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# Cation catalysis in high-temperature electrochemical synthesis of tungsten carbides in molten salts

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#### ABSTRACT

The paper presents a quantum-chemical model and experimental confirmation of cation catalysis phenomenon by the influence of magnesium cation on tungstate anion electroreduction to metallic tungsten in a chloride melt. Ab-initio calculations of the parameters of the  $\{Mg_n^{2+}[WO_4]^{2-}\}^{(2n-2)+}$  type species have been performed. Within the framework of this approximation the compositions for the most stable species in molten salts were obtained. The peculiarities of electroreduction of tungstate anion and carbon dioxide have been studied by the method of cyclic voltammetry in the binary NaCl-KCl melt on platinum electrodes at 750°C separately and jointly, in the presence and without magnesium chloride. It has been shown that addition of Mg<sup>2+</sup> in the melt is a necessary condition for the electrodeposition of tungsten in the same potential range as carbon from carbon dioxide and for the subsequent synthesis of tungsten carbides. The electrochemical synthesis of tungsten carbides WC and W<sub>2</sub>C in the form of dispersed powder has been effected in the system NaCl-KCl-Na,WO,-MgCl,-CO,. The optimal electrolysis conditions have been determined for the synthesis of single-phase WC powder. WC product was produced in the studied system with electrodeposition rate 0.3 g/A·h at CO<sub>2</sub> pressure over 1.7 MPa and at cathodic current densities 0.05 - 0.2 A/cm<sup>2</sup>. © 2012 Trade Science Inc. - INDIA

#### INTRODUCTION

Refractory metal carbides can be successfully produced either as coatings or as fine dispersed powders by high-temperature electrochemical synthesis (HTES) from molten salts. This method may compete with other known methods for the synthesis of the fine powders,

## **KEYWORDS**

Electrochemical synthesis; Tungsten carbides; Cation catalysis; Ab initio calculations; Outersphere cations; Electron transfer.

and be of interest in powder metallurgy. The HTES of tungsten carbides is based on multielectron processes that occur on a cathode and lead to the electroreduction of tungsten and carbon from ionic melts. The sources of metal and carbon are their oxygen containing compounds  $Na_2WO_4$  and  $CO_2$ . The discharge products can then react chemically on the cathode surface. It

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should be noted that the presence of electronic conductivity in the deposited compound (tungsten carbide) is a necessary condition for the realization of synthesis. The high-temperature electrochemical processes in molten salts differ greatly from low-temperature processes in aqueous solutions. At high temperature, the influence of catalytic properties of electrode material on the kinetics of electrode process becomes weaker. At the same time, the catalyzing role of the medium (electrolyte composition) becomes more important. The influence of the medium on electrode kinetics can be clearly revealed in the electroreduction processes of oxygen-containing anions (complex coordination compounds) of d-metals in the highest valent state. The specific mechanisms of electrochemically active species (EAS) formation and of multielectron reaction of charge transfer are characteristic features of electroreduction processes of the above compounds. A cation catalysis mechanism was proposed by<sup>[1,2]</sup> for the explanation of the electroreduction of complex oxygen-containing anions in melts. The essence of cation catalysis is the transformation of complex anions into the active state under the influence of cations of different concentration with strong polarizing effect (Li<sup>+</sup>, Ba<sup>2+</sup>, Ca<sup>2+</sup>, Mg<sup>2+</sup>). This leads to changes in the energy and electronic state of anion, formation of a new EAS, to changes in its composition, in rates of EAS formation and charge transfer reactions.

The necessary condition for effective HTES of carbides in the form of powders is the closeness of potentials of carbon and refractory metal deposition from different EAS. In the chloride melt NaCl-KCl the potential of NaWO<sub>4</sub> discharge is more negative by 0,8 V than the potential of carbon deposition from carbon dioxide in the same melt, and the cathodic product is tungsten bronze (Na<sub>x</sub>WO<sub>3</sub> (x = 0, 1-0, 9)). In order to produce metallic tungsten and to shift the potential of W deposition to more positive potential values, an approach to the formation of a new more electrophilic EAS (which is reduced at more positive potentials) by means of cation catalysis was proposed. A quantum-chemical model of the formation of tungstate complex cationized by Mg<sup>2+</sup> cations is proposed in this paper. To confirm this approach experimentally, the electrochemical behavior of each carbide component must be studied (determination of discharge potential range, partial currents, the Research & Reviews Dn

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mechanism of electrode processes, and methods of decreasing the difference between discharge potentials).

