Electrochemical Synthesis of Binary Carbides of Tungsten and Iron (Nickel, Cobalt) in Halide-Oxide Melts at 823 K

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Iron, cobalt and nickel powders are used as binding components for the production of articles of tungsten carbide by the hot pressing method. This fact and the unique properties of binary carbides of tungsten-iron triad metals encouraged the search for new ways of their synthesis. In the present work, the attempt to synthezise binary tungsten-nickel (cobalt, iron) carbides in molten KCl-NaCl-CsCl at 823 K was made.

As a result of voltammetry research, it was established that in eutectic KCl-NaCl-CsCl melts the deposition potentials of W and Ni (Co, Fe) differ by 150 – 350 mV from each other, which makes their co-deposition difficult. It is possible to shift the deposition potentials of tungsten and metals of the iron triad metals towards each other by changing the acid-base properties of the melt. The products of electrolysis in these molten system were identified by X-ray analysis. They are mixtures of tungsten and nickel (cobalt, iron) carbides: Ni_2W_4C, $W_6C_{2.54}$; Co_3W_3C, Co_6W_6C, W_2C, Co_3C; FeW_3C.

Key words: High-Temperature Electrochemical Synthesis; Binary Carbides; Voltammetry; Molten Halides.

Iron, cobalt and nickel powders are used as binding components for the production of articles of tungsten carbide by the hot pressing method. This fact and the unique properties of binary carbides of tungsten-iron triad metals encouraged the search for new ways of their synthesis. The method of high-temperature electrochemical synthesis is rather perspective for solving these problems.

The authors [1] carried out the electrochemical synthesis of binary carbides at 1023 K in a molten KCl-NaCl eutectic on the basis of processes of tungsten, iron triad metal and carbon electrochemical co-deposition.

In the present work, the attempt to synthezise binary tungsten-nickel (cobalt, iron) carbides in molten KCl-NaCl-CsCl at 823 K was made. We studied the electrochemical co-deposition of tungsten, iron (nickel, cobalt) and carbon with the help of cyclic voltammetry and potentiostatic electrolysis. The identification of the obtained samples was performed by X-ray analysis.

As a result of the voltammetry research, it was established that in eutectic KCl-NaCl-CsCl melts the deposition potentials of W and Ni (Co, Fe) differ by 150 – 350 mV from each other, which makes their co-deposition difficult. It is possible to shift the deposition potentials of tungsten and metals of the iron triad metals towards each other by changing the acid-base properties of the melt.

In an earlier work [2] we showed that changing the concentration of F^- and O^{2-} ions in the melt makes various tungsten fluoroxide complexes turn into one $[WOF_6]^{2-}$. In the present work we used NaF and K_2SiF_6 as the source of fluoride ions.

The voltammetry curves of molten KCl-NaCl-CsCl eutectic-NaF (7.5 wt%) that contains $3.0 \cdot 10^{-4}$ mol/cm^3 of $Na_3WO_3F_3$ at nickel (cobalt, iron) chloride consecutive addition are presented in Figure 1. As it can be seen, the introduction of nickel (cobalt) chloride ($1.0 \cdot 10^{-5}$ mol/cm^3) leads to the appearance of a nickel (cobalt) reduction wave at -(0.45 – 0.5) V versus the potential of a platinum-oxygen reference electrode. With an increase of the nickel (cobalt) chloride concentration in the melt the electrodeposition potentials of nickel (cobalt) and tungsten approach

