Electrochemical Synthesis of Niobium-Hafnium Coatings in Molten Salts

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Graphite is widely used in technology because of its unique properties. A drawback of graphite is its low heat resistance in oxidizing atmospheres. To increase its heat resistance, Nb-Hf protective coatings were synthesized. Electrodeposition of niobium coatings on graphite with subsequent precise surface alloying of niobium with hafnium was studied. Electrochemical synthesis of Nb-Hf coatings from molten salt systems containing compounds of niobium and hafnium was used too. It was shown that Nb-Hf coatings with a planar growing front can be obtained if the concentration and therefore the limiting current density of the more electropositive component Nb is kept low. Nb-Hf coatings with a thickness of 20 – 30 μm have been obtained in this way from an NaCl-KCl-K_2NbF_7 (1 wt%)-K_2HfF_6 (10 wt%)-NaF (5 wt%) melt, above the limiting current density of niobium deposition.

Key words: Graphite-Based Compositions; Heat Resistance; Protective Coatings; Precise Surface Alloying; Electrochemical Synthesis.

1. Introduction

Materials based on graphite are widely used in present-day technology because of the unique properties of graphite. However, a drawback of graphite is its low heat resistance in oxidizing atmospheres. To increase this heat resistance, siliciding and borosiliciding are currently used. Such articles are operable in a limited period of time at temperatures up to 1200 °C only.

In the USA, for a new generation of aerospace vehicles for defense in the program NASA SHARP-B2 composites on the basis of graphite, the next ultra-high temperature ceramics: ZrB_2/SiC, HfB_2/SiC and ZrB_2/SiC/C, were suggested [1]. The results of tests of ceramic materials are presented in Table 1.

As can be seen in Table 1, the highest temperature at which no ablation was observed in arc-jet tests was found for composition No. 1. This composition has the highest melting point. NASA proposed also: HfC/C and HfC+TaC/C.

The aim of this study is the description of electrochemical synthesis of niobium-hafnium coatings for improving the heat resistance of articles based on graphite.

Table 1. Tests of ultra-high temperature ceramics [1].

No.	Composition, vol%	t_{na}, °C	$t_{m.p.}$, °C
1	HfB_2-SiC (20%)	2277	2817
2	ZrB_2-SiC (20%)	2017	2587
3	ZrB_2-C (30%)-SiC (14%)	2110	2587

t_{na}, no ablation observed in arc-jet tests.

2. Experimental

2.1. Chemicals

Alkali chlorides (NaCl and KCl) were purchased from Prolabo (99.5% min.). They were dehydrated by continuous and progressive heating just above the melting point under gaseous HCl atmosphere in quartz ampoules. Excess HCl was removed from the melt by argon. NaF (Aldrich, 99.5% min.) was purified by double melt recrystallization: NaF was dried in a glassy carbon crucible (SU-2000) at 400 – 500 °C under vacuum, then heated up to a temperature 50 °C above its melting point and finally cooled to 50 °C below the melting point at a rate of 3 – 4 °C/h.

Sodium, potassium chlorides and sodium fluoride were mixed in the required ratio, placed in a glassy carbon ampoule (SU-2000 type) and transferred to a sealed stainless steel retort. The latter was evacuated to a residual pressure of 0.67 Pa, first at room temperature and then stepwise at 200, 400 and 600 °C. The cell was heated using a programmable furnace. The temperatures were measured using a Pt-Rh (10 wt%)-Pt thermocouple. The retort was then filled with high purity argon (U-grade: < 3 ppm H_2O and < 2 ppm O_2) and the electrolyte was melted.

Potassium hexafluorohafnate (K_2HfF_6) was obtained by dissolving type GFI-1 metallic hafnium or "pure-grade" hafnium tetrachloride in a solution of hydrofluoric acid, followed by precipitation by potassium fluoride. After being washed with ethanol and dried in vacuum, the precipitate was identified by X-ray powder diffraction, IR-spectroscopic, and optical crystallographic analyses.

To produce K_2NbF_7, high purity Nb_2O_5 was dissolved in chemically pure hydrofluoric acid solution (50 wt%). Precipitation of K_2NbF_7 occurred on adding a saturated solution of potassium chloride at 80 °C. The product was filtered, washed with rectified ethanol and dried under vacuum at 70 – 75 °C. The oxyfluoride content in K_2NbF_7 was determined by XRD and optical crystallographic analysis, and did not exceed 0.5%.

K_2HfF_6 and K_2NbF_7 were added to a NaCl-KCl equimolar mixture or to NaCl-KCl-NaF melt.

