloy is transformed into a mixture of X-ray amorphous and crystalline phases (Figure 1 b). Further increase of Na₂WO₄ concentration in the aqueous electrolyte solution leads to a decrease in the fraction of crystalline phase having α-Co structure and to an increase in the fraction of X-ray amorphous phase. At Na₂WO₄ concentration in the aqueous electrolyte solution equal to 11 g/l, the alloy is formed X-ray amorphous. Consequently, the Na₂WO₄ salt is an amorphizer.



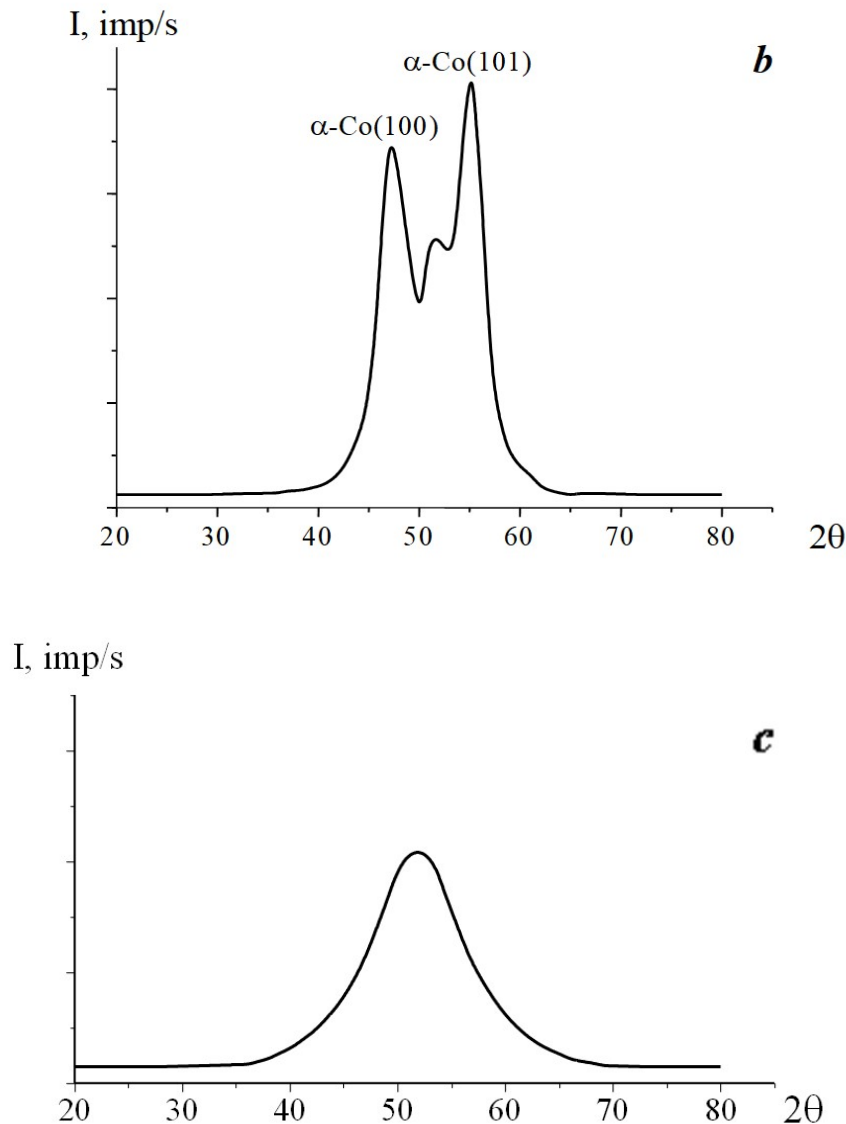


Figure 1: Diffraction patterns of Co-W alloys obtained from electrolyte with Na_2WO_4 concentration: 5 g/l (a); 9 g/l (b); 11 g/l (c)

In pulsed current electrodeposition, the concentration of Na_2WO_4 in the aqueous electrolyte solution plays the same role as in direct current deposition, i.e., as the concentration of amorphizing additive increased, the amount of crystalline phase having $\alpha\text{-Co}$ structure decreased and the amount of X-ray amorphous phase increased. However, the studies showed that in pulse electrolysis, the deposition mode, i.e. pulse current parameters such as pulse repetition rate and duty cycle, is also a factor affecting amorphization. In DC electrodeposition, the X-ray amorphous state was observed at a concentration of Na_2WO_4 in the aqueous electrolyte solution of not less than 11 g/l. Application of pulsed current allowed to obtain X-ray amorphous Co-W alloy at a lower concentration of Na_2WO_4 in the aqueous electrolyte solution. It was found that the minimum permissible values of Na_2WO_4 concentration, at which X-ray amorphous alloys are formed as a result of pulse electrodeposition, decrease with increasing 'hardness' of deposition modes, i.e. with increasing the duty cycle and decreasing the pulse repetition rate.