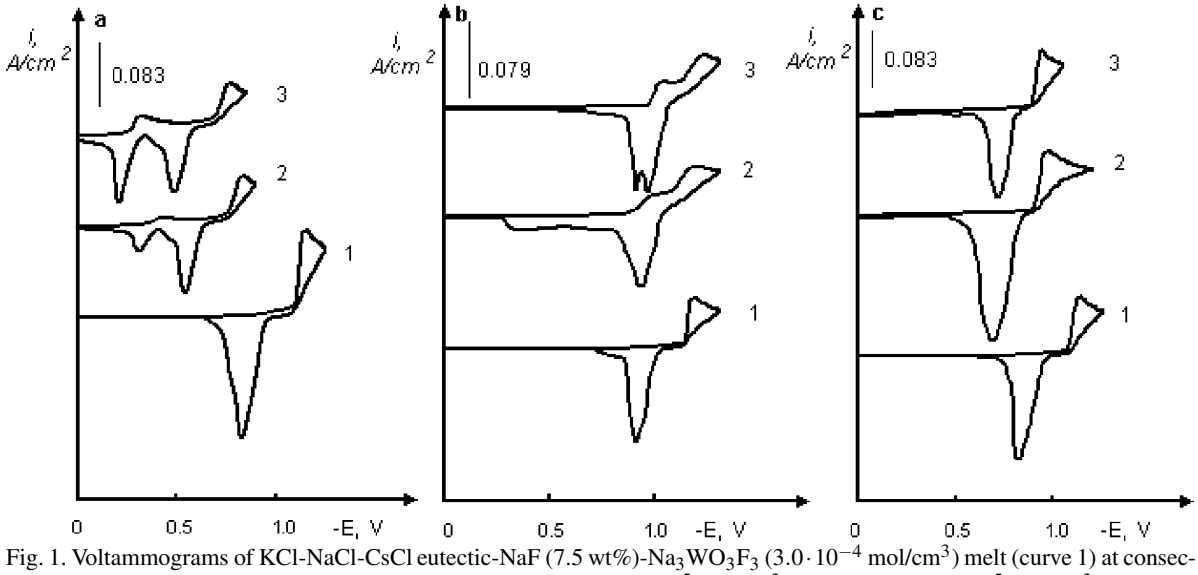

Fig. 1. Voltammograms of KCl-NaCl-CsCl eutectic-NaF (7.5 wt%)-$Na_3WO_3F_3$ ($3.0 \cdot 10^{-4}$ mol/cm^3) melt (curve 1) at consecutive addition (curves 2, 3) of: (a) nickel chloride; curve 2: $c = 1.0 \cdot 10^{-5}$ mol/cm^3; curve 3: $c = 3.0 \cdot 10^{-5}$ mol/cm^3; (b) cobalt chloride; curve 2: $c = 1.0 \cdot 10^{-5}$ mol/cm^3; curve 3: $c = 3.0 \cdot 10^{-5}$ mol/cm^3; (c) iron chloride; curve 2: $c = 3.0 \cdot 10^{-5}$ mol/cm^3; curve 3: $c = 5.0 \cdot 10^{-5}$ mol/cm^3. Polarization rate, 0.1 V/s; T, 823 K; working electrode, platinum.