2.2. Electrochemical Equipment

Alloy formation during electrodeposition of hafnium on a niobium cathode from a molten equimolar mixture of NaCl and KCl containing 10 wt% K_2HfF_6 was studied at 1023 K. The investigation was carried out by a chronopotentiometry method. The electrolysis of the melt, which was placed in a container made from type SU-2000 glassy carbon, was carried out with the aid of a P-5848 potentiostat in an electrochemical cell [2]. The recording of the potential of the niobium cathode (a rod with a diameter of 2 mm, which was obtained from an ingot by electron-beam melting) relative to a hafnium reference electrode (a 5 cm^2 plate) was carried out by a KSP-4 potentiometer and a V7-21 digital voltmeter. The potential scan rate for steady-state voltammograms was $5 \cdot 10^{-3}$ V s^{-1} and the experiments were carried out at 700 – 850 °C.

Electrodeposition and electrochemical synthesis were carried out in a hermetic electrolyzer made of Cr18N10T stainless steel. A sluice device made it possible to replace the cathodes without disturbing the inert atmosphere over the melt. A molybdenum crucible, whose walls and bottom were lined with metallic hafnium or niobium, which served as anodes, was employed as a container for the melt.

2.3. Coating Characterization

The uniformity of the protective coatings was studied by scanning electron microscopy (SEM). The roughness was determined on a Kalibr-252 profilograph-profilometer. The arithmetic mean deviation of the profile (R_a) was selected as a criterion of the roughness. Electron probe microanalysis (EPMA) was used to determine the distribution of alloying elements from the surface to the interior.

3. Results and Discussion

3.1. Electrodeposition of Protective Hafnium Coatings on Articles of Graphite

In the first stage of investigation for defense of graphite articles from high temperature oxidation hafnium coatings were used. Electrodeposition of hafnium coatings from chloride-fluoride melts [3], NaCl-KCl-K_2HfF_6 (10 wt%), NaCl-KCl-K_2HfF_6 (10 wt%)-NaF (5 – 10 wt%) and chloride melts [4], NaCl-KCl-$HfCl_4$ (4 – 10 wt%) on different substrates including graphite were studied in detail [5]. In these works the influence of the electrolysis parameters and composition of the first and second coordination spheres on the hafnium coatings roughness has been investigated. In [5] it was found that during electrodeposition of hafnium on graphite a thin layer (1 μm) of hafnium carbide is formed. Carbide of hafnium is a good barrier coating, which decreases the interdiffusion coefficient of hafnium and carbon by some orders of magnitude. The choice of hafnium as a protective coating for graphite was explained by the next unequal properties of the Hf-C composition:

1.) HfO_2 which is formed during oxidation is one of the most stable oxides.

2.) HfO_2 acts as a good thermal barrier coating.

3.) The interlayer HfC_xO_y is an oxygen diffusion barrier.

4.) The interlayer adheres well to both the residual carbide and the outer oxide.

Special tests on the heat resistance showed that hafnium coatings defense graphite articles up to 1700 °C in the best case. The top temperature 1700 °C for hafnium coatings is determined by the formation of HfO_2 during oxidation and transition of HfO_2 from monoclinic to tetragonal modifications [6]. Due to this phase transition, the composition HfC/C was refused and HfC-TaC/C was chosen, because experiments performed with mixed HfO_2-Ta_2O_5 revealed, that as little as 4 mol% of Ta_2O_5 stabilizes monoclinic HfO_2 as a solid solution without substantially decreasing the high melting point of HfO_2 [7].

It is possible to suggest that the temperature of graphite articles can be increased if niobium-hafnium protective coatings are used. Nb-Hf coatings on graphite can be obtained in two ways. The first includes electrodeposition of niobium coatings on graphite [8] with subsequent precise surface alloying of niobium by hafnium. The second way is electrochemical synthesis of Nb-Hf coatings from molten salt systems containing compounds of niobium and hafnium. Both methods for obtaining niobium-hafnium coatings were studied.

3.2. Precise Surface Alloying of Niobium by Hafnium

On the charging curves (the cathodic chronopotentiograms) in potential-time coordinates (Fig. 1), which allow for studying the ohmic component, there are four sections with different types of variation of the potential, in agreement with the niobium-hafnium equilibrium diagram [9]. The formation of hafnium in niobium takes place in a β-solid solution between 0 to τ_1. The concentration of hafnium in it increases. The formation of an (α+β)-solid solution takes place in the section from τ_1 to τ_2. After the limiting concentration of hafnium in the α-solid solution is achieved (at τ_3), a phase of hafnium forms, and pure hafnium grows.

