JOURNAL OF APPLIED ELECTROCHEMISTRY **22** (1992) 717–721

Electrodeposition of refractory carbide coatings from fluoride melts

K. H. STERN

Chemistry Division, Naval Research Laboratory, Washington, DC 20375, U.S.A.

Received 9 September 1991; revised 5 December 1991

Experimental studies relevant to the electrodeposition of the carbides of vanadium, niobium, titanium, and zirconium are reported. These focus on choices of suitable metal precursors, their solubility and reducibility. The state of knowledge in the field is summarized.

1. Introduction

In previous publications from this laboratory, methods for plating carbides of the refractory metals have been described [1–5]. Studies of tantalum [1, 2], tungsten [3], and chromium [4] were carried out in some detail, and molybdenum carbide was plated by Topor and Selman [6]. In this work we describe some studies relevant to plating carbides of vanadium, niobium, titanium, and zirconium and attempt a systematization of carbide plating, based on available data.

All the previous studies as well as the current one have used a single solvent: the ternary eutectic LiF–NaF–KF (FLINAK). This choice was based on the work of Senderoff and Mellors [7–10] who used this solvent in the successful plating of the refractory metals. Although the eutectic temperature of the melt is 453° C, Senderoff and Mellors found that metals could not be successfully plated from FLINAK below 700° C. For this reason all carbide plating has been carried out above this temperature, generally near 750° C.

In order to plate carbides it is necessary to have a source of carbon which can be reduced simultaneously with the metal-containing species. For carbides to form on the cathode surface it is also necessary that the metal and carbon react. Very few studies on carbonate reduction in molten fluorides, particularly in FLINAK, have been carried out. Topor and Selman [11] reported a reduction peak for CO_3^{2-} in this solvent very close to the reduction peak of the solvent itself, whereas Deanhardt and Stern [12] did not observe this peak and therefore concluded that CO_3^{2-} was reduced by an alkali metal, most likely lithium, in a chemical reaction, i.e.

$$4Li + CO_3^{2-} = C + 3O^{2-}$$

CO_3^{2-} has reduction has also been studied in chloride melts. Delimarskii *et al.* [13, 14] obtained carbon in a NaCl–KCl melt saturated with CO_2 at 680° C and accounted for their results by a two-step process

$$CO_2 + 2e^- = CO_3^{2-}$$

$$CO_3^{2-} + 2e^- = C + 2O^{2-}$$

In the presence of CO_3^{2-} the above partial reactions are preceeded by the chemical equilibrium

$$CO_3^{2-} = CO_2 + O^{2-}$$

which appeared to be the rate-controlling step. In the absence of added CO_2 the above mechanism is less likely than the direct reduction observed by Inman [15] in a ternary chloride melt at 450° C. The situation is further complicated by the effect of the melt cation on the reduction path, as was found by Bartlett and Johnson [16, 17] for pure alkali metal carbonates, for which reversible reduction potentials vary with the cations.

There are as yet no systematic studies of the effect of solvent cations and anions on the carbonate reduction mechanism and the situation must be regarded as unsettled. From a practical point of view, however, the carbonate reduction mechanism is less important than the fact that it occurs and that the product is carbon, and that therefore refractory carbides can be plated if (a) a suitable metal precursor can be reduced to the metal simultaneously with CO_3^{2-}, and (b) the metal and carbon react.

The introduction of CO_3^{2-} into FLINAK containing a refractory metal fluoride leads to CO_2 evolution as the result of an acid-base reaction between the acid metal salt and basic CO_3^{2-}. The implications of this reaction for carbide plating have been studied in considerable detail, at least for tantalum [2]. For the Ta–C system the acid-base reaction is

$$K_2TaF_7 + 3K_2CO_3 = KTaO_3 + 3CO_2 + 7KF$$

However, tantalum carbide is still plated from a K_2TaF_7 + K_2CO_3 melt because the reaction does not go to completion. This type of reaction seems to be quite general. A potential alternate path to carbide formation would exist if the metal oxyanion, TaO_3^- in the above example, were reducible. This requires that the alkali metal salt is (a) soluble and (b) reducible at or below the cathodic limit of the melt. This condition is fulfilled for MoO_4^{2-} and WO_4^{2-}, but not for the oxyanions of other refractory metals.

