

HIGH-TEMPERATURE ELECTROCHEMICAL SYNTHESIS OF CARBON-CONTAINING INORGANIC COMPOUNDS UNDER EXCESSIVE CARBON DIOXIDE PRESSURE

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(Received 10 January 2003; accepted 18 March 2003)

Abstract

Features of the electroreduction of carbon dioxide dissolved in the equimolar melt of sodium and potassium chlorides under excessive pressure of up to 1.7 MPa have been studied by cyclic voltammetry over a wide polarization rate range. It has been found that the electrode process occurs in two stages at sweep rates of $\leq 0.1 \text{ V s}^{-1}$, and its mechanism has been suggested. The cathodic product is polycrystalline graphite. Systems and conditions for producing two- and three-component refractory metal carbides using CO_2 as a synthesis component have been selected.

Keywords: electrochemical synthesis, voltammetry, carbon dioxide, carbon films, refractory carbides

1. Introduction

The interest in electrode processes involving gases in ionic melts is due to their wide use in high-temperature technological processes (electrometallurgy, high-temperature current sources, and electrochemical synthesis in melts). Processes of halogen ionization in halide melts, hydrogen oxidation and oxygen ionization in carbonate melts are most exhaustively studied [1]. However, there are only a limited number of publications dealing with the electrochemical decomposition of carbon dioxide dissolved in halide

melts [2, 3]. The authors pointed out poor reproducibility of the results obtained, particularly at low gas pressures and potential sweep rates. This is due to the low solubility of CO_2 gas, which interacts weakly with the melt. The only possible way to raise the rate of the electrode process is to generate an excessive gas pressure over the melt. The cathodic product of electroreduction is carbon, which was produced in the form of powder. Investigation of the electroreduction of just this gas is of high interest since CO_2 can be used in fuel cells, in the electrosynthesis of metal carbides as carbon source, and to produce carbon films (coatings) of different structure. In recent years, carbon films of various structures have been widely used as a new electrode material in various electrochemical processes. This is connected with several of their unique electrochemical characteristics [4]. Hence, the knowledge of the laws governing electrode processes involving carbon dioxide is interesting both in terms of elucidation of transport properties and general nature of gas solutions in molten salts. It is also interesting in terms of understanding the regularities and controlling the process of the electrosynthesis of carboniferous inorganic compounds. These investigations are also interesting in terms of ecology being one of the possible ways of the electrochemical utilization of carbon dioxide. The aim of the present work was to study the features of carbon dioxide electroreduction in molten salts of different composition in order to use this process for the electrosynthesis of binary and ternary refractory metal carbides, and assess the possibility of producing carbon films of different structure.

2. Experimental

The electrochemical behavior of carbon dioxide under excessive pressure was investigated in a three-electrode cell made of special stainless steel, which permitted measurements at temperatures up to 900 °C and at an excessive gas pressure of 1.5 MPa. Voltametry with single and cyclic potential sweep was chosen as the method of investigation. Voltametric curves were taken by means of a PI-50-1 potentiostat in the polarization rate range of 0.005–10 V/s. A glassy carbon or platinum crucible served as the anode and, at the same time, as melt container. A fully dipped and semi-dipped platinum pin electrodes (wire diameter 0.5±1 mm, area of the electrode ~0.2 cm²) were used as indicator electrodes.

A difficulty was experienced when choosing the reference electrode. Preliminary investigations showed that lead and silver chloride electrodes, which are commonly used in molten chlorides, lose their functions when increased gas pressures are generated, which may be due to the effect of carbon dioxide on their electrode reactions and diaphragm properties. Analysis of literature data on the use of different reference electrodes in molten salts [5, 6, 7] and experimental features of conducting the process under excessive pressure showed a non-polarizable platinum (or gold) electrode dipped in the melt under investigation, which is in carbon dioxide atmosphere, to be the most

suitable variant for our system. In some cases, a glassy carbon rod was used as the anode and a platinum crucible as the reference electrode. At this electrode, when there is some oxygen impurity in the applied gas, the following equilibrium exists:



The reversibility of such electrodes has been proven in Refs.[7, 8] However, this electrode can be called “reference electrode” only conditionally since its potential depends on the carbon dioxide pressure in the system.