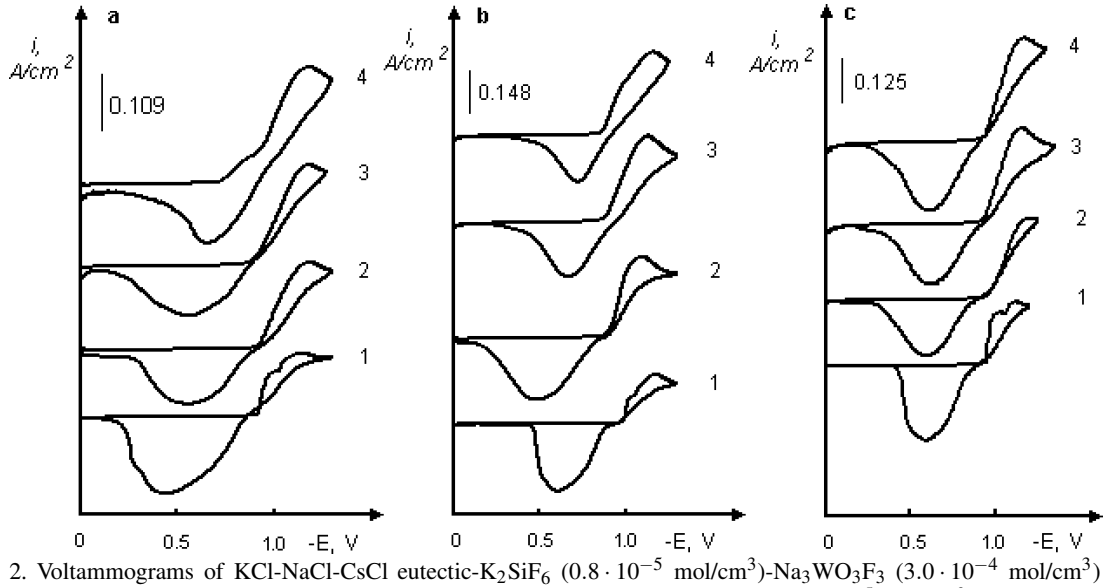

Fig. 2. Voltammograms of KCl-NaCl-CsCl eutectic-K_2SiF_6 ($0.8 \cdot 10^{-5}$ mol/cm^3)-$Na_3WO_3F_3$ ($3.0 \cdot 10^{-4}$ mol/cm^3) melt (curve 1) at consecutive addition (curves 2, 3) of: (a) nickel chloride; curve 2: $c = 1.0 \cdot 10^{-5}$ mol/cm^3; curve 3: $c = 3.0 \cdot 10^{-5}$ mol/cm^3; (b) cobalt chloride; curve 2: $c = 1.0 \cdot 10^{-5}$ mol/cm^3; curve 3: $c = 3.0 \cdot 10^{-5}$ mol/cm^3; (c) iron chloride; curve 2: $c = 3.0 \cdot 10^{-5}$ mol/cm^3; curve 3: $c = 5.0 \cdot 10^{-5}$ mol/cm^3. Polarization rate, 0.1 V/s; T, 823 K; working electrode, platinum.

each other. Also, a shift of the voltammogram towards more positive potentials is observed. The introduction of iron chloride ($3.0 \cdot 10^{-5}$ mol/cm^3) into the melt results in the appearance of a cathodic peak at -(1.00–1.15) V versus the potential of the platinum-oxygen reference electrode (Fig. 1c). The deposition potentials of W and Fe in a chloride-fluoride KCl-NaCl-CsCl eutectic-NaF (7.5 wt%) melt practically coincide,