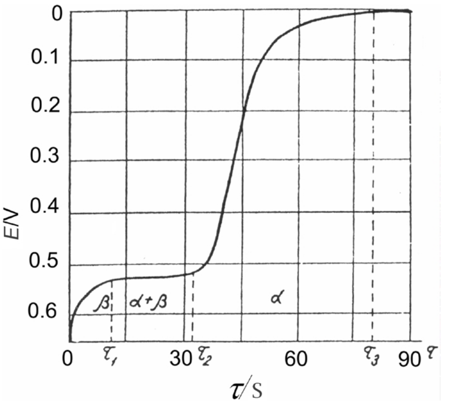

Fig. 1. Dependence of the potential (E, V) formed during electrodeposition of hafnium on the niobium cathode on the electrolysis time (τ, s); cathodic current density, $8.3 \cdot 10^{-3}$ A cm^{-2}; temperature, 750 °C.

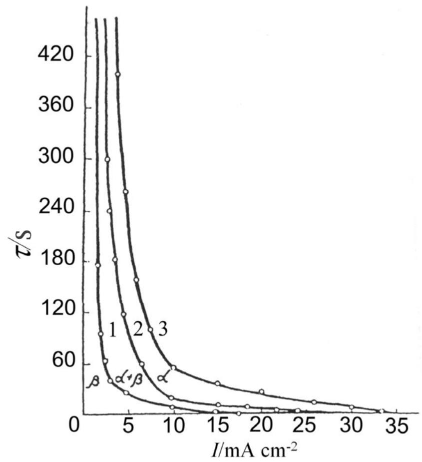

Fig. 2. Time interval for the phases formation and growth on the niobium cathode surface (τ, s) at different current densities (I, mA cm^{-2}). Atomic fraction of Hf on section 1: $C = 5.9$ at%, β-solid solution; section 2: $C = 95.9$ at%, (α+β)-solid solution; section 3: $C = 100$ at%, α-solid solution.

The absence of a potential dependence on the composition (the electrolysis time) is observed in the two-phase (α+β)-region owing to the constant activity of hafnium within the two-phase region. An abrupt variation of the potential is discovered within the α-phase, i. e. the activity of hafnium in the α-phase is very dependent on the concentration.

Charging curves were recorded during the deposition of hafnium on niobium at current densities from $4 \cdot 10^{-4}$ to $5 \cdot 10^{-2}$ A cm^{-2}. Plots of the dependence of the limiting concentration of hafnium in β-, (α+β)- and α-phases (Fig. 2) were obtained on the basis of these curves. The curves obtained made it possible to establish the variation of the phase composition during the electrodeposition of hafnium on niobium and to determine the time intervals for the formation and growth of the phases on the surface of the cathode at different current densities and 750 °C.

It follows from Fig. 2, that in order to obtain a β-solid solution of hafnium in niobium, the electrolysis process must be carried out at a very low current density, i. e., at a current density not exceeding $1 \cdot 10^{-3}$ to $2 \cdot 10^{-3}$ A cm^{-2}. Hafnium coatings can be obtained on a niobium substrate with intermediate layers of solid solutions of hafnium in niobium at current densities ranging from $4 \cdot 10^{-3}$ to $3 \cdot 10^{-2}$ A cm^{-2}. The formation of intermediate layers of solid solutions guarantees good adhesion of the hafnium coating to the niobium substrate. The use of a current density higher than $3 \cdot 10^{-2}$ A cm^{-2} results in the formation of metallic hafnium only on the surface of the niobium substrate.

On the basis of chronopotentiometric curves obtained at different cathodic current densities, the parameters of the solid state interdiffusion coefficients for the couple Hf-Nb can be determined. According to [10], the coefficient $\tilde{D}$ of interdiffusion in the case of solid solution formation of deposited metal with material of the cathode can be calculated by the Sand equation

$$N = 2V_{\mathrm{a}} I \tau^{1/2} / nF \pi^{1/2} \tilde{D}^{1/2}, \qquad (1)$$

where N is the atomic fraction of Hf, V_{a} the molar volume of the alloy (cm^3 mol^{-1}), I the cathodic current density (A cm^{-2}), τ the transition time of the solid solution formation, n the number of electrons involved in the reaction, F the Faraday constant (96487 C mol^{-1}), $\tilde{D}$ the interdiffusion coefficient for the couple Hf-Nb (cm^2 s^{-1}).