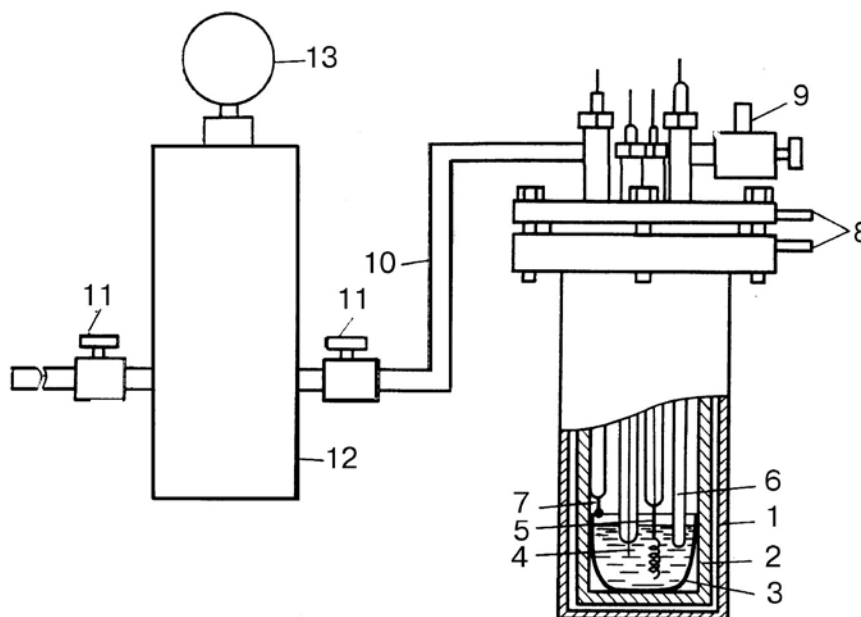


Figure 1. Principal circuit of the high-temperature cell for electrochemical investigations under excessive gas pressure: 1-high-temperature stainless steel box, 2-quartz box, 3-crucible, 4- indicator electrode, 5-reference electrode, 6-thermocouple, 7-Pt lead wire for crucible, 8-water cooling for cell cover, 9-valve of pressure release in cell, 10-hose coupling, 11-gas control valves, 12-intermediate gas container (filling volume-2 liters), 13-gauge-pressure manometer.

A mixture of extra pure potassium and sodium chlorides was used as the solvent melt. We used this system in the synthesis of tungsten carbide, and the solubility of CO_2 in these salt mixtures under atmospheric pressure has been studied well by different methods. The purity of the mixture was checked by measuring residual current magnitude ($i_{res}=1.2 \text{ mA/cm}^2$ at $E=-1 \text{ V}$). Investigations were carried out in the temperature range $700\div 850 \text{ }^\circ\text{C}$ at a CO_2 pressure of $0.1\div 1.52 \text{ MPa}$. The temperature was maintained with accuracy to $\pm 5 \text{ }^\circ\text{C}$. Polarization curves were taken after keeping the

system under isothermal and isobaric conditions for not less than 1 h, i.e. after attaining the equilibrium:

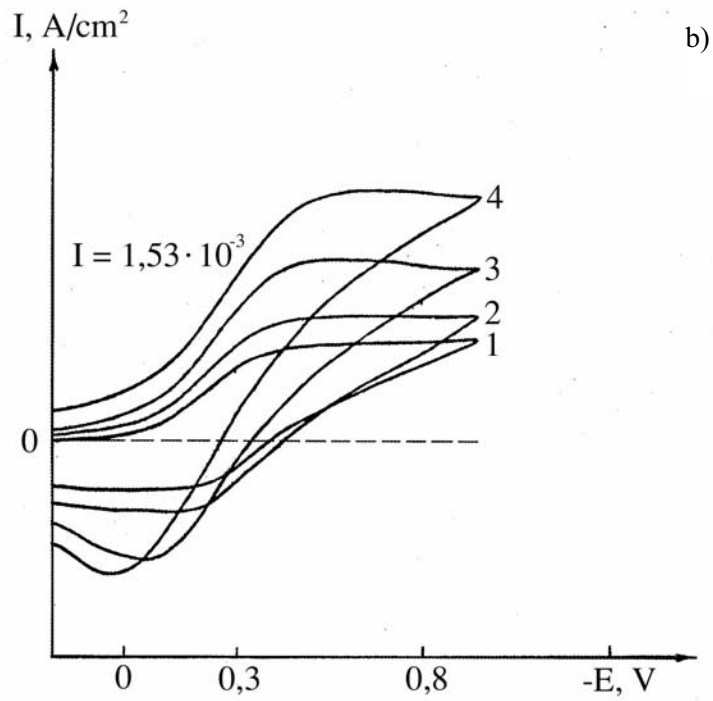
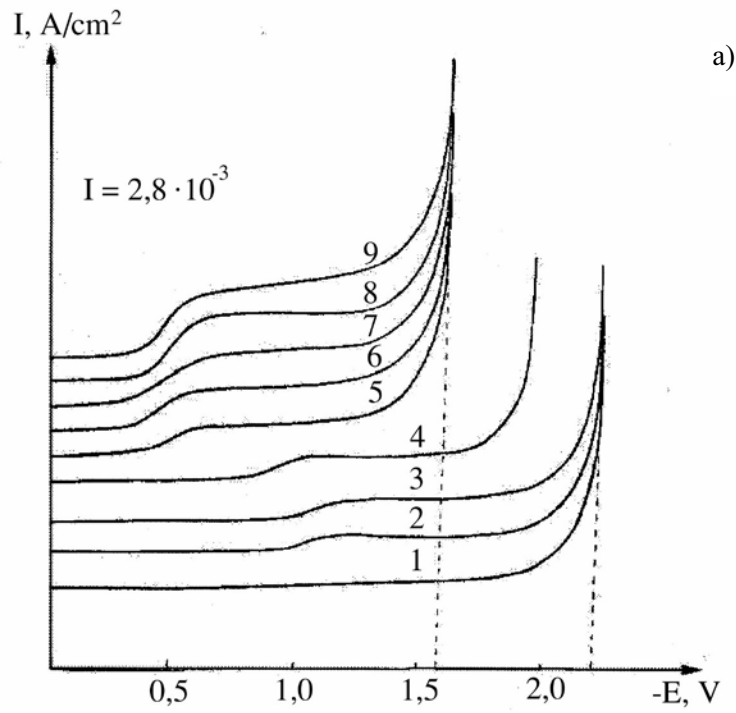