In this work we report relevant studies of titanium, vanadium, niobium, and zirconium.

0021-891X/92 © 1992 Chapman & Hall

2. Experimental details

The conditions of the experiments were as described previously [1–4] with respect to glove box atmosphere and FLINAK preparation. Reagent grade K_2TiF_6, K_2TiO_3, $NaVO_3$, Na_3VO_4, ZrF_4, and $LiNbO_3$ were dried for several days at 120° C.

Since it was only necessary to determine whether the above compounds were sufficiently soluble in FLINAK to permit electrochemical studies to be carried out, solubility was determined visually by adding the respective compounds to FLINAK and observing dissolution.

Compounds which were soluble were studied electrochemically. Current–voltage curves were obtained with a 5A potentiostat (Electrosynthesis Company) using a nickel working electrode consisting of a nickel 200 coupon welded to a nickel rod, glassy carbon counter, and platinum quasi-reference, consisting of a bare platinum wire immersed in the melt. It should be emphasized that the potential of this electrode is sensitive to the oxide activity of the melt [12] and that therefore the potentials measured are only significant for each particular melt.

3. Results

3.1. K_2TiO_3

The reaction between K_2TiF_6 and K_2CO_3 in FLINAK was studied visually. For C/Ti $\leqslant$ 2, the reaction proceeds with vigorous gas evolution, with very slight reaction, if any, for C/Ti > 2. By analogy with the tantalum case the most likely stoichiometry of the reaction is

$$K_2TiF_6 + 3K_2CO_3 = K_2TiO_3 + 3CO_2 + 6KF$$

It thus appears likely that the reaction does not go to completion and it might be possible to plate the carbide by a judicious choice of concentrations.

Potentiometric measurements [18] have shown that the solubility of K_2TiO_3 does not exceed 0.2 mol % (m/o). Current–voltage curves for incremental additions of K_2TiO_3 are virtually identical with those for FLINAK alone, indicating that the compound, even though slightly soluble, is not reducible below the cathodic limit of the melt.

3.2. $LiNbO_3$

The solubility of this compound is at least 0.3 m/o. The current–voltage plot is shown in Fig. 1. The curves show the current increasing with increasing $LiNbO_3$ concentration well below the cathodic reduction of the solvent. Since niobium is in its highest oxidation state the process is presumably a reduction, but not necessarily to the metal.

Attempts to plate at 1.1 V led to no coating, indicating that the reduction goes to some lower-valent, nonzero state. Thus carbides cannot be plated from a $LiNbO_3$–K_2CO_3 melt since the metal cannot be plated.

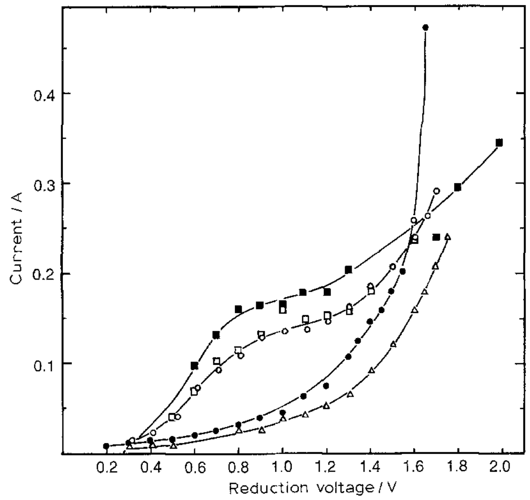

Fig. 1. Current–voltage curves for the potentiostatic reduction of $LiNbO_3$ in FLINAK at 750° C. Pt reference. Concentrations (in mol %): (●) 0.0, (▲) 0.027, (○) 0.066, (□) 0.135 and (■) 0.276.