Table 1 shows the results of the study of the influence of pulse electrodeposition modes on the phase composition of Co-W films obtained from an aqueous electrolyte solution with a Na_2WO_4 content of 8 g/l.

The studies have shown (Table 1) that the application of pulse electrodeposition mode with parameters $f=20$ Hz and $Q=6$ allowed to obtain X-ray amorphous Co-W alloy from aqueous electrolyte solution with Na_2WO_4 concentration equal to 8 g/l, whereas at DC electrodeposition the X-ray amorphous state of the alloy was achieved at Na_2WO_4 concentration of not less than 11 g/l in the aqueous electrolyte solution. Thus, the application of pulse electrolysis made it possible to reduce by 27% the concentration of Na_2WO_4 required for obtaining Co-W alloys in the X-ray amorphous state. Consequently, the formation of X-ray amorphous phase during pulse electrodeposition is influenced not only by the concentration of amorphizing agent, but also by the deposition modes (current pulse repetition rate and duty cycle).

Table 1 also shows that with an increase in the frequency and a decrease in the pulse duty cycle, the structure of Co-W alloys becomes more equilibrium under unchanged deposition conditions (composition and temperature of the aqueous electrolyte solution, average current density). The change in crystallization conditions can be explained by the fact that during pulsed electrolysis, with an increase in the current pulse repetition rate and a decrease in the duty cycle, the supersaturation value at the crystallization front decreases with a decrease in the rate of change of cathodic supersaturation [10-13], i.e. the conditions necessary for the formation of an X-ray amorphous state are not reached. The formation of two-phase alloys (X-ray amorphous and crystalline phases) is caused by the fact that during the pause between current pulses the cathodic supersaturation drops to some residual value not equal to zero. During the action of the current pulse, the cathode region reaches a supersaturation sufficient for the introduction of the amount of tungsten required for the formation of the X-ray amorphous state in the forming coating. The pause between current pulses is characterised by a small rate of change of cathode supersaturation, which can be regarded, to a large approximation, as areas of constant current. At the same time, the value of cathode supersaturation is much lower than in the pulse. It should be noted that the use of large duty cycles of current pulses at low pulse repetition rates leads to an increase in the pause duration, which favours the formation of the X-ray amorphous structure of electrolytic Co-W alloys.

Table 1: Phase composition of Co-W alloys obtained by pulse electrodeposition from electrolyte with Na_2WO_4 content of 8 g/l-
litre

Q	f, Hz		
	20	200	400
2	C	C	C
4	A+C	A+C	C
6	A	A+C	A+C

C – crystalline phase; A – X-ray amorphous phase; A+C – X-ray amorphous plus crystalline phase

In order to establish the temperatures of phase transitions and to determine the temperatures of isothermal annealing, DTA curves were considered. Figure 2 shows the most characteristic DTA curves of Co-W alloys of different compositions and process modes. Figure 2 demonstrates that the curves have a similar character of dependence of the differential ratio of the temperature of the investigated film to the reference standard. With the onset of heating, the DTA curves of alloys of all compositions behave without changes, and in the temperature range from 500 K to 720 K, the curves monotonically decrease, indicating the gradual ordering of the amorphous structure. The first transformation responsible for the separation of α -Co crystalline phases with HCP lattices in the amorphous matrix in $\text{Co}_{75}\text{W}_{25}$ alloys obtained at direct current (Figure 2, curve 2b) begins at a temperature of 720 K. In films of the same composition obtained with pulsed current, this transformation starts at a temperature of 740 K (Figure 2, curve 2a). With increased tungsten content in the films, the crystallisation temperature shifts towards higher temperatures. Thus, for $\text{Co}_{62}\text{W}_{38}$ alloys, crystallisation starts at temperatures of 750 K and 765 K, respectively, for DC and pulse current deposition modes (Figure 2, curves 1a and 1b).

