Electrolytic Generation of Nano-Scale Carbon Phases with Framework Structures in Molten Salts on Metal Cathodes

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Dedicated to the memory of Professor V.I. Shapoval, an outstanding scientist in the field of electrochemistry of molten salts
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An electrochemical study of mechanisms of electrodeposition of carbon solid phases from halide melts (Na,K|Cl; Na,K,Cs|Cl), saturated with carbon dioxide under an excessive pressure of up to 1.5 MPa, has been carried out in the temperature range 550 – 850 °C by cyclic voltammetry. It has been found that the cathode process occurs in three steps at sweep rates of less than 0.1 $V\,s^{-1}$, and its electrochemical-chemical-electrochemical (ECE) mechanism is suggested. It has furthermore been found that cathodic deposits contain nano-sized carbon particles of different forms and structure: blocks of amorphous carbon, crystalline graphite, carbon nanotubes (CNT), and nanofibres. The outer diameter of the tubes is 5 – 250 nm, and the internal diameter is 2 – 140 nm. A correlation between the product structure and yield against electrolysis conditions and regimes has been established.

Key words: Chloride-Oxide Melts; Carbon Dioxide; Excessive Pressure; Carbon Nanotubes; Product Characterization.

1. Introduction

Carbon, which is a unique chemical element, can form a great number of stable elementary solid substances (allotropes) owing to the fact that it can exist in different valence states. The new framework forms of carbon (fullerenes, nanotubes, onions), which have been discovered in the late 20-th century, attract great attention of researchers in view of their unique structure and hence unique physico-chemical properties, in terms of both development of new efficient methods of preparation and comprehensive investigation of their properties and possible ways of application. Framework carbon compounds are large (and sometimes giant) textural features, which consist solely of carbon atoms and are closed (sometimes semi-open) "shells" with cavities or voids inside.

One of the least developed but promising methods for the production of framework carbon structures is electrolysis of molten salts. Four variants of electrolytic synthesis of framework carbon phases are possible:

(1) Intercalation of alkali or alkaline earth metals, electroreduced from halide melts, into a graphite cathode [1, 2].

(2) Electroreduction of carbonate anions to condensed carbon from carbonate melts at metal cathodes [2, 3].

(3) Electroreduction of carbon dioxide, dissolved in a chloride melt under excess pressure, to condensed carbon at metal cathodes [4 – 6].

(4) Chemical or electrochemical chlorination of carbides (carbide anodes) in salt melts [2].

In the variant (1) of nanotube synthesis, the carbon source is a graphite cathode. The essence of this method is electrowinning on a graphite cathode of alkali (Li, Na, K) or alkaline earth (Mg, Ca) metals from their chloride salts followed by the formation of carbon tubes by the interaction of the metal being deposited at the cathode surface. The variants (2) and (3) of synthesis may be regarded, in our view, as two variants of one method. In this method, a condensed carbon phase is generated on a metal cathode from a liquid molten salt phase by electrochemical reactions.

This paper deals with the development of the variants (2) and (3) of electrogeneration of carbon nanotubes.

The electrowinning of carbon from soda melts was first mentioned in the late 19-th century [7]. In the early 20-th century, the authors of [8] reported deposition of carbon powder by the electrolysis of a solid $BaCl_2$-$BaCO_3$ electrolyte at about 600 °C. The properties and structures of the obtained carbon products and the mechanisms of the electrode processes have not been studied. In the mid 1960's, electrochemists in various countries have studied in considerable detail electrochemical processes in molten carbonate and halide-carbonate melts [9 – 14]. It was found that under certain conditions a solid carbon phase is formed on the cathode with 100% current yield. The questions of the morphology, structure and fineness of the product remained unelucidated because of the absence of high-resolution instrumentation in those years. Various schools of electrochemists proposed their own mechanisms of carbon phase formation:

(1) electrowinning of alkali metal on the cathode, which then chemically reduced carbonate anions to carbon;

(2) direct discharge of carbonate anions to carbon at the cathode;

(3) acid-base type preceding chemical reaction:

$$CO_3^{2-} \leftrightarrow CO_2 + O^{2-}, \quad (1)$$

followed by discharge of carbon dioxide to carbon at the cathode.