The electrolysis experiments were carried out in the same cells as voltametric measurements. The product settled down onto the crucible bottom and was extracted together with the solidified electrolyte, separated from it mechanically. The salt was grounded and the deposit was separated from it by successive leaching with hot water. Thereafter, the precipitate was washed with distilled water, filtered off and dried to a constant mass at 100-150°C. The electrolysis products were analyzed by X-ray and chemical methods.

3. Results and discussion

In view of the specific character of voltametric measurements in melts under excessive pressure, which was pointed out in the Introduction, we have studied the behavior of a platinum reference electrode, dipped in the melt under investigation, in the case of change of the gas phase over the melt. The variation of the function of the reference electrode on carbon dioxide content in the system was estimated from the alkali metal deposition potential (discharge of the base electrolyte), considering it to be independent of the gas atmosphere composition. Fig.2 shows voltamograms for a chloride melt in the case of carbon dioxide content at different pressures and polarization rates. It is seen from Fig.2(a) that gas content into the cell gives rise to a CO_2 reduction wave at potentials of $-0.9 \div -1.1$ V with respect to platinum-oxygen reference electrode. It has been found that when the gas pressure in the system is gradually increased, the reference electrode potential shifts towards values that are more positive. At low CO_2 pressures over the melt, the reference electrode still functions as a platinum-oxygen electrode (curves 2, 3 in Fig. 2(a)), and in the pressure range $0.5 \div 0.7$ MPa its function changes. Beginning with the pressure $P_{CO_2}=0.7$ MPa, the function of the reference electrode becomes constant and corresponds to that of platinum-carbonate reference electrode. The CO_2 discharge potential range in this case is $-0.3 \div -0.5$ V. If the cell is first evacuated and then filled with carbon dioxide, its reduction waves are observed at once at potentials of $-0.3 \div -0.5$ V, i.e. the reference electrode operates as a platinum carbonate electrode. Thus, the difference in equilibrium potential between platinum-carbonate and platinum-oxygen electrodes is 0.6 V. All experiments for investigation of the features of CO_2 reduction were performed firstly with evacuating the system and then passing carbon dioxide through the system for 10 minutes.

At polarization rates over 0.5 V s^{-1} , it was found that the process occurred in one stage (Fig.2 (b)). Cyclic sweeping shows the presence of an anodic dissolution wave of the cathodic-cycle product, whose height is practically equal to that of the cathodic wave. The use of semi-dipped indicator electrodes (the surface area of the dipped portion is the same as for fully dipped electrode) gives an increase of the order of 30 % in the wave height. The character of the charge transfer step of the process under study was



