

## Anodic Behavior of Hafnium in Water–Alcohol Solutions of Sodium Chloride

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**Abstract**—High-rate anodic dissolution of hafnium in water-isopropanol-glycerin chloride solutions is studied in relation to the alcohol concentration and electrolyte temperature by voltammetric, chronoamperometric, and photoelectric measurements. The dissolution mechanism varies with increasing potential: upon reaching a potential of 0.4 to 0.5 V, the diffusion control of the process is replaced by kinetic one. It is supposed that the anodic behavior of hafnium is determined by the properties of surface nonstoichiometric semiconducting films, which are present on the metal under all studied conditions.

Hafnium is among a few metals the anodic behavior of which is poorly studied [1, 2]. Studies of its anodic machining in nonaqueous or organo-aqueous solutions, in particular, high-rate electrochemical shaping, are lacking in the literature.

However, hafnium is used in the production of parts of vacuum electronic devices and nuclear reactors. The attempts to mechanically machine thin-walled, easily deformable hafnium parts remain unsuccessful. The problem may be solved by the use of electrochemical machining (ECM), which requires no mechanical force to be applied to a workpiece. Its advantage is also the absence of a defective layer, which impairs the electro-physical properties of a mechanically treated surface. Moreover, choosing the appropriate conditions of ECM and bath compositions, one can control the process and obtain the optimum roughness of a surface.

As was found empirically [3], chloride solutions based on organic solvents that contain both mono- and bi- or tribasic alcohols together enable one to enhance the localization degree of high-rate anodic shaping of the titanium-subgroup metals.

The aim of this study is to elucidate the mechanism (i.e., the essence of the limiting stage) of hafnium anodic dissolution in the sodium chloride–isopropanol (IP)–glycerin (G)–water systems and, incidentally, to estimate their corrosivity to hafnium.

Voltammetric measurements were carried out on a rotating disk electrode, simulating actual ECM conditions, under potentiodynamic (0.05 V/cm) and potentiostatic conditions with a PI-50-1 potentiostat and a PR-8 programmer. The curves were recorded with a PDA-1 two-coordinate potentiometer. The electrode's rotational speed was controlled with the use of an F5035 frequency meter.

The working-electrode potentials were measured and are given against a saturated silver-chloride reference electrode.

The surface state of the test metal was judged by measuring structure-sensitive values of photoelectric polarization [4].

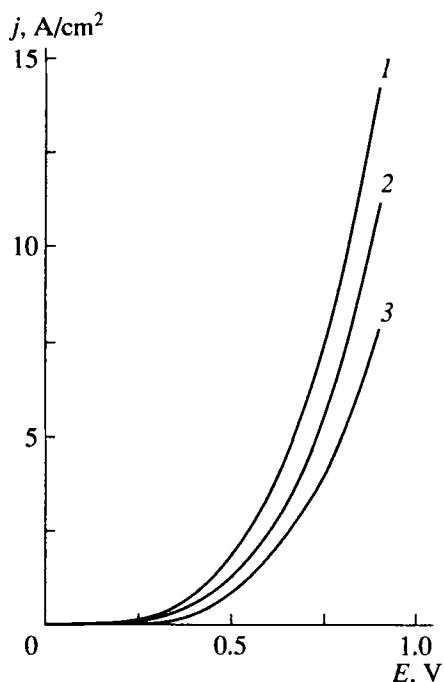
Isopropyl alcohol and glycerin were purified by the procedures proposed in [5] and [6], respectively. The electrodes were produced from hafnium rods (2.5 mm in diameter) obtained by remelting a 99.98% pure commercial hafnium of a vacuum-iodine purification<sup>1</sup>.

Two characteristic domains may be recognized in the hafnium voltammetric curves (Fig. 1). Until reaching the activation potential  $E_{act}$ , its anodic current density slowly increases with an increase in polarization, but starting from  $E_{act}$ , the current grows steeply.