Equation (1) is valid under the following conditions: the molar volume of the alloy is invariable; the interdiffusion coefficient is constant and does not depend on the concentration. Using (1) it was found that the interdiffusion coefficients for the couple Hf-Nb at 750 °C in β- and (α+β)-phases are $(2.2 \pm 0.6) \cdot 10^{-10}$ and $(3.2 \pm 0.4) \cdot 10^{-12}$ cm^2 s^{-1}, respectively.

Thus $\tilde{D}$ in the (α+β)-phase is by two orders of magnitude smaller than in the β-phase. These data confirm the correlation between the interdiffusion coefficients in phases of different compositions and their heat resistance. It is known that the heat resistance of Nb-Hf alloys corresponding to compositions of (α+β)-solid solutions is higher than those of the β-phase [11].

Parameters for the formation of the (α+β)-phase of niobium-hafnium alloys were used for the modification of niobium coatings on graphite substrates. The disadvantage of the above described method is the insignificant thickness of the Nb-Hf alloy that leads to a certain limitation of the composite working. Thicker coatings can be obtained by high temperature electrochemical synthesis from molten salts containing compounds of niobium and hafnium.

3.3. Electrochemical Synthesis of Niobium-Hafnium Coatings

The electrolyte NaCl-KCl-K_2NbF_7 (1 wt%)-K_2Hf F_6 (10 wt%)-NaF (5 wt%) and a niobium anode were used for electrochemical synthesis. In contact with the niobium anode, due to the interaction

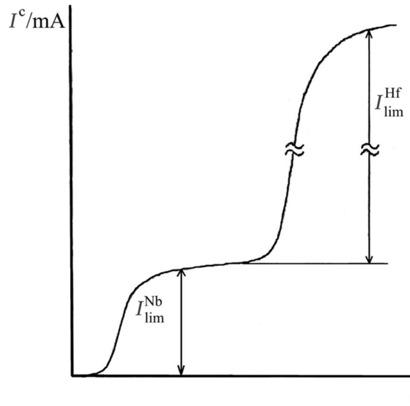

Fig. 3. Scheme of electrodeposition of niobium-hafnium alloys from an NaCl-KCl-K_2NbF_7 (1 wt%)-K_2HfF_6 (10 wt%)-NaF (5 wt%) electrolyte in contact with the niobium anode.

$$4\,\mathrm{Nb(V)} + \mathrm{Nb} \leftrightarrow 5\,\mathrm{Nb(IV)}, \qquad (2)$$

in the melt exist complexes of Nb(IV) only.

Electrodeposition of niobium-hafnium coatings occurs in the "kinetic regime" due to significant difference of formal standard potentials $E^*{}_{\mathrm{Nb(IV)/Nb}}$-$E^*{}_{\mathrm{Hf(IV)/Hf}}$ [12, 13]. A scheme of the electrodeposition of niobium-hafnium alloys is presented in Figure 3. As can be seen from Fig. 3 the deposition of niobium at current densities (I) less than the limiting current density of discharge niobium complexes $I_{\mathrm{lim}}^{\mathrm{Nb}}$ at the graphite cathode, is observed. At $I > I_{\mathrm{lim}}^{\mathrm{Nb}}$ electrodeposition of niobium and hafnium takes place simultaneously. With increasing current density the growth of the hafnium concentration in the alloy was observed.

The steady-state voltammetry method was used for the determination of the limiting current density of discharge Nb(IV) complexes in an NaCl-KCl-K_2NbF_7 (1 wt%)-K_2HfF_6 (10 wt%)-NaF (5 wt%) electrolyte, which was in equilibrium with metallic niobium. For steady-state voltammetry at constant temperature the equation

$$I_{\mathrm{lim}}^{\mathrm{Nb}} = kC_{\mathrm{Nb(IV)}} \qquad (3)$$

is valid [14], where k is the diffusion constant for the limiting current density (A cm^{-2} wt%$^{-1}$) and $C_{\mathrm{Nb(IV)}}$ the concentration of Nb(IV) complexes (1.25 wt% in our case).

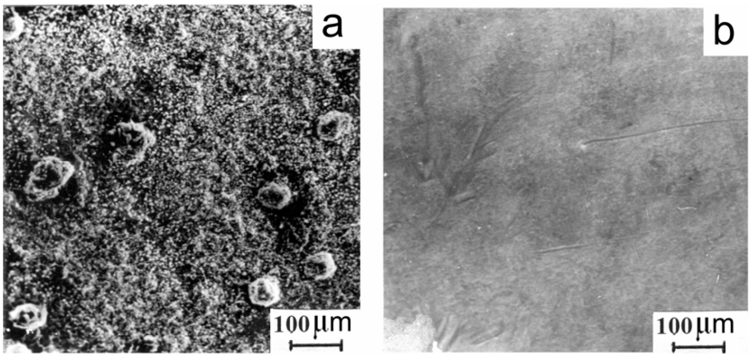

Fig. 4. SEM image of niobium-hafnium coating obtained from an NaCl-KCl-K_2NbF_7 (1 wt%)-K_2HfF_6 (10 wt%)-NaF (5 wt%) electrolyte with a niobium anode at the cathodic current density 0.12 A cm^{-2} and the temperature 750 °C; (a) outer side of the coating; (b) inner side after separation of the coating from the graphite substrate.