The aims of the study are: (a) creation of a quantumchemical model of cation catalysis for the reduction of tungstate anion; (b) determination of the conditions for carrying out the electroreduction of tungsten and carbon separately and simultaneously in chloride melt with MgCl<sub>2</sub> additives; (c) realization of the HTES of tungsten carbide powders and product characterization.

## QUANTUM-CHEMICAL ESTIMATION OF INFLUENCE OF OUTERSPHERE CATIONS (Mg<sup>2+</sup> CATIONS) ON CHARGE TRANSFER AT THE WO<sub>4</sub><sup>2-</sup> REDUCTION

The application only traditional electrochemical criteria for the estimation of characteristics and parameters of the electroreduction of anions with complex structure in molten salts is connected with overcoming considerable difficulties caused by multi-stage character of the processes, synchronous occurring of separate elementary stages on the cathode and very short lifetime of the intermediate products. That's why according to our point of view it cannot gives the complete and detailed information about thermodynamical and kinetic peculiarities of the electrochemical behavior of anions in melts. The methods of quantum chemistry, which are the effective means of the direct study of species and activated complexes with short lifetime allow to interpret the experimental data at the electronic level and are of great importance. In our previous works<sup>[3-5]</sup> efficiency of application the methods of quantum chemistry for modeling as interpartial interactions and solvations effects in a volume phase of the melts, and the processes occurring on interphase border an electrode-melts has been shown. The special attention is deserved by the results received by us on modeling nonoparticles at HTES from tungstencontained melts<sup>[6]</sup>, therefore applying only the representations which have received explanations on the methods of quantum chemistry, in a combination to experimental data, it is possible to reach decisions of tasks in view.

Quantum chemical calculations and its analysis give us possibility to prove the formation of stable cationized species of  $\{M_n^{m+}[WO_4]^{2-}\}^{(mn-2)+}$  (M=Li<sup>+</sup>, Ca<sup>2+</sup> and Mg<sup>2+</sup>) type in the bulk phase of diluted chloride melt<sup>[7]</sup>. This type of EAS has been proposed on the basis of the experimental data<sup>[8]</sup>. The calculations of the space structure, charge and energety characteristics for the  $\{Mg_n^{2+}[WO_4]^{2-}\}^{(2n-2)+}$  species were fulfilled within the framework of the programmed complex GAMESS/ FireFly in the basis set SBK-31G with the account of the electron correlation<sup>[9, 10]</sup>.

The possibility of the cationized particles formation in the bulk phase based only on the comparative analysis of energy characteristics does not give the full information about the character of the tungstate anion interaction with cations of melt. This initiates the study of the cation (for example Mg<sup>2+</sup>) influence on the changes of the geometrical and electronic structure of WO<sub>4</sub><sup>2-</sup> anions.

The potential energy surface (PES) of the interaction of  $nMg^{2+}...WO_4^{2-}$  is shown in the Figure 1. The topology of PES represents the three-holed potential and shows the possibility of the influence of the cation composition of the melt both on the reconstruction of the outer coordinate sphere and on the authentic places of "electronic attack" in the subsequent reactions of the electroreduction of EAS. So, it was found for n=1 that the bidentate interaction of one- and two- charged cations with the anion (Figure 1.(a) is the most energetically favorable in comparison with mono- and three dentate variants of the cation-anion interaction (Figure 1(b), (c). With growth of the n all minimums of the PES are realized for another positions of cations relative to anion.

 

 TABLE 1 : Charge (Q,a.u.) characteristic of atoms in tungstate anions of different type (sampled data)

Q,a.u. Species	n	W	<b>O</b> <sub>(1)</sub>	O <sub>(4)</sub>	Mg <sub>(1)</sub>
"isolated" [WO <sub>4</sub> ] <sup>2-</sup>	0	0,378	-0,595	-0,595	_
	1	0,698	-0,717	-0,370	1,472
$(2^{+})^{(2n-2)+}$	2	0,875	-0,535	-0,535	1,633
$\{Mg_n^{-1}[WO_4]^{-1}\}$	3	1,066	-0,695	-0,185	1,730
	4	1,186	-0,600	-0,600	1,800
	5	1,342	-0,589	-0,314	1,725



Figure 1–An example of the surface fragment of the potencial energy of the interaction  $Mg^{2+}$ ...  $WO_4^{2-}$ . The configuration (a) is the absolute minimum, (b) and (c) – are local minima of the surface of the potential energy (PES) of the interaction  $Mg^{2+}$ ... $WO_4^{2-}$ ; a)\* and b)\* – are transitional states of the system

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Comparative analysis of charge characteristics of atoms in the "isolated"  $WO_4^{2-}$  anion according to Lowdin<sup>[11]</sup> and cationized species showed that the outer-sphere cationization is accompanied by the redistribution of the charge from the anion to the cations (Figure 2). The degree of the charge transfer increases with the growth of the cation concentration (TABLE 1).