The first studies of direct electroreduction of carbon dioxide from chloride melts were started at the Institute of General and Inorganic Chemistry (IGIC) of the Ukrainian National Academy of Sciences (UNAS), Kyiv in the late 1960's by the Corresponding Member of UNAS V. I. Shapoval and coworkers [12, 14]. They developed carbonate fuel cells and examined the possibility of oxygen regeneration from CO_2. Because of the low solubility of carbon dioxide in halide melts [15], an excess gas pressure had to be applied to increase the rate of the electrochemical process. It was found that the cathodic product of reduction of an equimolar Na,K|Cl mixture saturated with carbon dioxide under a pressure of 0.15 MPa at 680 °C and current densities of 0.05 – 0.50 A/cm^2 is fine carbon. The structure peculiarities and morphology of the carbon produced, its current yield and the kinetic peculiarities of the CO_2 discharge were not studied. An advantage of isolating carbon from carbon dioxide over that from carbonate melts is that during the electrolysis of the carbonates, oxide accumulates in the electrolytic bath, leading to a change in its composition and hence to instability. In the case of carbon dioxide discharge in a wide current density and potential range, the only cathodic product is carbon and the anodic product is oxygen, i. e., an ecologically very important reaction, $CO_2 \rightarrow C + O_2$, is realized electrochemically. Besides, much less aggressive and cheaper halide melts may be used as carbon dioxide solvents.

In the 1980's and later, this reaction became an object of investigation at the IGIC in connection with the development of high-temperature electrochemical synthesis of fine molybdenum and tungsten carbide powders by the codeposition on the cathode of refractory metal, which is introduced in the melt as an oxy salt, and carbon from CO_2 [16 – 18]. But the carbon product separately was not studied then either.

The aim of the present work is to offer an electrochemical investigation of the mechanism of discharge (cathodic and anodic) of carbon dioxide, dissolved in halide melts under an excess pressure of 0.5 – 1.5 MPa at 550 – 850 °C, at platinum, gold and glassy carbon electrodes; to elucidate the mechanisms and kinetics of the electrode processes; to establish the correlation between the chemical properties, the phase composition, the morphology and structure of the cathode deposits formed and the electrolysis regimes and their conditions.

2. Experimental

2.1. Chemicals and Materials

Mixtures of extra-pure sodium, potassium, and cesium chlorides of different compositions were used as the solvent melt. Two electrolytes were employed: a ternary eutectic (NaCl : KCl : CsCl with molar ratio 0.3 : 0.245 : 0.455 and melting point 480 °C) and a binary mixture (NaCl : KCl with molar ratio 1 : 1 and melting point 660 °C). Each electrolyte was prepared first by thermally drying each salt in air at 150 °C during 12 h and then by pre-melting 60 g of the appropriate mixture in a platinum crucible. The purity of the mixture was checked by residual current magnitude ($i_{res} = 1.2$ mA/cm^2 at $E = -1$ V). Carbon dioxide was used from a gas cylinder of trade mark (99.8% of the

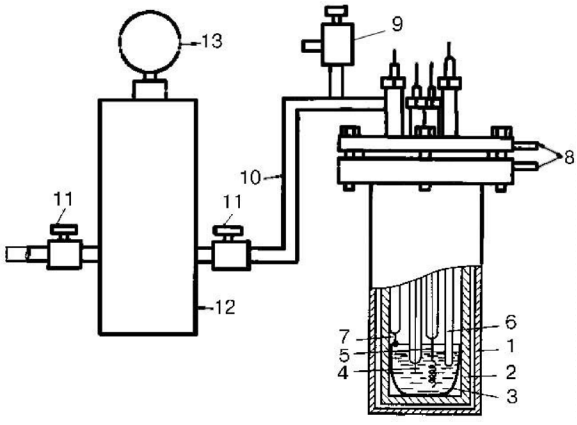

Fig. 1. Principal scheme of the high-temperature cell for voltammetry investigations under excess gas pressure. 1, High-temperature stainless steel reactor; 2, quartz beaker; 3, crucible and counter electrode; 4, indicator (working) electrode; 5, reference electrode; 6, thermocouple; 7, Pt lead wire 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 l); 13, gauge-pressure manometer.

main compound) after drying by silica gel, which was in the intermediate gas container, cf. 12 in Figure 1.