The addition of K_2CO_3 to K_2NbF_7 in FLINAK leads to gas evolution which ceases when Nb/C = 1. Since, by analogy with the tantalum case, the reaction most likely is

$$K_2NbF_7 + 3K_2CO_3 = KNbO_3 + 3CO_2 + 7KF$$

the reaction does not go to completion and the carbide probably could be plated, although Senderoff and Mellors [9] found that because of oxidation–reduction reactions, a niobium valence of 4.5 is required (see below).

3.3.1. $NaVO_3$. The solubility is at least 1.0 m/o and current–voltage curves (Fig. 2) exhibit increased current with increasing concentration. Plating experiments at 1.0–1.1 V produce small amounts of a dark coating which is not very adherent, and difficult to identify by X-ray diffraction. The current efficiency is < 10%, based on metallic vanadium.

If K_2CO_3 is added to the melt (V/C = 1), the dark coating produced is completely non-adherent.

3.3.2. Na_3VO_4. The solubility of this compound is at least 0.3 m/o. Current–voltage curves (Fig. 3) up

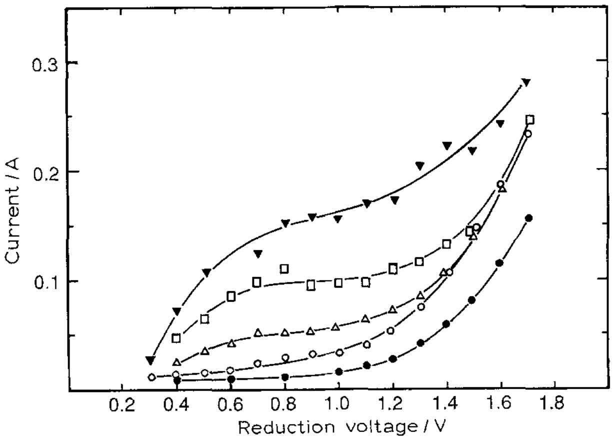

Fig. 2. Current–voltage curves for the potentiostatic reduction of $NaVO_3$ in FLINAK at 750° C. Pt reference. Concentrations (in mol %): (●) 0.0, (○) 0.092, (▵) 0.200, (□) 0.434 and (▿) 0.886.

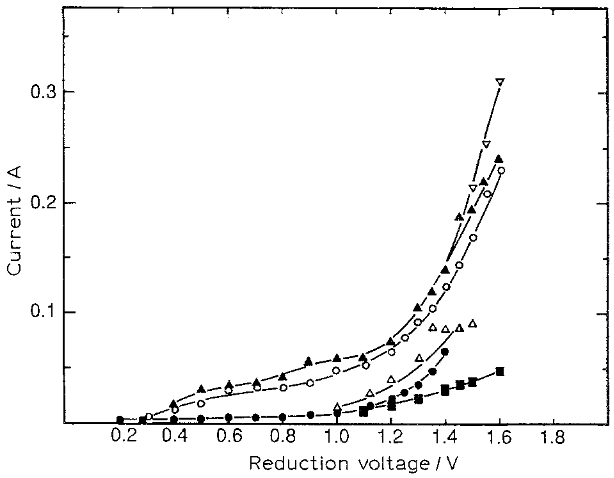

Fig. 3. Current–voltage curves for the potentiostatic reduction of Na_3VO_4 in FLINAK at 750° C. Pt reference. Concentrations (in mol %): (●) 0.0, (△) 0.012, (■) 0.040, (○) 0.286, (▲) 0.539 and (▼) 0.957.

to this concentration show only slightly increased current with increased concentration, in contrast to $NaVO_3$ in which vanadium also has a valence of + 5.