In the case of interaction of one  $Mg^{2+}$  cation (n=1) with  $[WO_4]^{2-}$  anion the charge is changed by 0.320 a. u. on W atom, by 0.122 a. u. on  $O_{(1)}$ , as on  $O_{(2)}$  atoms and by 0.225 a. u. on  $O_{(3)}$  as on  $O_{(4)}$  atoms in the tungstate anion. Another words the presence of cations in the coordinate sphere of the anion stimulates the display of donor properties of the central atom (W) of the anion (bigger in comparison with such properties of oxygen atom). So W atom becomes the possible center of the "electronic attack" together with cations in the subsequent reactions of the electroreduction of EAS at the cathode. The growth of number of cations in the coordinate sphere of the anion (for example, n=2; 4; Figure 2, TABLE 1) increases the effect of the charge transfer.

The comparative analysis of the occupation of atom



Figure 2 : Conceptional chart of the charge redistribution in WO<sub>4</sub><sup>2</sup> anion under the influence of 2 and 4 cations Mg<sup>2+</sup> Research & Restance On

Electrochemistry An Indian Journal orbitals (AO) according to Lowdin showed that the distribution of the electron density in the "isolated" anion was changed under the influence of cations; and the main "load" in the direction of this process is taken by d-orbits of tungsten atom.

#### EXPERIMENTAL

#### **Chemicals and materials**

A binary mixture of extra pure potassium and sodium chlorides with molar ratio 1:1 and melting point  $660 \,^{\circ}$ C was used as the solvent melt. Electrolyte was prepared firstly by thermally drying each salt in air at 150  $\,^{\circ}$ C during 10 h and then by pre-melting 50 g of the mixture in a platinum crucible. The purity of the mixture was checked by residual current magnitude ( $i_{res}$ =1,2 mA/sm<sup>2</sup> at E=-1V). Sodium tungstate of "chemically pure" grade was dried for 5 h in vacuum at a temperature 500  $\,^{\circ}$ C. Magnesium chloride (fused anhydrous) was prepared by the method described in<sup>[12]</sup>. Carbon dioxide was used from gas cylinder of trade mark (99,8 % of the main compound) after drying by silica gel, which was in the intermediate gas container.

Platinum wire (diameter 0,5 mm; area of electrode  $\sim 0,2 \text{ cm}^2$ ) was used as fully-doped working electrode. Crucibles made of glassy carbon 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<sup>2</sup>). The electrochemical behavior of this reference electrode in the case of change of the gas phase over the chloride melt has been described in<sup>[13]</sup>.

#### Apparatus, measurements and analysis

The experiments were performed in an electric resistance furnace of vertical type at 700–800 °C. The temperature of the melt was maintained within  $\pm 2$  °C. The cell for the measurements of electroreduction of tungstate anion was in the form of a test tube made of quartz. Its upper part was provided with a cooling jacket and was closed with an air-tight Teflon head with inlet ports for electrodes sealed with rubber packings. A special feeder in the view of "spider" was used for addition of MgCl, in the melt.

The electrochemical behavior of carbon dioxide under excessive pressure was investigated in a hermeti-

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cally sealed three-electrode cell made of special stainless steel, which permitted measurements at temperatures up to 900 °C and at excessive gas pressure up to 2.0 MPa and described in<sup>[13]</sup>.

Voltammetry with single and cyclic potential sweep was chosen as the electrochemical method of investigation. I – E curves were obtained with a PI-50-1 potentiostat in a polarization rate range of 0.01 - 10 V/s. Investigations were carried out at a CO<sub>2</sub> pressure of 0.1 - 1.7 MPa. All experiments were carried out by evacuating the system firstly to -13.3 Pa and then passing carbon dioxide through the system for 10 minutes. After that the needed pressure was produced in the cell. Polarization curves were taken after keeping the system under isothermal and isobaric conditions for no less than 1 h, i.e. after attaining the equilibrium:  $CO_2$  (gas, P, T) =  $CO_2$  (in the melt, P, T)

The electrolysis of the studied systems was carried out in the same cell as voltammetry measurements in the mode of either constant cathode current or potential. Semi-immersed platinum and glassy carbon plate electrodes (cathode area 5 cm<sup>2</sup>, anode area 10 cm<sup>2</sup>) were used in electrolysis experiments.