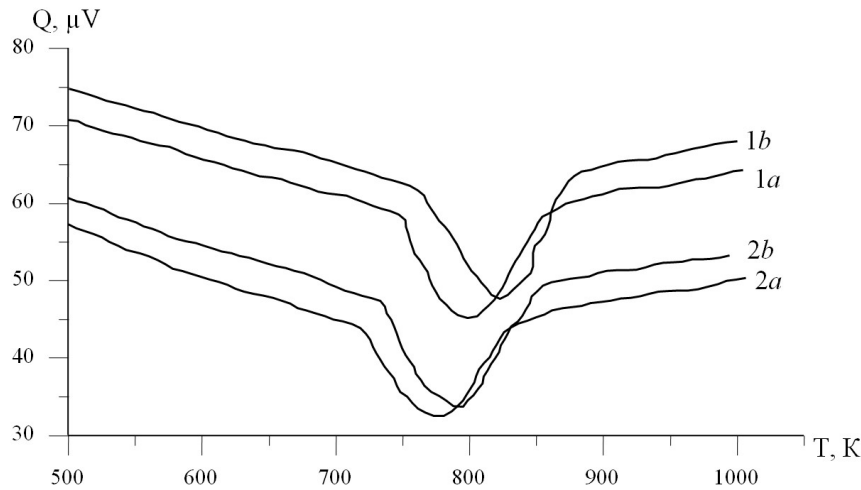


Figure 2: DTA curves of Co-W alloys: 1a – $\text{Co}_{62}\text{W}_{38}$ (direct current); 1b – $\text{Co}_{62}\text{W}_{38}$ (pulsed current); 2a- $\text{Co}_{75}\text{W}_{25}$ (pulsed current); 2b – $\text{Co}_{75}\text{W}_{25}$ (direct current)

The further temperature increase result in transformation processes associated with the subsequent separation and increase in the fraction of the crystalline α -Co phase, as well as the separation of the Co_3W phase from the remaining amorphous phase. Increasing of the annealing temperature to 870 K leads to the final decomposition of the amorphous phase in all the alloys considered, the coating structure being a mixture of crystalline α -Co and Co_3W phases. Thus, it was found that as a result of heating, the crystallisation process in alloys with lower tungsten content is more intense and occurs at lower temperatures. It should be noted that obtaining amorphous coatings by means of pulse current allows increasing the temperature of the beginning of their crystallisation by 15-20 degrees compared to films deposited in more equilibrium conditions, i.e. at direct current. As a result of the analysis of DTA curves, isothermal annealing points of 590 K, 650 K, 710 K, 770 K, 830 K, 890 K, 950 K were selected, which allowed us to investigate the temperature stability of the films under study.

Table 2 shows the changes in the structure of Co-W alloys after isothermal annealing. In films with 25 at. % tungsten content, α -Co release occurs already at 720 K, indicating the presence of crystalline α -Co in the initial state. All alloys of all compositions obtained by pulsed current are more heat resistant than films obtained by direct current. By increasing tungsten concentration, the temperature stability of the films increases, which is caused by the inhibition of the processes of nucleation of crystalline phases in more disordered alloys.

Table 2: Dependence of the Co-W film structure on the annealing temperature

Alloy composition	Deposition mode	Annealing temperature, K						
		720	740	750	765	835	850	870
$\text{Co}_{62}\text{W}_{38}$	Direct current	A	A	A+ α	A+ α	A+ α	α + β	α + β
$\text{Co}_{62}\text{W}_{38}$	Pulsed current($f=20$ Hz, $Q=6$)	A	A	A	A+ α	A+ α	A+ α	α + β
$\text{Co}_{75}\text{W}_{25}$	Direct current	A+ α	A+ α	A+ α	A+ α	α + β	α + β	α + β
$\text{Co}_{75}\text{W}_{25}$	Pulsed current($f=20$ Hz, $Q=6$)	A	A+ α	A+ α	A+ α	A+ α	α + β	α + β

Figure 3 shows the diffraction patterns of $\text{Co}_{75}\text{W}_{25}$ films electrodeposited at pulse mode ($f=20$, $Q=6$) after isothermal annealing for 30 minutes, which can be used to trace the crystallisation process of the alloy.