3.4. *ZrF_4*

This compound is quite soluble in FLINAK and was, in fact, used by Mellors and Senderoff [10] as the precursor for successful zirconium plating. The addition of K_2CO_3 to a 0.55 m/o ZrF_4 melt produces only slight gas evolution, in contrast to most other refractory metal fluorides. However, near Zr/C = 1 the solution turns cloudy because an insoluble material is being formed, most likely ZrO_2 or K_2ZrO_3:

$$ZrF_4 + 2K_2CO_3 = ZrO_2 + 2CO_2 + 4KF$$

or

$$K_2ZrF_6 + 3K_2CO_3 = K_2ZrO_3 + 3CO_2 + 6KF$$

The present experiment does not allow a distinction between these two reactions.

4. Discussion

At least some information related to carbide formation is now available for all the refractory metals except hafnium. In this section the current state of knowledge for the eight elements for which results have been reported are summarized.

4.1. *Titanium*

No carbide plating studies have been done, but any attempt to plate titanium carbide requires the use of K_2TiF_6, although this salt undergoes an acid-base reaction with K_2CO_3, because TiO_3^{2-} is only very slightly soluble in FLINAK and is not reducible. Little is known about TiC, which seems to be the only carbide in the Ti–C system. It seems to oxidize somewhat more easily than other refractory carbides [20].

4.2. *Vanadium*

Two carbides of vanadium appear in the V–C phase diagram; VC and V_2C. They are quite hard, but are reported to oxidize rapidly in air at 800° C.

Mellors and Senderoff report in their patent [7] that vanadium can be plated from a fluoride melt containing V(III), but otherwise give no details. Since the sources of V(III), i.e. VF_3 or K_3VF_6, are very expensive, they are probably not practical precursors for large-scale plating. In this work the oxyanions containing V(V), i.e. VO_3^- and VO_4^{3-} have been studied. Figure 2 shows *V–i* curves for $NaVO_3$ in FLINAK which shows that (a) the salt is quite soluble and (b) that it can be reduced below the cathodic limit of the melt. A black, porous deposit appears on the cathode when plating is carried out at 1.1 V, whose by X-ray diffraction pattern does not correspond to a known compound, but it is not metallic vanadium.

Similar results were obtained for Na_3VO_4 (Fig. 3), but the solubility of this compound seems to be less than that of $NaVO_3$.

There is no gas evolution from a $NaVO_3$–K_2CO_3 melt, but attempts to plate a carbide at 1.1 V only results in a black deposit, probably carbon, which is completely non-adherent. Further work is required to elucidate the reduction mechanism of the vanadium oxyanions.

4.3. *Niobium*

There are two forms of niobium carbide: NbC and Nb_2C. NbC is fairly unreactive toward oxygen [20] and would therefore make a useful high temperature wear coating. NbC has been electrodeposited from a melt containing $Na_2B_4O_7$, Na_2CO_3, NaF, and KF as solvent and Nb_2O_5 as the solute [21], but as crystals rather than as a coating. Perhaps changing concentration and/or electrochemical parameters would be useful for producing coatings by this method.

Senderoff and Mellors studied the reduction of niobium in considerable detail [19]. They found that the valence of the niobium species is extremely important and must be close to + 4.5 for high current efficiency because of the interconversion between the intermediate species Nb(IV) and Nb(I).

As found in this work, K_2NbF_7 reacts with K_2CO_3 in an acid-base reaction to evolve CO_2. By analogy with tantalum [2], this reaction probably does not go to completion and carbides can probably be plated from FLINAK containing K_2NbF_7 and K_2CO_3, but this has not yet been investigated, nor is it known under what conditions each carbide can be plated, and which one has better coating properties.

Current-voltage curves for $LiNbO_3$ in FLINAK (Fig. 1) show that NbO_3^- can be reduced below the cathodic limit of the melt. It is not clear why a doubling of concentration from 0.066 to 0.135 results in virtually no increase in current, and why some of the curves cross the curve for pure (unelectrolysed) FLINAK. The curve for 0.027 m/o is below that for FLINAK alone, possibly because NbO_3^- reacts with some impurity in FLINAK, perhaps O^{2-}. Such behaviour has been observed for other refractory metal oxyanions [9].