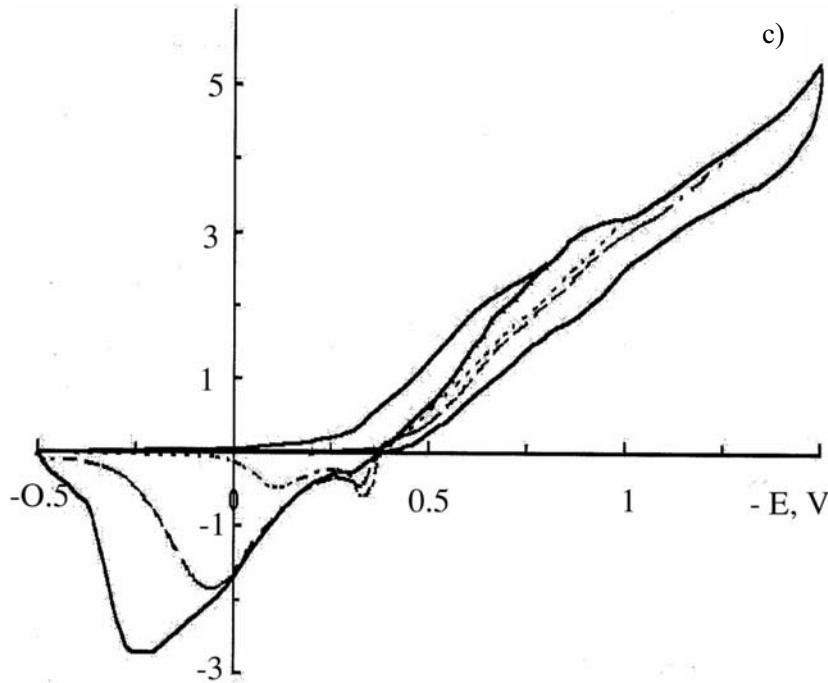


Figure 2. Voltammograms of NaCl-KCl(1:1)-CO₂ melt at a Pt electrode:
 (a) at various gas pressures, $\times 10^5$ Pa: 1-0, 2-1, 3-2.5, 4-5, 5-7.5, 6-10, 7-12.5, 8-15, 9-17. $T=700$ °C, $V=0.1$ V·s⁻¹;
 (b) at various potential scan rates, V·s⁻¹: 1-1, 2-2, 3-5, 4-10, $T=700$ °C, $P_{CO_2}=5 \times 10^5$ Pa;
 (c) at various potential reverses. $V=0.1$ V·s⁻¹, $PCO_2=5 \times 10^5$ Pa.

determined by the known diagnostic criteria of non-stationary voltametry, viz. Matsuda-Ayabe criterion [9] for peak half-width:

$$E_{p/2} - E_p = 1.857RT/\alpha n_\alpha F \quad (3)$$

And criterion of the dependence of half-peak potential on the logarithm of polarization rate (Delahay equation [10]):

$$E_{p/2} = -C RT/\alpha n_\alpha F - \ln(D^{1/2})RT/\alpha n_\alpha F + \ln(k_{fh}^o)RT/\alpha n_\alpha F - \ln(\alpha n_\alpha \nu^{1/2})RT/\alpha n_\alpha F \quad (4)$$

where D is the diffusion coefficient of the species being discharged, cm²·s⁻¹; ν is the electrode polarization rate, V·s⁻¹; k_{fh}^o is charge-transfer rate constant, cm²·s⁻¹; C is

temperature-dependent constant, E_p , $E_{p/2}$ are peak and half-peak potentials, V; α is the apparent coefficient of charge transfer, n_α is the number of electrons transferred in the potential-determining step.

As it is seen from Fig.2b, the cathodic and anodic peak potentials of the cyclic voltamograms depend on polarization rate, and their difference exceeds that for reversible four-electron process. This points to the rate-determining role of the charge-transfer step. The linear dependence of the wave current on gas pressure (Fig.2a) and the dependence of the peak current, as well as the formal value of αn_α on polarization rate (Fig.3), indicate a mixed nature of the electrode process. Thus, the electroreduction of CO_2 is controlled by both transfer rate and the rate of gas diffusion to the electrode.

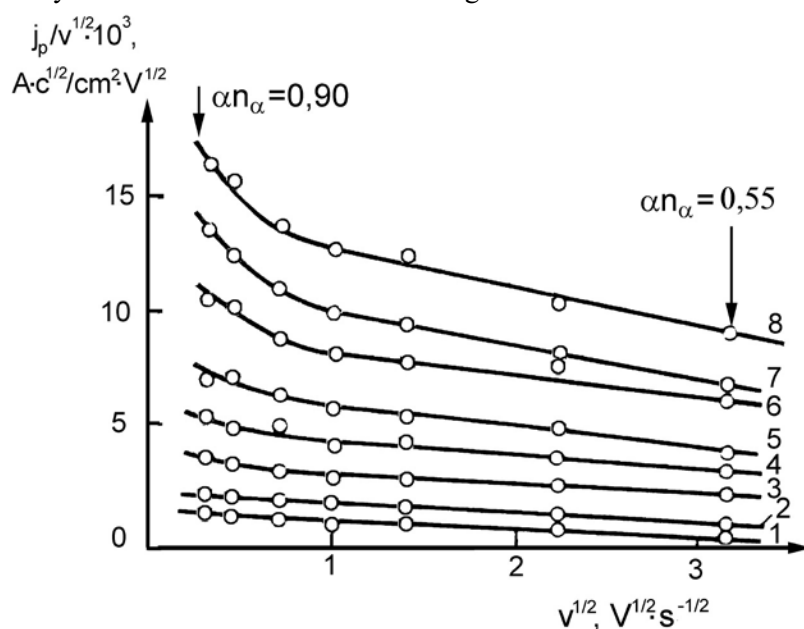


Figure 3. Plots $I_p/v^{1/2}$ against $v^{1/2}$ for the CO_2 electroreduction wave at different gas pressures, $\times 10^5$ Pa: 1-1, 2-2, 3-2.5, 4-5, 5-7.5, 6-10, 7-12, 8-15.