Platinum and gold wires and glassy carbon (GC) cores (diameter, 0.5 – 1 mm; area of the electrodes, $\sim 0.2 - 0.5$ cm^2) were used as fully or semi-doped indicator electrodes. Crucibles made of GC or platinum served as the counter electrode and melt container at the same time. The potentials were measured versus the quasi-reference electrode – platinum wire (diameter, 1 mm; area, 5 cm^2). The mechanisms of the electrochemical behaviour of this reference electrode in the case of change of the gas phase over the chloride melt have been described in [18].

2.2. Apparatus, Measurements and Analysis

The electrochemical behaviour of carbon dioxide under excessive pressure was investigated in a hermetically sealed three-electrode cell made of special stainless steel, which permitted measurements at temperatures up to 900 °C and at excessive gas pressures up to 2.0 MPa (Fig. 1).

Voltammetry with single and cyclic potential sweep was chosen as the electrochemical method of investigation. Current-voltage (*I–E*) curves were obtained with a PI-50-1 potentiostat in a polarization rate range of 0.005 – 0.1 V/s. Investigations were carried out in a temperature range of 550 – 850 °C and at a CO_2 pressure of 0.1 – 1.5 MPa. The temperature of the melt was maintained within ±2 °C. All experiments were made by evacuating the system first to 13.3 Pa and then passing carbon dioxide through the system for 10 min. After that the needed pressure was produced in the cell. 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

$$CO_2(\text{gas}, P, T) = CO_2(\text{in the melt}, P, T). \qquad (2)$$

The electrolysis of the studied systems was carried out in the same cell as used for the voltammetry measurements in the modes of either constant current or constant voltage. In the constant current mode, the applied current density was in the range of 0.01 – 0.2 A/cm^2 with reference to the surface area of the cathode before starting the electrolysis. Semi-immersed platinum and GC plate electrodes (cathode area, 5 cm^2; anode area, 10 cm^2) were used in the electrolysis experiments.

A powder product was either settled down onto the crucible bottom or was assembled on the cathode in the form of electrolytic "pear". The deposit was cleaned from salts by successive leaching with hot water. Then the precipitate was washed with distilled water several times by decantation and dried to a constant mass at 100 – 150 °C. The electrolysis products were analyzed by chemical and X-ray phase analyses [DRON-UM1 diffractometer with Bragg-Brentano geometry ($R = 192$ mm) using Cu-K_α monochromatic radiation], electron diffraction, and electronic microscopy [transmission (TEM) and scanning (SEM)]. Microscopy and electron diffraction experiments were carried out using a transmission electron microscope JEM-100CX II at 60 kV, below the threshold for knock-on damage in CNTs. Sample preparation for TEM observations was performed by dropping a dilute acetone suspension of as-produced carbon deposit (after washing with water) onto a copper grid. To reduce agglomeration, the dilute suspension was subjected to ultrasonic dispersion for 10 min.

3. Results and Discussion

A cathodic voltammetry study carried out on platinum and gold needle-shaped electrodes has shown that at low electrode polarization rates (≤ 0.1 V/s) the voltammograms exhibit two well-defined cathodic waves of carbon dioxide electroreduction with limiting currents and the half-wave potentials (A) $E_{1/2} =$