4.4. *Tantalum*

The factors affecting the electrodeposition of tantalum carbide have been studied in considerable detail [2], but not all aspects are yet understood. K_2TaF_7 and K_2CO_3 undergo an acid-base reaction with CO_2 evolution, but this reaction does not go to completion, and either TaC or Ta_2C can be plated, depending on the concentration. However, since only Ta_2C is produced as a hard, adherent coating, our studies have been concentrated on this carbide. Successful plating requires careful control of the C/Ta ratio. For C/Ta $\geqslant 3$ the electrode becomes passivated for Ta reduction, perhaps because too much insoluble $KTaO_3$ is produced on the electrode. Since the solubility of $KTaO_3$ in FLINAK is very low [18], and it seems to be irreducible it cannot be used as a precursor for tantalum plating.

In addition to the work described above, TaC has been synthesized electrochemically from a borate-fluoride melt by Hockman and Feigelson [21] but the material did not have the characteristics of a coating.

4.5. *Chromium*

Three carbides appear on the Cr–C phase diagram: $Cr_{23}C_6$, Cr_7C_3, and Cr_3C_2. Oxidation of the bulk materials does not begin until 1000° C [20]; thus these carbides would make excellent high temperature wear coatings.

Several possible paths to the electroplating of the chromium carbides have been studied [4]. K_2CrO_4 is quite soluble in FLINAK, producing intensely yellow solutions, but CrO_4^{2-} cannot be reduced below the cathodic limit of the melt. The most useful precursor to carbide plating is CrF_2 since Cr(III) is not easily reduced, probably because the reduction Cr(III) → Cr(II) is difficult. CrF_2 undergoes the usual acid-base reaction with K_2CO_3, but chromium carbide can still be formed, probably because the reaction does not go to completion. The reduction of Cr(II) requires a temperature $\geqslant 850°$ C which tends to increase evaporation of carbonate.

Because the X-ray spectra of the three carbides are similar, it has not been possible to distinguish between them. Further work would also be required to increase the current efficiency above 10%.

4.6. *Molybdenum*

Work on molybdenum carbide deposition from molten salts has been carried out primarily by Shapoval and coworkers [22–25], and by Topor and Selman [6]. The former work utilizes mostly chloride melts to which Mg^{2+} is added to bring the deposition potentials of Mo, added as MoO_4^{2-}, and carbon, added as CO_2 under pressure, close together. Most of this work is concerned with the mechanism of Mo_2C deposition, rather than a detailed study of the coating. However, in their most recent work [25] they report obtaining adherent, non-porous Mo_2C coating ~ 50-μm thick, with a current efficiency of 40–50% from a NaCl–LiF melt containing Na_2MoO_4 and Na_2CO_3.

Topor and Selman [6] report obtaining excellent Mo_2C coatings by the simultaneous reduction of MoO_4^{2-} and CO_3^{2-} in FLINAK. Electrode kinetic studies [11] indicate that Mo(VI) is first reduced to Mo(III), and that then the simultaneous reduction to Mo and C occurs in the same narrow potential range.

4.7. *Zirconium*

As shown in the previous section, ZrO_2 and K_2ZrO_3 are insoluble. Electroplating zirconium carbide would therefore require ZrF_4 or K_2ZrF_6 as precursor. However, since ZrO_2 and K_2ZrO_3 are only slightly soluble, very careful adjustment of concentrations and concentration ratios would be required to avoid precipitating these materials, rather than reducing the precursors electrochemically.