Further investigations showed that at low electrode polarization rates (below 0.1 V s^{-1}), voltamograms exhibit two well-defined waves. The first at $E_{1/2} = -0.44 \text{ V}$ and the second at $E_{1/2} = -0.78 \text{ V}$. The difference between the waves is $0.3\text{-}0.4 \text{ V}$. On the reverse sweep, no anodic current is observed after the first wave (Fig. 2c). If reversal of the sweep takes place after the limiting current of the second wave, two waves appear on the reverse sweep. As the reversal potential shifts towards more negative values, the first-

wave current decreases, and the potential remains unchanged; the peak potential of the second wave shifts towards more positive values, and its current increases. To elucidate the mechanism of the processes occurring at the cathode, the potentiostatic electrolyses at first-wave and second-wave potentials have been carried out. Electrolysis at the first-wave potential gave unsound deposits with fairly good adhesion but with a low current efficiency. In electrolysis at the second wave potential, also unsound but black deposits were obtained. In the case of galvanostatic electrolysis, the adhesion and homogeneity of the film are better than those of films deposited under potentiostatic conditions. We failed to determine the current efficiency for black films because many of them crumbled on cooling down and on washing them free from salts. Electrolysis of different duration has been carried out at several pressures and several temperatures, but this had no noticeable effect on the quality of the deposits obtained. A microprobe analysis of the deposits obtained has been performed; it showed the gray deposits to consist only of electrolyte impurities (*Ca, Mg, Si, Zn* and some others) which should not have deposited at the given potentials, and the black deposits to consist mainly of carbon. Scanning electron micrographs of deposits have been obtained and shown in Fig. 4. Electron-diffraction method showed that the deposit is a polycrystalline graphite (Fig. 4b IV).

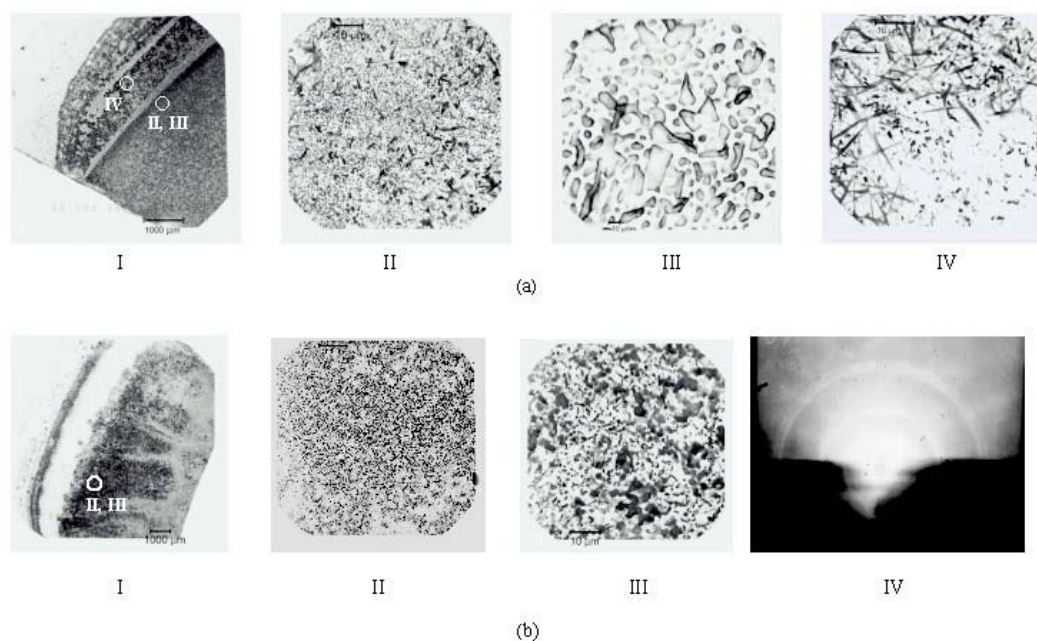


Figure 4. Photomicrographs and electron (-beam) image (b IV) of the films obtained under potential-controlled electrolysis conditions in the system $\text{NaCl-KCl}(1:1)\text{-CO}_2$:

(a) at $E_{\text{cathode}} = -0.6 \text{ V}$, $P_{\text{CO}_2} = 10 \times 10^5 \text{ Pa}$, $\tau = 4.5 \text{ h}$, $T = 750^\circ\text{C}$;

(b) at $E_{\text{cathode}} = -0.9 \text{ V}$, $P_{\text{CO}_2} = 5 \times 10^5 \text{ Pa}$, $\tau = 2 \text{ h}$, $T = 850^\circ\text{C}$, $\eta = 18.5 \%$.

Based on the analysis of the data obtained, it may be suggested that a two-stage charge-transfer process, separated by an irreversible chemical stage, occurs at the platinum electrode, i.e. the CO_2 electroreduction process occurs by the ECE mechanism: First stage: quasi-reversible reduction of CO_2 to CO_2^{2-} radical: $CO_2 + 2e^- = CO_2^{2-}$. The radical formed is an unstable species, which possesses strong reducing properties and reduces small impurities in the electrolyte.