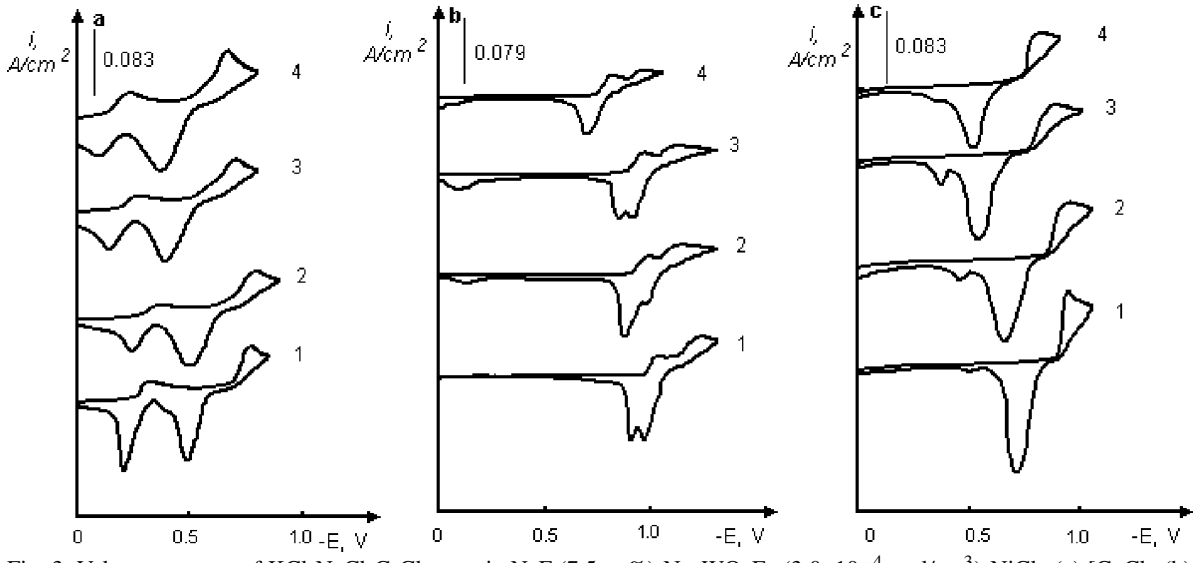

Fig. 3. Voltammograms of KCl-NaCl-CsCl eutectic-NaF (7.5 wt%)-$Na_3WO_3F_3$ ($3.0 \cdot 10^{-4}$ mol/cm^3)-$NiCl_2$ (a) [$CoCl_2$ (b), $FeCl_2$ (c), $2.0 \cdot 10^{-5}$ mol/cm^3] at consecutive increase of CO_2 pressure: curve 1: $p(CO_2) = 0 \cdot 10^5$ Pa; curve 2: $p(CO_2) = 4 \cdot 10^5$ Pa; curve 3: $p(CO_2) = 8 \cdot 10^5$ Pa; curve 4: $p(CO_2) = 12 \cdot 10^5$ Pa. Polarization rate, 0.1 V/s; T, 823 K; working electrode, platinum.