4.8. *Tungsten*

The formation of W_2C is analogous to that of Mo_2C. Excellent coatings of columnar structure were obtained by Stern and Deanhardt [3] by the simultaneous reduction of WO_4^{2-} and CO_3^{2-} in FLINAK at 750° C over a fairly wide range of composition and voltage. More recently, Ito and coworkers [26, 27] have investigated the effect of WO_4^{2-}–O^{2-} equilibria on tungsten and tungsten carbide electrodeposition, and found that the melt basicity has considerable influence on the character of the deposit, probably by controlling the concentration of the tungsten-containing species.

Conditions for the simultaneous reduction of $[WO_2F_4]^{2-}$ and CO_2 in a chloride-fluoride melt have also been described [28], but the resultant carbide has not yet been well characterized.

4.9. *General comments*

In Table 1 the state of carbide chemistry described above is summarized.

From Table 1 it appears that the ease of carbide plating increases from group IVA of the periodic table to group VIA and with increasing atomic weight of the metal. If we consider the two metal species that have been used as precursors in FLINAK, complex fluorides and oxyanions, separate generalizations can be made. Complex fluorides: It is known from the work of Senderoff and Mellors that all the complex fluorides can be reduced to the metal. All the fluorides which we have studied – Ti, Nb, Ta, Cr, and Zr – react with CO_3^{2-} in an acid-base reaction to produce CO_2. For tantalum and chromium, which were studied in detail, these reactions do not go to completion and carbide plating is feasible for appropriate concentrations, concentration ratios, and voltages. Each system requires

Table 1. The state of molten salt carbide plating from FLINAK

Ti TiO_3 solubility low, not reducible. TiF_6^{2-} reacts with CO_3^{2-} to form TiO_3	**V** VO_3^-, VO_4^{3-} soluble and reducible, but not necessarily to V^0	**Cr** CrO_4^{2-} soluble, but not reducible; carbides can be plated from Cr(II) + CO_3^{2-}
Zr ZrF_4 reacts with K_2CO_3 to form ZrO_2 or ZrO_3^{2-} – insoluble	**Nb** NbO_3^- soluble and reducible, but not necessarily to Nb^0. NbF_7^{2-} – No carbide plated yet	**Mo** Mo_2C plated from MoO_4^{2-} + CO_3^{2-}
Hf Not studied	**Ta** Ta_2C plated from TaF_7^{2-} + CO_3^{2-} over narrow concentration range. TaO_3^- solubility low, not reducible	**W** W_2C plated from WO_4^{2-} + CO_3^{2-}

separate study to determine the most feasible precursor, e.g. Cr(II) rather than Cr(III), and conditions.

4.9.1. Oxyanions. The utility of oxyanions as precursors for carbide plating depends on (a) solubility of their alkali metal salts and (b) their electrochemical reducibility. The solubility appears to be inversely related to the melting point, as shown in Table 2.

The alkali metal ions shown are for the most readily available anhydrous compounds. The solubility increases (melting point decreases) from IVA to VIA and is greater from the lighter elements, e.g. vanadate is quite soluble, tantalate is slightly soluble.

It is obvious that for those metals whose oxyanions are the least soluble, plating from fluoride-carbonate mixtures is likely to be the most difficult, because of the competition between the precipitation and reduction reactions.

5. Conclusions

It is obvious from the work described that progress toward producing practical carbide coatings has reached very different stages for different carbides. Molybdenum and tungsten are further advanced, with the main need for controlling the microstructure of the coatings, possibly by careful concentration and voltage control. Tantalum carbide has been shown to be plateable, if careful control over the melt composition and electrochemical parameters is exercised. Chromium carbide can be plated, but the current efficiency achieved so far is too low to be practical. The carbides of titanium, zirconium, and niobium have not yet been plated, and the effect of the acid-base reactions on the plating process remain to be determined. For titanium and zirconium the low solubility of their oxyanions probably precludes them from being precursors for plating. The oxyanions of vanadium and niobium are reducible, but possible methods for reducing them to metal have not yet been studied. Hafnium has not yet been investigated at all.