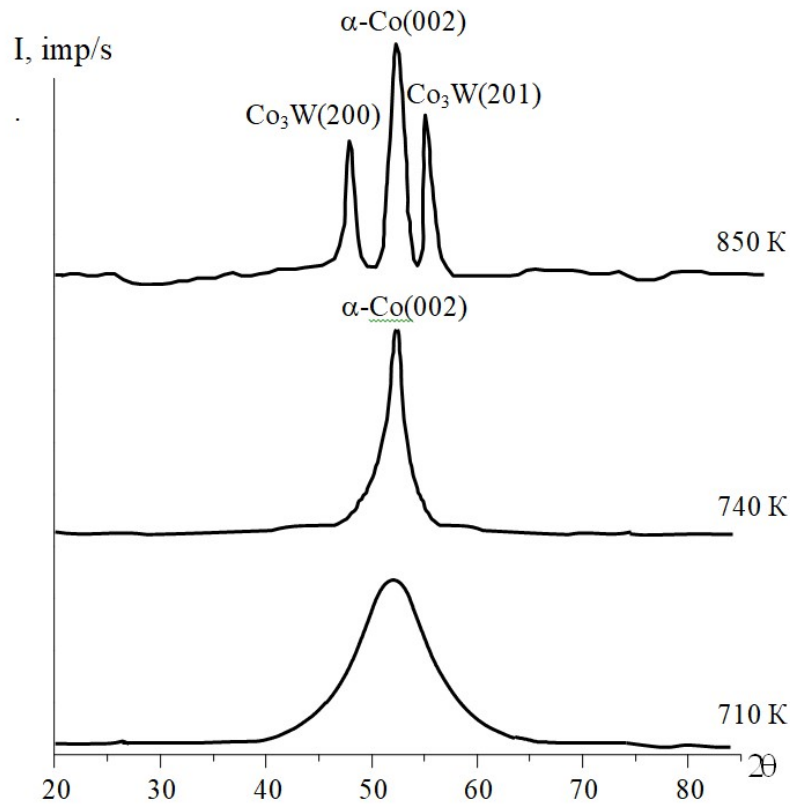


Figure 3: Diffraction patterns of $\text{Co}_{75}\text{W}_{25}$ films after isothermal exposures

It follows from the diffraction patterns that at annealing temperatures up to 740 K there is no significant change in the structure of $\text{Co}_{75}\text{W}_{25}$ films and the amorphous phase remains the main structural component. At the annealing temperature of 740 K, the line (002) of α -Co HCP lattice appears on the diffraction pattern, and at 850 K, the lines (200) and (201) of Co_3W phase appear.

The increase in the thermal stability of amorphous alloys, in addition to the tungsten content in the films, is also influenced by the conditions of their production. In films, which are close in composition, but obtained under pulse modes as opposed to steady ones, the onset of the metastable state decay, formation and growth of crystalline nuclei is shifted towards higher temperatures. The same can be said about the temperature of completion of phase transformations in alloys obtained using pulsed and steady modes. This feature can be explained, on the one hand, by the fact that the overvoltage at the cathode and its rate of change can be compared with the rate of supercooling. As the cooling rate increases, the amorphous state is fixed at higher glass formation temperatures, so the amorphous structure corresponds to higher liquid temperatures. As a consequence, amorphous alloys deposited at different cathode overvoltages have different viscosity values in the initial state, and consequently, different values of the diffusion coefficient [14].

The second reason, which gives rise to a shift in the onset temperature of the metastable state decay, may be related to impurity inhibition of the interfacial boundary between the nuclei that were formed at the moment of the current pulse action. Then these data can be explained in the framework of the theory of impurity inhibition [15, 16], which is based on the experimental fact that impurity atoms (in our case, tungsten) are adsorbed on inhomogeneities of the structure, on intergrain and interphase boundaries, in this case on the side faces of the nuclei (clusters) of the metallic phase. The smaller the nuclei, the higher their total surface area, which is covered by impurities. As a result of heating, nucleation growth occurs, which leads to enrichment of the interphase boundary with impurities, due to a decrease in the total area of the boundary and redistribution of impurities between phases. The boundary becomes "loaded" with impurities, and its migration, as a result of growth of a new phase, requires

energy expenditure. This leads to a decrease in the speed of migration of the boundaries, as they must spend energy to "advance" in front of them impurities (tungsten accumulations), which, in turn, causes a shift in time of the temperature of the beginning and end of the phase transition.

Conclusions

1. The formation of the amorphous state in Co-W alloy is significantly influenced by the non-equilibrium of the crystallisation process during pulse electrodeposition, which depends on the rate of change of the cathodic overvoltage. At pulse deposition the amorphous state in Co-W alloy is achieved at a lower content of sodium tungstate (8 g/l) in the aqueous electrolyte solution than in films obtained at direct current (11 g/l).
2. During heating of amorphous Co-W alloys, crystallisation starts at temperatures above 740 K with the release of crystalline α -Co from the amorphous component of the phases. At further temperature increase above 850 K, the formation of Co_3W phase occurs with simultaneous increase in the fraction of crystalline base metal phase. The final products of the decomposition of amorphous Co-W alloys during heating are a mixture of the equilibrium phases of α -Co and Co_3W .
3. The crystallisation kinetics of amorphous Co-W alloys is influenced not only by the sodium tungstate content in the aqueous electrolyte solution, but also by the non-equilibrium conditions of the crystallisation process during pulse electrodeposition. In alloys with the same concentration of tungsten obtained under pulse deposition modes, the onset of crystallisation during annealing shifts to the region of higher temperatures, compared to alloys obtained with direct current.

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