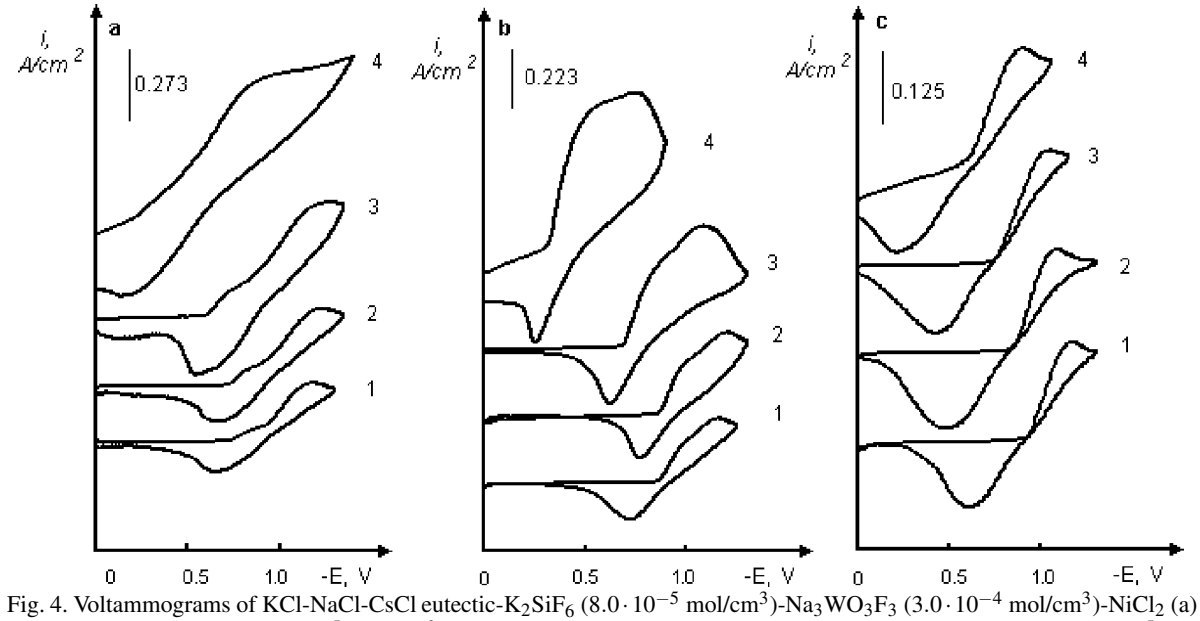

Fig. 4. Voltammograms of KCl-NaCl-CsCl eutectic-K_2SiF_6 ($8.0 \cdot 10^{-5}$ mol/cm^3)-$Na_3WO_3F_3$ ($3.0 \cdot 10^{-4}$ mol/cm^3)-$NiCl_2$ (a) [$CoCl_2$ (b), $FeCl_2$ (c), $2.0 \cdot 10^{-5}$ mol/cm^3] at consecutive increase of CO_2 pressure: curve 1: $p(CO_2) = 0 \cdot 10^5$ Pa; curve 2: $p(CO_2) = 4 \cdot 10^5$ Pa; curve 3: $p(CO_2) = 8 \cdot 10^5$ Pa; curve 4: $p(CO_2) = 12 \cdot 10^5$ Pa. Polarization rate, 0.1 V/s; T, 823 K; working electrode, platinum.

which enables obtaining their alloys and intermetallic compounds.

The voltammograms of KCl-NaCl-CsCl eutectic-K_2SiF_6-$MeCl_2$ (Me = Ni, Co, Fe) melt are shown in Figure 2. It can be seen that the deposition potentials of nickel, cobalt and iron are -0.75 V, -0.87 V and -1.12 V, respectively, versus the potential of the platinum-oxygen reference electrode.