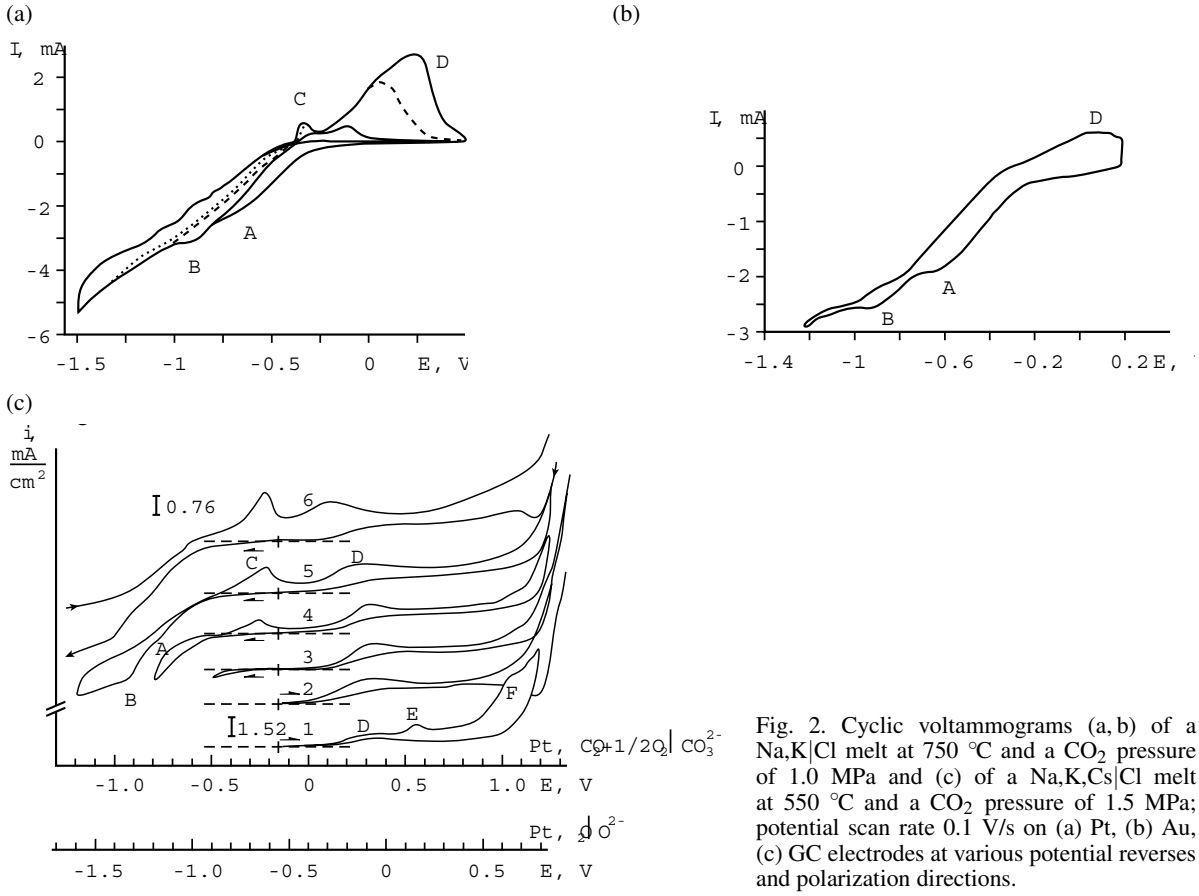

Fig. 2. Cyclic voltammograms (a, b) of a Na,K|Cl melt at 750 °C and a CO_2 pressure of 1.0 MPa and (c) of a Na,K,Cs|Cl melt at 550 °C and a CO_2 pressure of 1.5 MPa; potential scan rate 0.1 V/s on (a) Pt, (b) Au, (c) GC electrodes at various potential reverses and polarization directions.

-0.44 V and (B) $E_{1/2} = -0.78$ V vs. the platinum-carbonate reference electrode (Figs. 2a, b).

At the reverse sweep, no anode current is observed on the Pt electrode after the first wave. If the reversal of sweep takes place after the limiting current of the second wave, two waves, (C) and (D), appear on the reverse sweep (Fig. 2a). As the reversal potential is shifted towards more negative values the first wave (C) current decreases and its potential remains unchanged; the peak potential of the second wave (D) shifts towards more positive values and its current increases. The difference in the *I-E* curves obtained on the gold electrode (Fig. 2b) consists in the presence of only one wave (D) at the reverse sweep, which is presumably connected with hindering of the formation of gold compounds.

To elucidate the mechanisms of cathodic and anodic processes on a GC electrode in the system Na,K,Cs|Cl-CO_2 (1.5 MPa), voltammetric investigations with different reversal potentials and different sequences of the indicator electrode polarization directions have been carried out. For instance, when the GC electrode is polarized by the stationary potential first to the cathodic region to -1.7 V and then to the anodic region to $+1.4$ V (Fig. 2c, curve 6), two waves with limiting currents and half-wave potentials are observed on the forward cathodic sweep: (A) $E_{1/2} = -0.73$ (-0.43) V and (B) $E_{1/2} = -0.98$ (-0.68) V vs. platinum-oxygen, Pt, $1/2O_2|O^{2-}$ (platinum-carbonate; Pt, $CO_2 + 1/2O_2|CO_3{}^{2-}$) reference electrodes. Thus in this part of the voltammetric curve, the results for the three indicator electrodes agree. At the reverse cathodic sweep, two waves, (C) and (D), are observed as in the case of the platinum electrode. But in contrast to the platinum electrode, the wave (C) at the GC electrode already appears at the reversal potential after the first cathodic wave (A), and its potential does not depend on the reversal potential. When the reversal potential increases in the negative direction, only an increase of the wave current is observed (Fig. 2c,