A powder product was either settled down onto the crucible bottom or assembled on the cathode in the form of electrolytic "pear". The deposit was separated from salts by successive leaching with hot water. Thereafter, the precipitate was washed with distilled water by decantation method several times and dried to a constant mass at 100 °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\_alpha monochromatic radiation), methods of electron diffraction, scanning electronic microscopy (JEM -100 CX).

#### **RESULTS AND DISCUSSION**

## Electroreduction of CO<sub>2</sub>, dissolved in Na,K|Cl

At polarization rates over 0,1 V s<sup>-1</sup> it was found that the process of carbon dioxide reduction occurred in one stage in the potential rage - 0,3 - 0,5 V against platinum carbonate reference electrode, and the linear dependence of the wave current on gas pressure is observed (Figure 3a, b). The product produced under the constant potential mode electrolysis (E = -0.9 V) at

CO<sub>2</sub> pressure 1,0 MPa is dispersed powder of carbon. Kinetic peculiarities of this process and obtained carbon characterization were described in detail in<sup>[13]</sup>. In this process CO<sub>2</sub> acts both as carbon source and as an acid, which binds the oxygen anions that is liberated in the near-electrode space. Therefore, the cathodic reaction may be represented as

$$3 \operatorname{CO}_2 + 4e \to C + 2 \operatorname{CO}_3^{2}$$
 (1)

# Influence of Mg<sup>2+</sup>ions on WO<sub>4</sub><sup>2-</sup> electroreduction.

Figure 4a shows current-voltage curves in tungstate-

I,mA cm<sup>2</sup>

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Figure 3a : Voltammograms of the Na, K|Cl melt on Pt electrode at 750°C saturated with CO, under excess pressure (MPa): 1-0, 2-0.1, 3-0.2, 4-0, 3, 5-0.5, 6-0.7, 7-1.0, 8-1.2, 9-1.5; potential scan rate 5 V/s. Figure 3b : Dependence of peak current (ip) of the CO2 wave against CO, pressure, potential scan rate 5 V/s.

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containing chloride melt. The tungstate anion is electrochemically inactive in NaCl-KCl melts when  $Mg^{2+}$  cations are not present (curve 2) in the electrolyte. When  $Mg^{2+}$  ions are added in the melt waves of the reduction of  $WO_4^{2-}$  appear in the current-voltages curves at potentials – 0,8 and -1,1 V against a platinum oxygen reference electrode. The wave is shift in the positive direction with increasing  $Mg^{2+}$  ion concentration, and the limiting (or peak) currents increase. A metallic tungsten powder is the electrolysis product obtained under potentiostatic condition (E = -1,2 V) in the system NaCl-KCl – Na<sub>2</sub>WO<sub>4</sub> (3 mol. %) – MgCl<sub>2</sub> (6 mol.%).

Figure 4b shows plot of wave current against Mg<sup>2+</sup> ion concentration. The current is directly proportional L mA-cm<sup>-2</sup>



Figure 4a : Voltammograms of the Na,K|Cl melt on Pt electrode at 750°C, 1 – pure, 2 – with Na<sub>2</sub>WO<sub>4</sub> (5·10<sup>-5</sup>mol/cm<sup>-3</sup>), 3 to 8 as (2) but with increasing concentration of MgCl<sub>2</sub> (10<sup>-5</sup> mol/cm<sup>-3</sup>): 3 - 4.6, 4 - 7.6, 5 - 26, 6 - 42, 7 - 62; the potential scan rates: 1 to 7 - 1, 8 - 5 V/s. Figure 4b : Peak current as function of MgCl<sub>2</sub> concentration in the melt Na,K|Cl - Na<sub>2</sub>WO<sub>4</sub> (5·10<sup>-5</sup> mol/cm<sup>-3</sup>), potential scan rate 5 V/s.

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**Electrochemistry** An Indian Journal to Mg<sup>2+</sup> ion concentration up to a 3 to 3,5-fold excess of Mg<sup>2+</sup>. The highest limiting current are attained when [Mg<sup>2+</sup>]  $\approx$  4 [WO<sub>4</sub>]<sup>2-</sup>. Under this conditions the ratio of i<sub>d</sub>/nFc = 2,0 · 10<sup>-3</sup> cm/s is commensurate with diffusion constant. Limiting currents that are proportion to the Mg<sup>2+</sup> concentration and values of i<sub>d</sub>/nFc are indication for diffusion character of the steady-state waves.