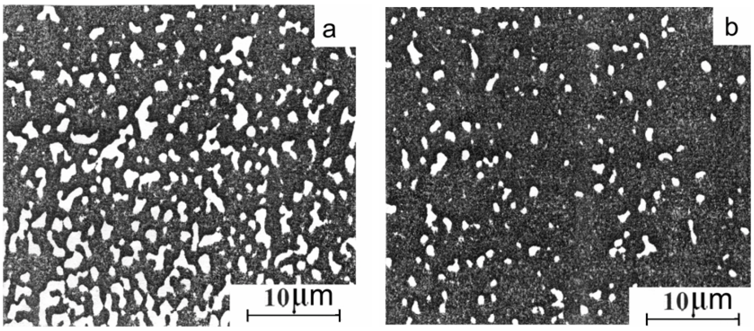

Fig. 5. Scanning images of niobium-hafnium alloys in characterizing rays Nb-L_α; (a) 78.1 wt% Nb; (b) 33.8 wt% Nb.

The dependence of the diffusion constant on the temperature can be described by the equation [14]

$$k = A \cdot 10^{-B/T}, \tag{4}$$

where A and B are constants.

Taking (3) and (4) into account, the expression for the limiting current density is formulated as

$$I_{\mathrm{lim}}^{\mathrm{Nb}} = A \cdot 10^{-B/T} C_{\mathrm{Nb(IV)}}. \tag{5}$$

The limiting current density is satisfactorily fitted by the empirical dependence

$$I_{\mathrm{lim}}^{\mathrm{Nb}} = 15.2 \cdot 10^{-2342/T} C_{\mathrm{Nb(IV)}}. \tag{6}$$

Equation (6) allows to calculate the limiting current density for the abovementioned electrolyte at different temperatures.

In the case of the “kinetic regime”, the ratio of the niobium and hafnium concentrations in the alloy is described by the equation [15]

$$C_{\mathrm{Nb}}/C_{\mathrm{Hf}} = (I_{\mathrm{lim}}^{\mathrm{Nb}} n_{\mathrm{Hf}})/[(I - I_{\mathrm{lim}}^{\mathrm{Nb}}) n_{\mathrm{Nb}}], \tag{7}$$

where n_{Hf} and $n_{\mathrm{Nb}} = 4$, C_{Nb} and C_{Hf} are the concentrations of niobium and hafnium in the alloy.

Table 2. Electron probe microanalysis of Nb-Hf coatings.

Current density, A cm^{-2}	Composition, wt%			
	$\mathrm{Nb_{experimental}}$	$\mathrm{Nb_{Eq.\,7}}$	$\mathrm{Hf_{experimental}}$	$\mathrm{Hf_{Eq.\,7}}$
0.12	81.7	78.1	18.3	21.9
0.25	33.8	39.2	66.2	60.8

So, for the “kinetic regime” the synthesis of Nb-Hf alloys takes place if the applied current density is higher than the limiting current density of the electropositive component (Nb). It was shown that Nb-Hf coatings with a planar growing front can be obtained if the concentration of the more electropositive component is low and therefore the limiting current density ($I_{\mathrm{lim}}^{\mathrm{Nb}}$) is low too. Optimal cathodic current densities for the electrodeposition of Nb-Hf coatings with the thickness 20 – 30 microns were determined. The SEM image of the niobium-hafnium coating obtained from an NaCl-KCl-K_2NbF_7 (1 wt%)-K_2HfF_6 (10 wt%)-NaF (5 wt%) electrolyte with a niobium anode at a cathodic current density of 0.12 A cm^{-2} and the temperature 750 °C is presented in Figure 4. EPMA of some Nb-Hf alloys obtained at different cathodic current densities shows a good agreement between calculated (7) and experimental data (Table 2). The scanning images of niobium-hafnium alloys with 78.1 and

33.8 wt% Nb in characterizing rays Nb-L_α are shown in Figure 5.

Thus, in this study the possibility of the production of Nb-Hf coherent coatings with a thickness of 20 – 30 microns on objects of graphite by electrochemical synthesis is shown.

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