Second stage: chemical formation of carbon monoxide: $CO_2^{2-} \rightarrow CO + O^{2-}$

Third stage: irreversible electroreduction of CO to polycrystalline graphite: $CO + 2e^- \rightarrow C + O^{2-}$

In this process, CO_2 acts both as a carbon source for deposit formation and as an acid, which binds the oxygen anion that is liberated in the near-electrode space. Therefore, the cathodic reaction may be represented as $3CO_2 + 4e^- \rightarrow C + 2CO_3^{2-}$.

Carrying out electrolysis at controlled potentials and current densities, under reversible electrolysis conditions, as well as through preparation of the electrode surface (to improve the adhesion of the product to the electrode) could make it possible, in our view, to govern the form and morphology of the cathodic product. Thus, electroreduction of carbon dioxide to carbon can be taken as the basis of high-temperature electrochemical synthesis (HTES) of various carboniferous inorganic compounds: carbon films, refractory carbides. If single-stage electrodeposition of a refractory metal is effected only at the minimum and fixed concentration of oxide ion in the electrolyte (e.g. Ti , Ta), this way of introduction of carbon component into the melt is the only possible one for carrying out electrosynthesis of the carbides.

3.1. Synthesis of molybdenum and tungsten carbide powders under excessive carbon dioxide pressure

The use of CO_2 (whose concentration in the melt can be controlled by excessive pressure) as carbon source can extend the range of potential applications of HTES of refractory carbides. This makes it possible to prepare a molten buffer electrolyte based on low melting metal chlorides. They can have specific acid-base properties and make it possible to carry out direct electrochemical synthesis of carbides. This method of introducing the carbon component into an electrolyte has several advantages:

- a) Decreased operating temperature for the synthesis of refractory-metal monocarbides.
- b) Use of cheaper, non-aggressive and non-hygroscopic solvent electrolytes.
- c) Carbides can be separated from the salt phase much more easily owing to the absent of secondary chemical processes (formation of slightly soluble oxides, fluorides, tungstates of alkali and alkaline-earth metals).
- d) The process is wasteless, for the electrolyte can be regenerated.

The electrodeposition of molybdenum and tungsten from their oxy-anions in a chloride melt takes place at a potential that is 0.5-0.8 V more negative than the

deposition potential of CO_2 . Therefore, the deposition potentials of refractory metals must be shifted towards more positive potentials to meet the requirements of the thermodynamic conditions of HTES. According to [11, 12], where the mechanisms of electroreduction of complicated complex anions of refractory metals has been established, methods of controlling metal deposition potentials have been developed. To this end, electrochemical species of refractory metal of different composition and structure, which are discharged at the potential of carbon deposition from CO_2 , have been formed in the melt by means of acid-base interactions. References [12, 13] showed the possibility of effecting electrochemical co-reduction of carbon dioxide and different ionic forms of molybdenum and tungsten (cationized $\{Me^{z+}_x[MO_4]^{2-zx-2}\}$, dimeric $[M_2O_7]^{2-}$, oxy-fluoride $[MO_2F_4]^{2-}$ forms) and direct HTES of carbides under excessive carbon dioxide pressure. Several compositions of plating baths for the synthesis of molybdenum and tungsten carbides have been developed and Table 1 gives the conditions for their preparation.

Table 1. Dependencies of the phase composition of cathodic products, obtained from baths of different composition, on carbon dioxide pressure in the electrolyzer at 750 °C

CO ₂ pressure, 10 ⁻¹ MPa	NaCl-KCl-Na ₂ WO ₄ (3 mol. %)-MgCl ₂ (6 mol. %) Bath voltage – 2.4 V, $\Delta_{\text{cathode}}=-1.4$ V	NaCl-KCl-Na ₂ WO ₄ (5 mol. %)-NaPO ₃ (0.75 mol. %) Bath voltage – 2.5 V, $\Delta_{\text{cathode}}=-1.5$ V	NaCl-KCl-NaF(1 mol. %)-Na ₃ WO ₃ F ₃ (3 mol. %) Bath voltage – 1.9 V, $\Delta_{\text{cathode}}=-1.1$ V
	I	II	III
0	W, MgO, MgWO ₄	W	W
2.5	W, MgO, MgWO ₄ , traces of W ₂ C	W, W ₂ C	W, traces of W ₂ C
5	W, W ₂ C, MgO, MgWO ₄	W, W ₂ C	W, W ₂ C
7.5	W ₂ C, WC, traces of W, MgO, MgWO ₄	W ₂ C, WC, traces of W	W, W ₂ C, WC
10	W ₂ C, WC, MgO, MgWO ₄	WC, W ₂ C	W ₂ C, WC
15	WC, W ₂ C, MgO, MgWO ₄	WC, traces of W ₂ C	WC, W ₂ C
17÷20	WC, MgO, MgWO ₄	*WC	*WC

* - Single phase monocarbides powder contain up to 2 wt% free carbone

Analysis of the data showed that the composition of electrolyte II is most suitable for the electrosynthesis of carbides. In these system, higher product electrodeposition rates (0.50 g/A·h) are realized, and washing of the product does not require the use of ammonium salt solutions as in the case of system I.