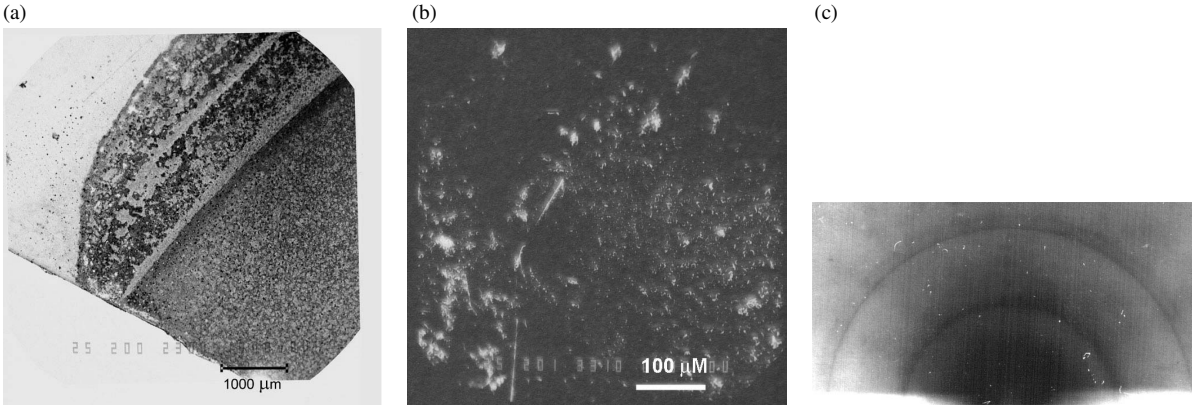

Fig. 3. Micrographs (SEM) of cathode films obtained in the system NaCl-KCl-CO_2 at different electrolysis conditions: (a) gray coating ($E_K = -0.6$ V; $P_{CO_2} = 1.0$ MPa; $T = 750$ °C), (b) black coating and (c) its electron-beam image ($E_K = -1$ V; $P_{CO_2} = 0.5$ MPa; $T = 850$ °C).

curves 4, 5, 6). As the wave (D) is concerned, investigations with different polarization directions (first to the anodic and then to the cathodic region) showed that it is observed and practically does not change either in current or potential on all curves (curves 1, 2, 3, 4). If the reverse sweep is performed after the cathodic wave (A) potential, the wave (D) potential is shifted in the negative direction (Fig. 2c, curves 5, 6). Thus, the wave (D) on the curves 5, 6 results from oxidation processes that occur both in the case of anodic polarization of the GC electrode and in the case of oxidation of the cathodic product. At present we do not have enough experimental data for a unambiguous interpretation of the electrode reactions, being responsible for the origin of the wave (D). This requires further detailed investigations of the anode processes on different electrode materials. We may assume that the origin of the stable and reproducible wave (D) during the anodic polarization of the GC electrode is connected with the oxidation of oxygen. Such assumption is based on experimental facts, well known in literature [19, 20], as well as on the fact, that the indicated wave was fixed also in base electrolyte in air atmosphere. With making a CO_2 atmosphere above the melt and with increase of its pressure surplus, a linear dependence of the current rise of this wave on pressure was not revealed. The problem of a proper definition of the oxygen-containing parts (O_2, O^{2-}, ${O_2}^{2-}$, ${O_2}^{-}$) is still open. It should also be noted that in the case of anodic polarization of the freshly prepared surface of the GC electrode (held in the melt without applied potential for not less than 0.5 h), the voltammogram exhibited extra waves, (E) and (F) (Fig. 2c, curve 1). These waves are not observed again on a repeated sweep after 5 min. They are apparently due to the oxidation of functional groups adsorbed on the surface of the GC electrode.