In accordance with the mechanism of cation catalysis of anion electroreduction that has been described above the following mechanism for the formation of EAS in tungstate-anion containing melts acidified with  $Mg^{2+}$ cations can be suggested:



The cathodic reaction under experiment conditions (way I) can be formulated as

 $\{Mg_n[WO_4]\}^{(2n-2)+} + 6e = W+nMgO + (4-n)O^{2-}$  (3)

Reaction (2) can be shifted according to the way II when the  $Mg^{2+}$  ion are present in a higher than 10-fold excess. In this case coefficient *n* assumed values larger than unity, i.e. the  $[WO_4]^{2-}$  anions will be under the strong polarizing effect of the  $Mg^{2+}$  ions that leads to the formation of volatile tungsten oxychlorides. The calculated heterogeneous charge-transfer rate constant (k<sub>s</sub>) of the studied process increases from  $8.34 \cdot 10^{-4}$  to  $24.62 \cdot 10^{-3}$  cm/s with increasing of  $Mg^{2+}$  ion concentration from  $4.6 \cdot 10^{-5}$  to  $62 \cdot 10^{-5}$  mol/cm<sup>-3</sup>.

The experimental date indicate that the multielectron electroreduction of tungstate ions to metallic tungsten can be accomplished within a narrow range of potentials which are close to the potentials of carbon isolation from  $CO_2$ , and that the potential and mechanism of the process can be controlled via the acid-base properties (Mg<sup>2+</sup> concentration) of the melt.

## Joint electroreduction of [WO<sub>4</sub>]<sup>2-</sup> and CO<sub>2</sub> in chloride melts having different acidities

The joint electroreduction of  $CO_2$  and  $WO_4^{2-}$  in chloride melts acidified with  $Mg^{2+}$  ions was studied as follows. Firstly we set up certain melt acidity by addition of  $Mg^{2+}$  cations, and recorded the current-voltage curve of  $WO_4^{2-}$  electroreduction corresponding to this melt acidity. Then the carbon dioxide was fed to the

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system under different pressures. The arrival of CO<sub>2</sub> in the system does not give rise to any additional wave, but is recognized merely in terms of increasing height of existing wave for  $WO_4^{2-}$  reduction and a minor shift of this wave (by 100 mV) to more positive potentials (Figure 5). A special feature of behavior of the system is the considerable shift of the wave seen at pressures of 0.5-0.7 MPa due to change in function of the reference electrode described in<sup>[13]</sup>. Loss of CO<sub>2</sub> pressure leads to a return to the original reduction situation, both with respect to potential and with respect to current.

Thus the summary process of the electrochemical synthesis of tungsten carbide can be described by the overall reaction

 ${\rm Mg_n[WO_4]}^{(2n-2)+} + {\rm CO_2} + 10 e \rightarrow {\rm WC} +$ 

I,mA.cm<sup>-2</sup>



Figure 5 : Voltammograms of the Na, K|Cl melt on Pt electrode at 750 0C, 1 - pure, 2 - with Na2WO4 (5.10-5 mol/cm-3), 3 - with Na2WO4 (5.10-5 mol/cm-3) and acidified with MgCl, (1.5.10-4 mol/cm-3), 4 to 10 as (3) but saturated with CO2 under excess pressure (MPa): 4 – 0.1, 5-0.25,6 – 0.5, 7 -0.75, 8-1.0, 9-1.25, 10-1.5, 11 as 3, but after a pressure drop down to zero; potential scan rate 0.1 V/s

 $n MgO + (6 - n) O^{2}$ 

(4)The electrolysis in the system NaCl – KCl –  $Na_2WO_4$  (3 mol.%) –  $MgCl_2$  (6 mol.%) –  $CO_2$  with different cathode current densities  $(i_{\mu})$  and at various gas pressures was carried out for producing cathodic product. The single-phase WC powder was produced in the studied system with electrodeposition rate 0.3 g/ A·h at CO<sub>2</sub> pressure over 1,7 MPa and at current density interval 0.05 - 0.2 A/cm<sup>2</sup>. The dependences of powder specific surface and its dispersity are observed in the indicated current density values. Specific surface and particles size of the product are 10(25) m<sup>2</sup>/g and 2-5 (05)  $\mu$ m correspondingly at i<sub>k</sub> = 0.05 (0.2) A/cm<sup>2</sup>. If  $i_{\nu} > 0.2 \,\text{A/cm}^2$  the cathode product consisted of mixture of carbides WC +  $W_2C$ . If  $i_k < 0.05 \text{ A/cm}^2$  the cathode powder was a mixture of  $W_2C + C$ . The composition of cathodic product depends also on the CO<sub>2</sub> pressure in the cell (TABLE 2).