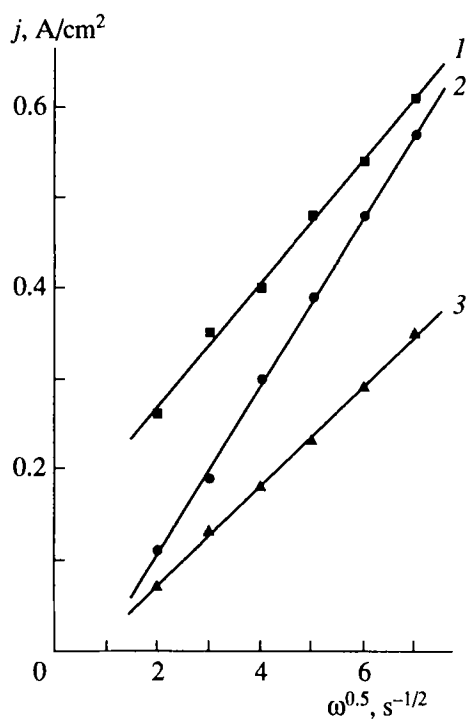
In order to characterize these domains, the plots of  $j$  vs.  $\omega^{0.5}$  were constructed at  $E = 0.4$  V (the first domain) and at  $E = 0.8$  V (the second domain) (Fig. 2). At low potentials, the  $j$  vs.  $\omega^{0.5}$  curve is linear, and we can say that the anodic reaction kinetics is determined primarily by the diffusion of electroactive species in the solution. In the second domain of the polarization curve, the process seemingly proceeds under the kinetic (electrochemical) control, inasmuch as  $j$  is independent of  $\omega^{0.5}$ .

A further evidence that supports the above reasoning is provided by a chronoamperometric study (Fig. 3). The character of a plot of  $j$  vs.  $t^{-0.5}$  also points to the essence of the limiting stage of electrochemical reaction. For the first region of the polarization curve (at low potentials), the dependence of  $j$  on  $t^{-0.5}$  is a straight line corresponding to the diffusion nature of the limiting stage. At high potentials, the dependence is nonlinear.

<sup>1</sup> The remelting (in an inert gas atmosphere) was carried out by B.A. Goncharenko in the Baikov Institute of Metallurgy, Russian Academy of Sciences.



**Fig. 1.** Anodic potentiodynamic (0.05 V/s) voltammetric curves of hafnium rotating disk electrode in water-alcohol 1 M sodium chloride solutions: (1) 1 M NaCl + 1 M IP + 1 M glycerin + water; (2) 1 M NaCl + 2 M IP + 2 M glycerin + water; (3) 1 M NaCl + 3 M IP + 3 M glycerin + water.  $T = 298$  K;  $\omega = 1500$  rpm.