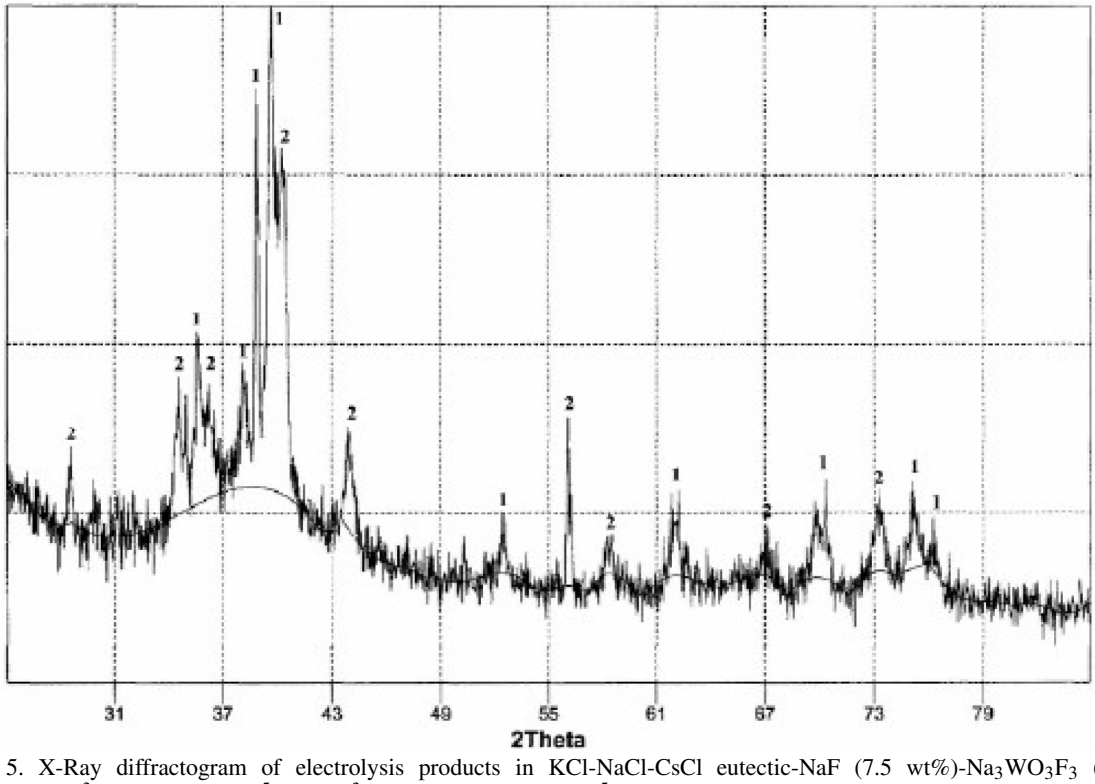

Fig. 5. X-Ray diffractogram of electrolysis products in KCl-NaCl-CsCl eutectic-NaF (7.5 wt%)-$Na_3WO_3F_3$ ($3.0 \cdot 10^{-4}$ mol/cm^3)-$NiCl_2$ ($2.0 \cdot 10^{-5}$ mol/cm^3)-CO_2 [$p(CO_2) = 15 \cdot 10^5$ Pa] melt. 1, Standard lines of W_2C; 2, standard lines of Ni_2W_4C.

It is possible to assume from these data that the formation of tungsten and iron compounds is the most probable process, as the condition of two components co-deposition [W and Ni (Co, Fe) in our case] is closeness of the potentials of their electrochemical deposition.

To obtain binary carbides, $Me_xW_yC_z$, we investigated the process of electrochemical co-deposition of tungsten fluoroxide complexes, iron (nickel, cobalt) ions and carbon dioxide in KCl-NaCl-CsCl eutectic-NaF (7.5 wt%) (Fig. 3) and KCl-NaCl-CsCl eutectic-K_2SiF_6 ($8 \cdot 10^{-5}$ mol/cm^3) (Fig. 4) melts.

The introduction of carbon dioxide (under excessive pressure) into the system does not result in the appearance of additional carbon reduction waves in the voltammograms (Figs. 3, 4). The increase of carbon dioxide pressure leads to an increase in the difference between cathodic and anodic peak potentials, while the voltammogram elongates along the potential axis, which tells the electrode process becomes more irreversible. When the carbon dioxide pressure is above $8 \cdot 10^5$ Pa, the voltammetry dependences shift towards more positive potentials because of the change in the potential of the reference electrode.

We investigated the electrochemical synthesis of the binary carbides of W-Ni (Co, Fe) based on the voltammetry results shown above. We carried out potentiostatic electrolysis in the range of -(1.1 – 1.3) V in the molten systems KCl-NaCl-CsCl eutectic-K_2SiF_6 ($1.2 \cdot 10^{-4}$ mol/cm^3)-$Na_3WO_3F_3$ ($3.0 \cdot 10^{-4}$ mol/cm^3)-$MeCl_2$ ($2.0 \cdot 10^{-5}$ mol/cm^3)-CO_2 ($15 \cdot 10^5$ Pa) and KCl-NaCl-CsCl eutectic-NaF (7.5 wt%)-$Na_3WO_3F_3$ ($3.0 \cdot 10^{-4}$ mol/cm^3)-$MeCl_2$ ($2.0 \cdot 10^{-5}$ mol/cm^3)-CO_2 ($15 \cdot 10^5$ Pa), where Me = Ni, Co, Fe.

The products of electrolysis in these molten systems are mixtures of tungsten and nickel (cobalt, iron) carbides: Ni_2W_4C, $W_6C_{2.54}$; Co_3W_3C, Co_6W_6C, W_2C, Co_3C; FeW_3C. The X-ray diffractograms of the electrolysis products are shown in Figs. 5 and 6.