#### **Product characterization**

Cathodic products were identified by the methods of X-ray and chemical analysis. The agreement between

TABLE 2 : Cathodic product composition in the system NaCl- $KCl - Na_{4}WO_{4}$  (3 mol. %) - MgCl, (6 mol.%) - CO<sub>2</sub>, bath voltage 2,4 V,  $\dot{E}_{cathode} = -1,4 V, T = 750 \,^{\circ}C$ 

Pressure CO <sub>2</sub> , · MPa	0	0,25	0,5	0,75	1,0	1,5	1,7
Product		W +	W +	$W_2C +$	$W_2C$	WC +	
approximation	W	trace	WC	trace	+	trace	WC
composition	W	$W_2C$	w <sub>2</sub> C	WC	WC	$W_2C$	

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. WC powder has a hexagonal lattice with the following parameters:  $a = 2.8973 \cdot 10^{-10}$  $m^2$ ,  $\Delta a = 0.00414 \cdot 10^{-10} m^2$ ,  $c = 2.8381 \cdot 10^{-10} m^2$ ,  $\Delta c =$  $0.00885 \cdot 10^{-10} \text{ m}^2$ . The shape and the size of cathode deposit particles were determined with a scanning electron microscope. Two types of particles (Figure 6) are characteristic of WC powders:

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

The results of chemical analysis of the obtained singlephase WC product are presented in the TABLE 3:

According to the TABLE 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 ab-





b

Figure 6 : Photomicrographs and electron (-beam) image of WC powders, obtained in the system NaCl–KCl–Na2WO4 (3 mol.%)–MgCl2 (6 mol.%)-CO2(1.5 MPa), Ebath = 2,5 V. T= 750oC: (a)-individual needle crystals of 0.5-1  $\mu$ m size, (b)-lamellar conglomerates of 10-20  $\mu$ m size.

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TABLE 3: Chemica	l composition of V	VC powder
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Element	W	C (total)	C (pure)	C (bound)
W, mass %	$86.9\pm1$	$7.4\pm0.5$	$2.2 \pm 0.2$	5.2

sence of oxygen peak from Auger spectrograms after 20 min long ionic etching to a depth of  $200 \cdot 10^{-10}$  m indicates the adsorbed nature of oxygen.

#### CONCLUSIONS

Thus, the peculiarities of the cation influence on the change of the geometrical and electronic structure of  $WO_{4}^{2}$ - anion obtained by quantum chemical calculations of energy, charge and geometrical parameters of the interaction  $nMg^{2+}...WO_4^{2-}$  and the profile of the PES of this interaction allow to determine the specific features of the deformation polarization of tungstate anion under the influence of cations. The essence of these specific features is the outer-sphere cationization of the  $WO_4^{2-}$  anion that stimulates the display of the donor properties of the central atom (W) of anion more than those of oxygen atoms. The main "load" in the process is taken by d-orbitals of W atom, making it and cations possible centers of the "electronic attack" in the subsequent reactions of the electroreduction of EAS. Performed quantum chemical calculations in the framework of the proposed model allow one to conclude that the cation composition of the melt catalyzes processes of the preformation of EAS both in the homogenous bulk phase of the melt and at the electrode-melt interface.

Joint deposition of refractory metal and carbon (at the same potentials) is a necessary condition for the electrochemical synthesis of single-phase WC powders in a wide current density range. The phenomenon of cation catalysis can be successfully used for the realization of this synthesis variant. It has been shown by the method of voltammetry that addition of Mg2+ cations to tungstate-containing chloride melts leads to the formation of new EAS (cationized complexes) in melt bulk and to the change of the nature of electrode process. Metallic tungsten deposits at the cathode instead of tungsten bronze. Increasing the magnesium ion concentration in melt leads to a change in the composition of cationized complexes and to an increase of an order of magnitude in heterogeneous charge-transfer rate constant. At the same time the tungsten deposition potential shifts to the positive potential region up to carbon deposition potentials.

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