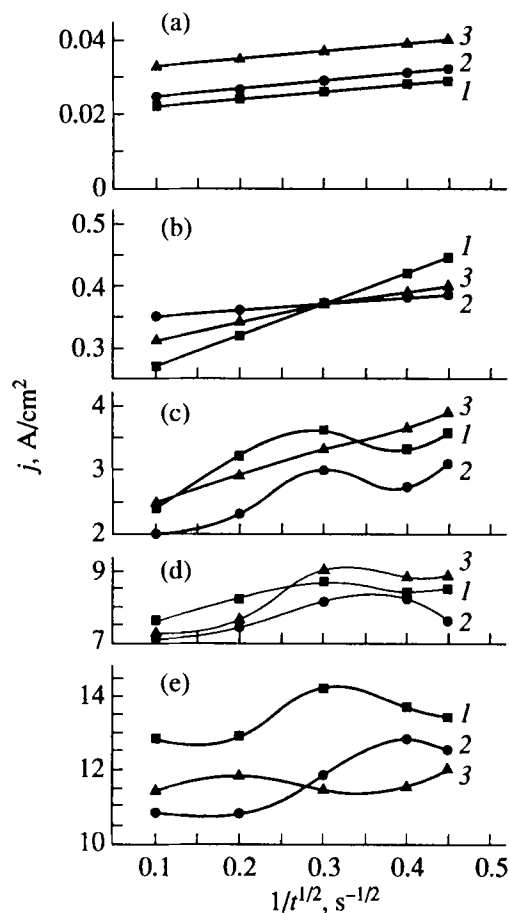


**Fig. 2.** Plots of anodic current of hafnium dissolution in water-alcohol sodium chloride solutions vs.  $\omega^{0.5}$ : (1) 1 M NaCl + 1 M IP + 1 M glycerin + water; (2) 1 M NaCl + 2 M IP + 2 M glycerin + water; (3) 1 M NaCl + 3 M IP + 3 M glycerin + water. The anodic potential is 0.4 V.

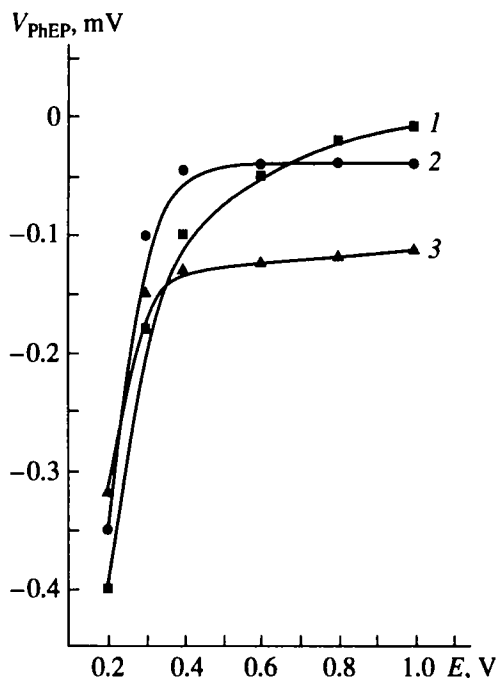
It can be proposed that a change in the essence of the limiting-stage is associated with the structure variation of the metal surface being machined. At low potentials, hafnium surface oxides are modified (alloyed) with the components of the machining solution, while a subsequent increase in the dissolution rate (and the anodic current density) may indicate that the defective film formed on the metal surface does not prevent it from the anodic dissolution.

The presence of a film on hafnium surface in the course of its anodic dissolution is supported by the data of photoelectropolarization (PhEP) measurements (Fig. 4).

At low potentials, the photoresponse is negative, thus indicating that the surface film is the n-type semiconductor. With an increase in the potential, the number of anionic vacancies in the surface layer decreases (as well as the negative photoresponse). This process corresponds to a slight increase in the anodic dissolution rate (the first segment of the polarization curve). Upon

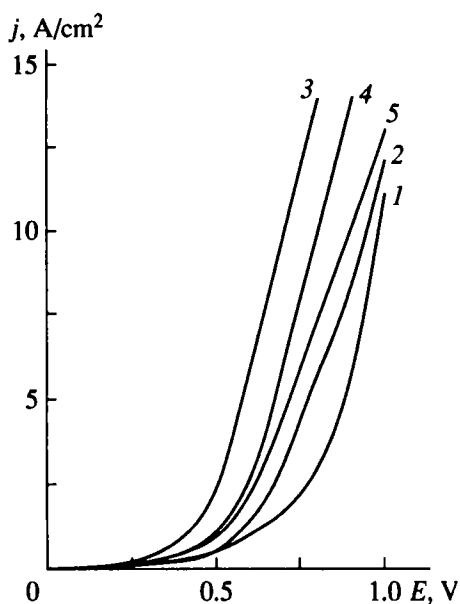


**Fig. 3.** Chronoammograms of anodic dissolution of hafnium rotating disk electrode ( $T = 298$  K;  $\omega = 1500$  rpm) in water-isopropanol-glycerin 1 M sodium chloride solutions. The potential (V): (a) 0.2; (b) 0.4; (c) 0.6; (d) 0.8; (e) 1.0. (1) 1 M NaCl + 1 M IP + 1 M glycerin + water; (2) 1 M NaCl + 2 M IP + 2 M glycerin + water; (3) 1 M NaCl + 3 M IP + 3 M glycerin + water.