To elucidate the mechanism of the processes occurring during electrolyses at the cathode in the constant potential current mode first wave and second wave potentials have been applied. Electrolysis at the first-wave potential gave gray unsound deposits with fairly good adhesion to the platinum electrode, but with low current densities ($i_k \leq 0.005$ A/cm). During electrolysis at the second wave potential, also unsound but black deposits were obtained. In case of electrolysis in the constant current mode, the adhesion and homogeneity of the film are better than those of films deposited under potentiostatic conditions. Electrolyses of different duration at several CO_2 pressures and several temperatures (700, 750, 800, 850 °C) were carried out, but this had no noticeable effect on the quality of the obtained films (Fig. 3a, b).

A microprobe analysis of the deposits 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 ($\geq 98\%$) of carbon. The electron diffraction method with reflection showed that they are polycrystalline graphite (Fig. 3c).

Based on the analysis of the obtained data, the following ECE (electrochemical-chemical-electrochemical) mechanism of CO_2 electroreduction can be suggested:

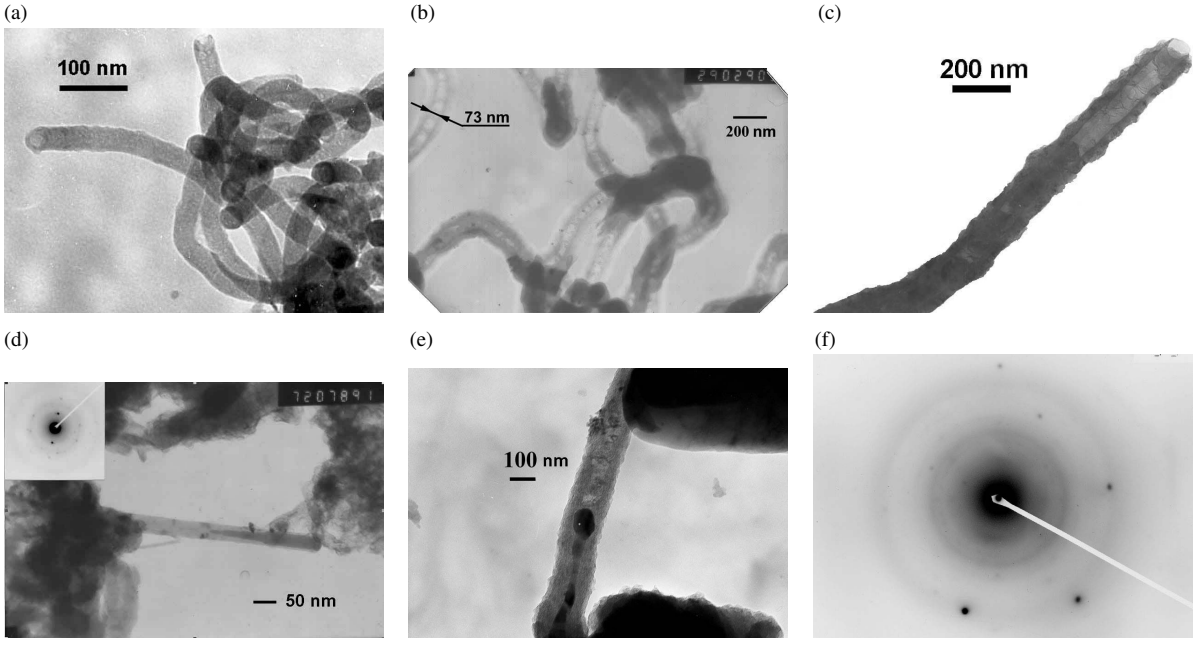

Fig. 4. (a – e) Micrographs (TEM) and (d, inset in the upper left and f) electron(-beam) images of fragments of black powders produced in the system NaCl-KCl-CO_2, obtained at different electrolysis conditions: (a – e) $P_{CO_2} = 1.0$ MPa; $T = 750$ °C; $i_k = 13.5, 28, 42, 56, 72$ mA/cm^2.

First step: (wave A) reduction of CO_2 to a ${CO_2}^{2-}$ radical:

$$CO_2 + 2e^- = {CO_2}^{2-}. \quad (3)$$

The radical formed is an unstable species, which possesses strong reducing properties and reduces small impurities in the electrolyte.