Cathodic products were identified by the methods of X-ray phase and chemical analysis. The agreement between the experimental and tabulated interplanar spacing and relative line intensity values identified unambiguously the *WC* phase. The lattice parameters of *WC* powder were calculated on an attachment to the diffractometer N26-ChA (Zeiss, Jena) using a standard lattice parameter computation program. Synthesized *WC* powder has a hexagonal lattice with the following parameters: $a=2.8973 \cdot 10^{-10}$ m, $\Delta a=0.00414 \cdot 10^{-10}$ m, $c=2.8381 \cdot 10^{-10}$ m, $\Delta c=0.00885 \cdot 10^{-10}$ m. The shape and the size of cathodic deposit particles were determined by transmission electron microscopy. Two types of particles (Fig.5) are characteristic of *WC* powders:

- a) individual needle crystals of 0.5-1 μm size;
- b) layered, loose conglomerates of 10-20 μm size.

The results of chemical analysis of the single-phase cathodic product obtained are:

Element	W	C (total)	C (pure)	C (bound)
W, wt. %	86.9 \pm 1	7.4 \pm 0.5	2.2 \pm 0.2	5.2

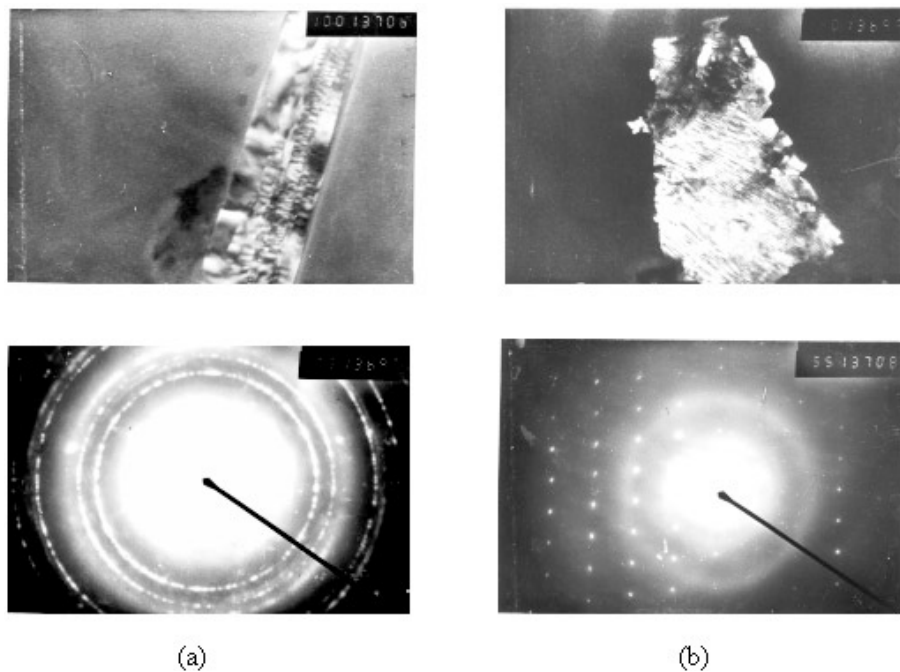


Figure 5. Photomicrographs and electron (-beam) image of *WC* powders, obtained in the system $\text{NaCl-KCl-Na}_2\text{WO}_4(5 \text{ mol. \%})-\text{NaPO}_3(0.75 \text{ mol. \%})-\text{CO}_2(15 \times 10^5 \text{ Pa})$, $E_{\text{cathode}}=-1.5 \text{ V}$, $T=750 \text{ }^\circ\text{C}$: (a) individual needle crystals of 0.5-1 μm size, (b) layered, loose conglomerates of 10-20 μm size.

According to the data, the *W/C* ratio corresponds to the stoichiometric compound *WC*. Auger spectra were taken for powdery *WC* deposits (on an IUMP 10C Auger microprobe). The presence of the carbide phase *WC* and oxygen, which was not bound into chemical compound and was apparently adsorbed during air drying of the powder, was shown. The absence of oxygen peak in Auger spectrograms after 20 min long ionic etching to a depth of 20 nm indicates the adsorbed nature of oxygen.