**Fig. 4.** PhEP emf of the polarized hafnium electrode as a function of potential: (1) 1 M NaCl + 1 M IP + 1 M glycerin + water; (2) 1 M NaCl + 2 M IP + 2 M glycerin + water; (3) 1 M NaCl + 3 M IP + 3 M glycerin + water.

the formation of the surface film, the number of its defects remains virtually constant: the PhEP emf is close to zero in this domain, with small positive or negative deviations. The negligibility of PhEP allows us to



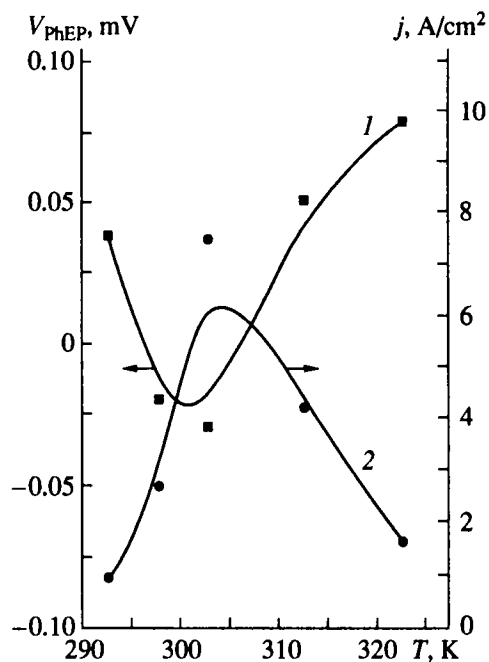
**Fig. 5.** Anodic potentiodynamic (0.05 V/s) voltammograms of hafnium rotating disk electrode in 1 M NaCl + 2 M IP + 2 M glycerin + water electrolyte at the following temperature, K: (1) 293, (2) 298, (3) 303, (4) 313, and (5) 323;  $\omega = 1500$  rpm.

propose that, in this case, the reaction rate is determined by a transfer in the solid surface film having a nearly stoichiometric composition [7].

One more feature of high-rate anodic dissolution of hafnium is worth noting. The temperature dependence of its rate has a maximum (Figs. 5 and 6, curve 2). According to [8], this is due to the change in the mechanism of metal dissolution with an increase in temperature. Probably, highly dispersed  $\text{Hf}(\text{OH})_4$  hydroxide is one of the basic components of the surface film on hafnium before the maximum, and it converts into difficultly soluble  $\text{HfO}(\text{OH})_2$  with an increase in temperature.

The change in the mechanism of hafnium anodic dissolution caused by the elevation of temperature, and associated with the presence of varying oxide film on its surface, can also explain the correlation between the temperature dependences of the anodic dissolution rate and the PhEP dependences of the test electrode (Fig. 6). A decrease in the negative PhEP emf above a temperature of 303 K points to an increase in the hafnium fraction of the surface film composition. This agrees well with the above supposition that, with an increase in temperature,  $\text{Hf}(\text{OH})_4$  converts into  $\text{HfO}(\text{OH})_2$ , the latter compound being richer in metal than the former.

The results of the study indicate that the mechanism of hafnium anodic dissolution changes with an increase in either the anodic potential or the temperature of the bath in which the electrochemical machining is performed. The change in the mechanism is caused by the



**Fig. 6.** Plots of (1) PhEP emf and (2) current density of hafnium anode vs. the temperature of 1 M NaCl + 2 M IP + 2 M glycerin + water electrolyte;  $\omega = 1500$  rpm at a potential of 0.6 V.

change in the composition and properties of oxide film on the metal surface.

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