Second step: chemical formation of CO:

$${CO_2}^{2-} \rightarrow CO + O^{2-}. \quad (4)$$

Third step: (wave B) irreversible electroreduction of CO to elementary carbon:

$$CO + 2e^- \rightarrow C + O^{2-}. \quad (5)$$

At the same time, CO_2 acts as acceptor of oxide anions, and the overall cathode reaction may be represented as:

$$\boxed{C} \quad 3CO_2 + 4e^- \rightarrow C + 2{CO_3}^{2-}. \quad (6)$$

Carbonate ion discharge takes place at the anode to produce CO_2 and oxygen:

$$\boxed{A} \quad 2{CO_3}^{2-} \rightarrow 2CO_2 + O_2 + 4e^-. \quad (7)$$

The overall electrode reaction is:

$$CO_2 = C + O_2. \quad (8)$$

In order to determine the current yield and to study the phase and structural composition of the cathodic carbon product, the electrolyses with different current densities ($i_k = 10 – 200$ mA/cm^2) were carried out in the system KCl-NaCl (1 : 1)–CO_2 ($P_{CO_2} = 0.5 – 1.0$ MPa and $T = 750$ °C). It was found that the structures of the cathode carbon deposits depend on the melt temperature, the carbon dioxide pressure, the current densities, and contain nano-sized carbon particles of different forms and structure: blocks of amorphous carbon, crystalline graphite, carbon nanotubes (CNT) and nanofibres. Most of the obtained CNTs are multi-walled and have a bent (curved) form. Most often CNTs agglomerate into bundles or, more rarely, are arranged as individual tubes. As a rule, tubes of one diameter make up one bundle. The outer diameter of the tubes is 5 – 250 nm, and the internal diameter is 2 – 140 nm. Almost all tubes are filled partly with electrolyte salt. With increase in current density the tube diameter decreases (although every product obtained with the studied current densities has tubes of different

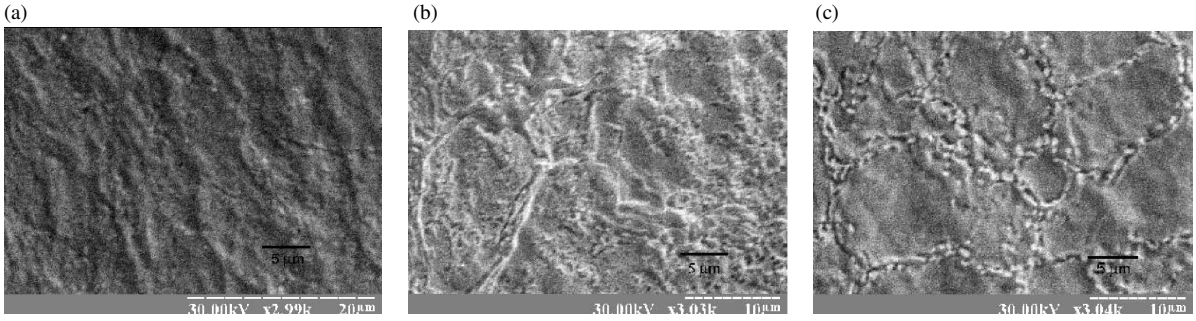

Fig. 5. Micrographs (SEM) of the platinum cathode after electrolysis in the system Na,K,Cs|Cl in various parts: (a) the section of platinum electrode surface not immersed in the electrolyte; (b) three-phase (gas-metal-electrolyte) boundary of the electrode; (c) surface completely immersed in the melt. $P_{CO_2} = 1.0$ MPa; $T = 550$ °C; $i_k = 15$ mA/cm^2; $E_k = -2.2$ to -1.30 V; duration 1 h.

diameters). At the same time, the carbon product yield and the proportion of the CNTs in the total mass of this product increase. The results of the microscopic investigations of the obtained carbon powders are presented in Figure 4.

In all electrolyses, a platinum cathode surface erosion was found (Fig. 5), and in some cases there were cathode mass losses (tenths of mg).

A metal phase, which is inside or on the ends of the tubes, has been found in carbon deposits by TEM, electron diffraction and X-ray analysis. It was found with the help of the last method (Fig. 6) that in all products, synthesized in the system Na,K|Cl-CO_2 (1.0 MPa), $T_{melt} = 750$ °C, there are 2 halos on the XRD pattern fixed in the regions 2Θ (Cu): (1) from $15° - 32°$ with center 26.5°; (2) from $38° - 48°$ with center 42° (Fig. 6a). The presence of the first halo testifies the availability of graphitized planes (002) with $d \approx 2.37 - 2.71$ Å. Also, the product contains a different quantity of face-centered cubic (fcc) lattice based on γ-Fe (austenite).