Table 2. Melting points of oxyanion salts of the refractory metals

$KTiO_3$ 1615°C	$NaVO_3$ 630°C Na_3VO_4 860°C	K_2CrO_4 968°C
$KZrO_3$ unknown	$LiNbO_3$ 1248°C	Na_2MoO_4 687°C
$KHfO_3$ unknown	$KTaO_3$ 1370°C	Na_2WO_4 698°C

References

[1] K. H. Stern and S. T. Gadomski, *J. Electrochem. Soc.* **130** (1983) 300.

[2] K. H. Stern and D. R. Rolison, *ibid.* **136** (1989) 3760.

[3] K. H. Stern and M. L. Deanhardt, *ibid.* **132** (1985) 1891.

[4] K. H. Stern and D. R. Rolison, *ibid.* **137** (1990) 178.

[5] K. H. Stern, *U.S. Patent 4 430 170*, February 1984.

[6] D. C. Topor and J. C. Selman, *J. Electrochem. Soc.* **135** (1986) 384.

[7] G. W. Mellors and S. Senderoff, Canadian Patent No. 688 546, 9 June 1964.

[8] *Idem, Science* **153** (1986) 1475.

[9] *Idem, J. Electrochem. Soc.* **112** (1965) 266, 841.

[10] *Idem, ibid.* **113** (1966) 60, 66.

[11] D. C. Topor and J. R. Selman, Extended Abstract 21-09-12G Int. Soc. Electrochem., Kyoto, Japan, September 1989.

[12] M. L. Deanhardt, K. H. Stern and A. Kende, *J. Electrochem. Soc.* **133** (1986) 1148.

[13] Yu. K. Delimarskii, V. I. Shapoval, V. F. Ghishchenko and V. A. Vasilenko, *Doklady A.N. U.S.S.R.* **183** (1968) 1332.

[14] Yu. K. Delimarskii, V. I. Shapoval and V. A. Vasilenko, *Elektrokhim.* **7** (1971) 1301.

[15] D. Inman, in Proceedings of the Fifth International Symposium on Molten Salts, (edited by M. L. Saboungi, D. S. Newman, K. Johnson and D. Inman), The Electrochemical Society Series 86-1, Pennington, NJ (1986) p. 109.

[16] H. E. Bartlett and L. E. Johnson, *Can. J. Chem.* **44** (1966) 2119.

[17] *Idem, J. Electrochem. Soc.* **114** (1968) 457.

[18] K. H. Stern, *ibid.* **136** (1989) 439.

[19] G. W. Mellors and S. Senderoff, *ibid.* **112** (1965) 266.

[20] E. K. Storms, 'The Refractory Carbides', Academic Press, New York (1967).

[21] A. J. Hockman and R. S. Feigelson, *J. Electrochem. Soc.* **130** (1983) 221.

[22] Kh. B. Kushkhov, V. I. Shapoval and I. A. Novoselova, *Elektrokhim.* **24** (1988) 1496.

[23] Kh. B. Kushkhov, I. A., Novoselova, D. G., Supatashvili and V. I. Shapoval, *ibid.* **26** (1990) 48.

[24] V. A. Polishchuk, Kh. B. Kushkhov and V. I. Shapoval, *ibid.* **26** (1990) 305.

[25] Kh. B. Kushkhov, V. V. Malyshev and V. I. Shapoval, *Zashch. Met.* **26** (1990) 1019.

[26] H. Yabe, Y. Ito, K. Ema and J. Oishi, in 'Proceedings of the Sixth International Symposium on Molten Salts', The Electrochem. Soc., Series 87-7, (1987) p. 804.

[27] H. Yabe, K. Ema and Y. Ito, *J. Electrochem. Soc.* **137** (1990) 1739.

[28] Kh. B. Kushkhov, I. A. Novoselova, D. G. Supatashvili and V. I. Shapoval, *Elektrokhim.* **24** (1990) 1496.