It has been established that in a KCl-NaCl-CsCl eutectic-$Na_3WO_3F_3$ melt tungsten exists in the form of two fluoroxide complexes, $[WO_2F_4]^{2-}$ and $[WOF_6]^{2-}$. The conditions of electrochemical co-reduction of tungsten fluoroxide complexes, carbon dioxide and

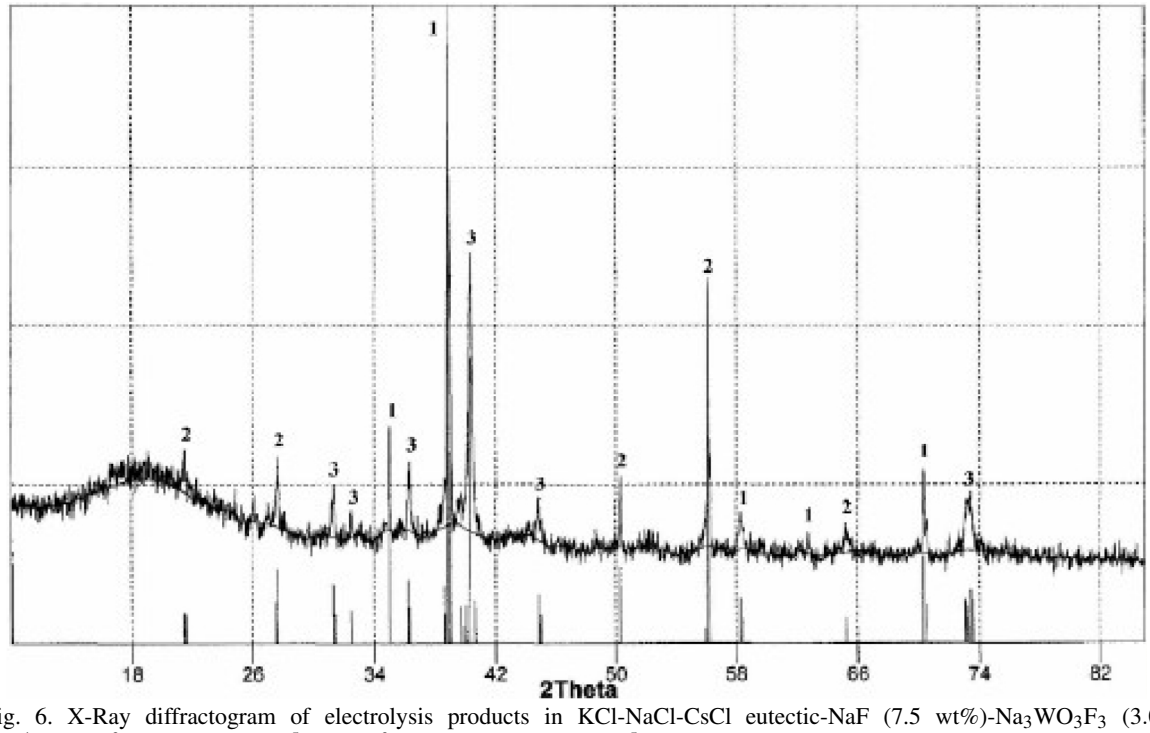

Fig. 6. X-Ray diffractogram of electrolysis products in KCl-NaCl-CsCl eutectic-NaF (7.5 wt%)-$Na_3WO_3F_3$ ($3.0 \cdot 10^{-4}$ mol/cm^3)-$FeCl_2$ ($2.0 \cdot 10^{-5}$ mol/cm^3)-CO_2 [$p(CO_2) = 15 \cdot 10^5$ Pa] melt. 1, Standard lines of W_2C; 2, standard lines of Co_3W_3C; 3, standard lines of Co_6W_6C.

nickel (cobalt, iron) ions in KCl-NaCl-CsCl-based halide-oxide melts have been found.

As a result of the performed research, the feasibility of binary tungsten-nickel (cobalt, iron) carbides (Co_6W_6C, Ni_2W_4C, Ni_3W_3C, Co_3W_3C, FeW_3C) electrochemical synthesis in the above-mentioned halide-oxide melts at of 823 K has been shown.

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[2] H. B. Kushkhov, M. N. Adamokova, and R. Z. Oshroeva, in: Proceedings of the 7th International Symposium on Molten Salts Chemistry and Technology, August 29 – September 2, 2005, Toulouse, France, pp. 899-902.