The typical XRD pattern of the cathodic product powders produced with the system Na,K,Cs|Cl-CO_2 (1.5 MPa), $T = 550$ °C (Fig. 6b) is characterized by the presence of all Pt peaks with symmetrical halos in the region 2Θ: $19° - 32°$ with the center at 26.5°.

The origin of the above fcc phase is explained by a non-controlling interaction of the reactor material and the crucible holder (stainless steel) with the carbon phase formed.

These facts together with the data on the cathode erosion (Fig. 5) allow to conclude that the metal phase (cathode material and metallic impurities in the electrolytic bath) plays an active role in the formation of the framework structures.

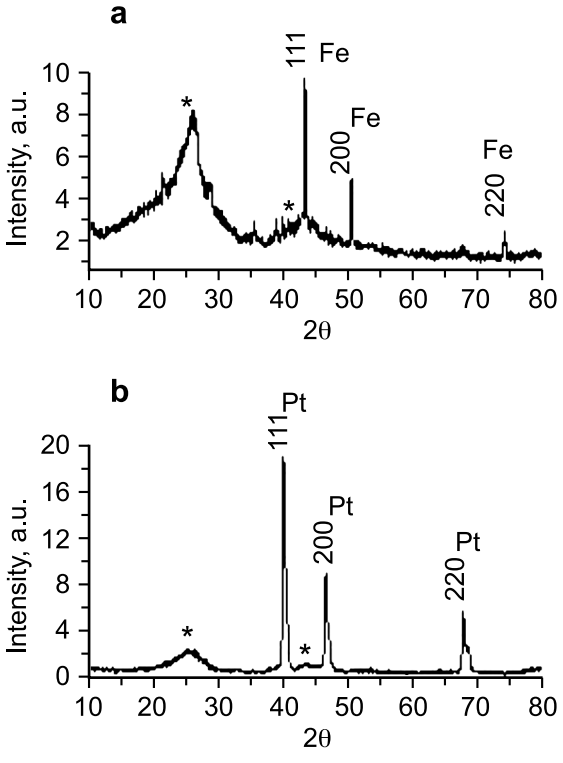

Fig. 6. XRD patterns of samples obtained in the systems: (a) Na,K|Cl-CO_2, $i_k = 42$ mA/cm^2 and (b) Na,K,Cs|Cl-CO_2, $i_k = 6$ mA/cm^2. The respective Miller index is presented for the peaks of (a) austenite (face-centered cubic lattice, based on γ-Fe) and (b) Pt. The $*$ indicate the halo centers.

The maximum current yield of the carbon phase in the melt NaCl-KCl does not exceed 30%, which apparently is connected with the cathodic product loss due to the following reaction at temperatures above 600 °C:

$$CO_2 + C = 2CO. \quad (9)$$

In order to increase the current yield of the carbon phase it is advisable to use lower-melting electrolytes. For this purpose, electrolysis of CO_2 in the ternary eutectic Na,K,Cs|Cl at 550 °C was carried out. In this system the current yield of carbon was increased by 50%, and the cathodic product contained a fullerene phase (according to X-ray analysis and Raman spectroscopy) together with other carbon phases, obtained in the NaCl-KCl melt. The low-current yield of carbon in the ternary eutectic may be connected with current loss due CO formation ($CO_2 + 2e^- = CO + O^{2-}$); CO leaves the reaction zone because of the low rate of the third stage of the CO_2 cathodic discharge.

4. Conclusion

(1) Electroreduction of carbon dioxide to carbon can be taken as the basis of high-temperature electrochemical synthesis of various nano-scaled carboniferous inorganic compounds: carbon films and powders of different structures and morphology.

(2) It has been shown that it is possible, in principle, to produce carbon nanotubes by electrolysis of molten salts saturated with carbon dioxide. The advantages of the method are the simplicity of the apparatus, ecological cleanness, economy, possibility of control of the product structure and morphology by the choice of the optimum electrolysis conditions.

(3) The electrochemical method under development enables fairly easy production of carbon nanotubes filled with metal phase. To this end, metal compounds and their concentrations must be chosen, for which the metal deposition potential would be close to the potential of carbon isolation from CO_2, but there would be no carbide phase formation.

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