3.2. Synthesis of three-component hard alloy compositions

In powder metallurgy, cobalt and nickel powders, which act as a binder component, are added to the charge, when articles of molybdenum or tungsten carbides are made using hot pressing. This fact and other unique properties of ternary alloys stimulated the search for systems and conditions for simultaneous electroreduction of carbon, tungsten (molybdenum) and cobalt (nickel) aimed at the HTES of binary carbides. The most suitable carbon source for this purpose is CO_2 . The co-deposition of three components [*C*, *Mo(W)*, *Co(Ni)*] was realized in systems with differences in discharge potential of not greater than 200 mV. In this case, carbon dioxide acts not only as carbon source but also as acidic additive that shifts the molybdenum (tungsten) deposition potential towards more positive values. The compositions of the electrolytic bath and the conditions for the synthesis are summarized in Table 2. In all the systems potentiostatic electrolysis is used at the potentials corresponding to the co-deposition of the three components. Pure single-phase binary carbide was obtained only in one system 7. The yield of the single-phase product Co_3W_3C is $0.4-0.6 \text{ g}\cdot\text{A}^{-1}\cdot\text{h}^{-1}$, the particle size is $0.3-1.0 \text{ }\mu\text{m}$. Evidently, the composition of the ternary alloy and its purity are determined by

Table 2. Systems and conditions for the synthesis of ternary compounds from melts based on $NaCl-KCl(1:1)$ mixtures (temperature 1023 K, $P_{CO_2}=1.5 \text{ MPa}$)

System no.	Other components of the electrolytic bath	Electrolysis parameters, $-E_{\text{cathode}}$ (V)	Cathodic product phase composition
1	$Na_2MoO_4-MgCl_2-CoCl_2-CO_2$	1.3	Co_6Mo_6C, Mo_2C
2	$Na_2MoO_4-NaPO_3-CoCl_2-CO_2$	1.2	Co_6Mo_6C, Mo_2C
3	$Na_2MoO_4-NaPO_3-NiCl_2-CO_2$	1.1	Ni_6Mo_6C, Mo_2C, Ni_4C
4	$Na_2MoO_4-Na_2Mo_2O_7-CoCl_2-CO_2$	1.1	Co_6Mo_6C, Mo_2C, Mo_2O
5	$Na_2WO_4-Na_2W_2O_7-CoCl_2-CO_2$	1.3	Co_3W_3C, W_2C, WC
6	$Na_2WO_4-Na_2W_2O_7-NiCl_2-CO_2$	1.2	Ni_6W_6C, W_2C, WC
7	$NaF-WO_3-CoCl_2-CO_2$	1.1	Co_3W_3C
8	$NaF-WO_3-NiCl_2-CO_2$	1.1	Ni_6W_6C, W_2C, WC

several factors: the ratio of the partial currents of the reacting components, the energetics of their interaction, and the possibility of parallel reactions between any two components. These reactions are responsible for the presence of high-melting metal carbides.

4. Conclusions

1. On the basis of the voltametric study of the electroreduction of CO_2 dissolved in a chloride melt under an excessive pressure of up to 1.5 MPa, it has been found that the electrode process occurs in one stage at polarization rates of $\leq 0.5 \text{ V}\cdot\text{s}^{-1}$, and that the electrode process is controlled both by the charge transfer rate and by the rate of gas diffusion to the electrode. At polarization rates of $\leq 0.1 \text{ V}\cdot\text{s}^{-1}$, the electrode process is observed to occur in two stages; its mechanism has been suggested. The cathodic product is polycrystalline graphite.
2. The electrodeposition of carbon from CO_2 was taken as the basis for high-temperature electrochemical synthesis of two- and three component carbides; systems and conditions for producing tungsten and molybdenum carbides and double carbides with cobalt and nickel by ionic melt electrolysis under excessive carbon dioxide pressure have been selected.

References

1. L.E. Ivanovsky, V.N. Nekrasov, Gases and Ionic Melts, Nauka, Moscow, 1979.
2. Yu.K. Delimarskiy, V.I. Shapoval, V.A. Vasilenko, V.F. Grishenko, Russian J. Appl. Chem., 43 (1970) 2634.
3. H.B. Kushkhov, V.I. Shapoval, I.A. Novoselova, Russian J. Electrochem., 23 (1987) 952.
4. Yu.V. Pleskov, Russian Chemical Reviews, 68 (1999) 416.
5. G. Janz, F. Colom, J. Electrochem. Soc., 107 (1960) 581.
6. A.F. Alabyshev, M.F. Lantratov, A.G. Morachevsky, Reference Electrodes for Fused Salts, Sigma Press, Washington, 1965.
7. B.K. Andersen, Thermodynamic Properties of Molten Alkali Carbonates, Lyngby: Technical University of Denmark, 1975.
8. A. Boruka, Fuel Cell System, Washington D.C., 1960, vol. 2, p. 242.
9. H. Matsuda, I. Ayabe, Z. Elektrochem., 59 (1955) 494.
10. P. Delahay, J. Am. Chemical Science, 75 (1953) 1190.
11. V.I. Shapoval, V.V. Malyshev, I.A. Novoselova et al., Ukrainian Chemistry Journal (in English), 60 (1994) 29.
12. V.I. Shapoval, V.V. Malyshev, I.A. Novoselova, et al., Russian Chemical Reviews, 64 (1995) 133.
13. I.A. Novoselova, V.V. Malyshev, V.I. Shapoval, et al., Theoretical Foundations for Chemical Engineering, 31 (1997) 286.