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The Oxidation of ZrB_2, TaB_2, NbB_2, and W_2B_5 in Atomic Oxygen and by Anodic Polarization

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The oxidation of ZrB_2, TaB_2, NbB_2, and W_2B_5 in atomic oxygen and by anodic polarization was studied. All the investigated materials, both in the gas medium and in the electrolyte, were highly resistant to corrosion. The composition of the surface compounds was examined during the oxidation. High resistance to oxidation is explained by the B_2O_3 oxide. Oxidation of borides in both atomic oxygen and in 1 N H_2SO_4 takes place at comparable rates, the corrosion resistance in the two media being similar.

INTRODUCTION

The reactions taking place during anodic polarization are extremely complex. A characteristic feature of these reactions is that they involve the participation of both acid anions and hydrous hydroxyl. Of particular importance are oxygen atoms which form from hydroxylic ions, becoming adsorbed on the surface of an electrode and ultimately leading to the formation of a primary film. In the case of thermal corrosion by oxygen atoms, the process is much less complex, i.e., the primary film forms as a result of direct interaction between the atomic species and the surface of the material. Since the interaction with atoms is one of the most essential stages of the passivation process in an electrolyte, a comparative investigation of oxidation in atomic oxygen and by anodic polarization was of interest. As the subject of our

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research we have chosen ZrB_2, TaB_2, NbB_2, and W_2B_5, which find application in modern technology because of their refractoriness, mechanical strength, and high thermal and electrical conductivity.

EXPERIMENTAL PROCEDURES

Two techniques were applied in this work. The interaction with oxygen atoms in the gas phase was investigated employing the microweight vacuum method[1] at a temperature of 1000°C and total gas pressure of 0.1 Torr. The oxygen atoms were generated in a high-frequency glow discharge (generator power, 100 W; frequency, 12 MHz). The degree of gas atomization in the system was 15–20 % and remained virtually constant during the experiment. The concentration of atomic oxygen was controlled employing the electronic paramagnetic resonance method. For this purpose a reactive quartz pipe was placed into the port of the resonator of radiospectrometer RÉ 1301. Diphenylpicrilhydrazile was used as a standard. The concentration of oxygen atoms was about 10^{15} cm^{-3}. The kinetics of the corrosion processes in the electrolyte was studied by the potentiostatic method[2] using anodic polarization curves taken potentiodynamically. The rate of change of potential was 400 mV per 50 min. The chosen medium was 1*N* H_2SO_4 at 25°C in purified argon from which traces of oxygen were removed.

Borides of transition metals (ZrB_2, TaB_2, NbB_2, and W_2B_5) were produced by the hot forming method.[3] The impurity content was about 1%. The porosity of the samples, determined by the hydrostatic weighing method, did not exceed 5–7%. Before starting the experiment, the surface was thoroughly ground and washed with acetone and alcohol. The corrosion product on all the borides was examined employing the methods of petrographic and electron diffraction analyses.

RESULTS AND DISCUSSION

During the course of the experiments it was established that all the investigated materials, both in the gas medium and in the electrolyte, were highly resistant to corrosion. On the basis of values of K (the corrosion weight index) of the order of about 0.09 g/m^2-h, these materials were classified as highly resistant ones. According to the data in Refs. 4 and 5, tungsten and zirconium borides were also oxidation-resistant in molecular oxygen.

The processes of interaction of metal borides and a medium containing atomic oxygen are characterized by the kinetic curves presented in Fig. 1. An increase of sample mass was observed for ZrB_2 for 60 min and for TaB_2 and NbB_2 for 20 min. Subsequently the sample weight decreased. For W_2B_5

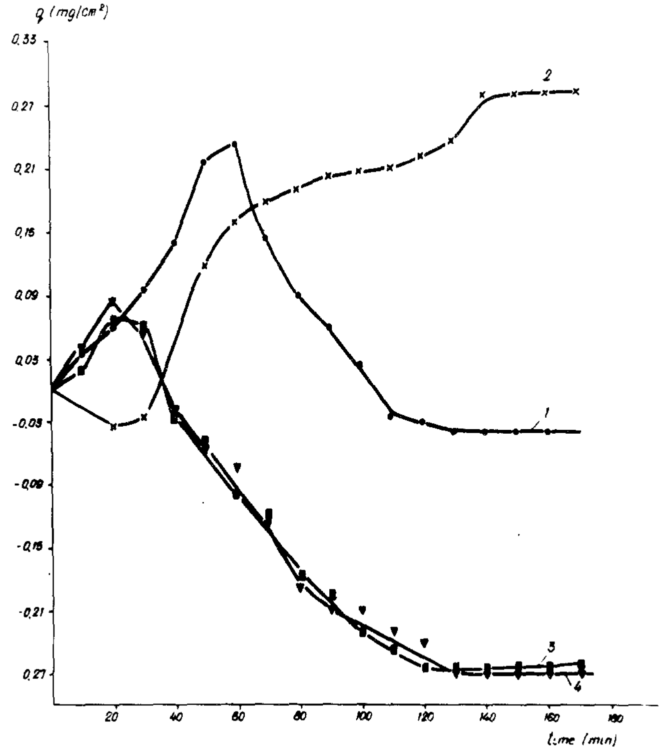

Fig. 1. Oxidation of (1) ZrB$_2$, (2) W$_2$B$_5$, (3) NbB$_2$, and (4) TaB$_2$. Weight change of oxidized specimens as a function of time in oxygen atoms at 1000°C.

during the first 20–30 min the sample mass decreased slightly and then increased. The relative oxidation rates in atomic oxygen of the borides were as follows:

$$W_2B_5 > TaB_2, NbB_2 > ZrB_2$$

The anodic polarization curves (Fig. 2) show that transition metal borides, within the range of potentials beginning with the corrosion potential (φ_{cor}) and up to 0.35 V, were in a passive state. (All the values of the potentials are given with respect to a normal hydrogen electrode.) The passive state achieved was also maintained for ZrB$_2$, TaB$_2$, and NbB$_2$ at higher potentials (up to $\varphi = 1.8$ V) as distinct from W$_2$B$_5$, for which the passive state was maintained only up to a potential of about 0.45–0.47 V. A further increase of potential resulted in the dissolution of W$_2$B$_5$ at a considerable rate. On the basis of polarization measurements, the anodic dissolution rates were found

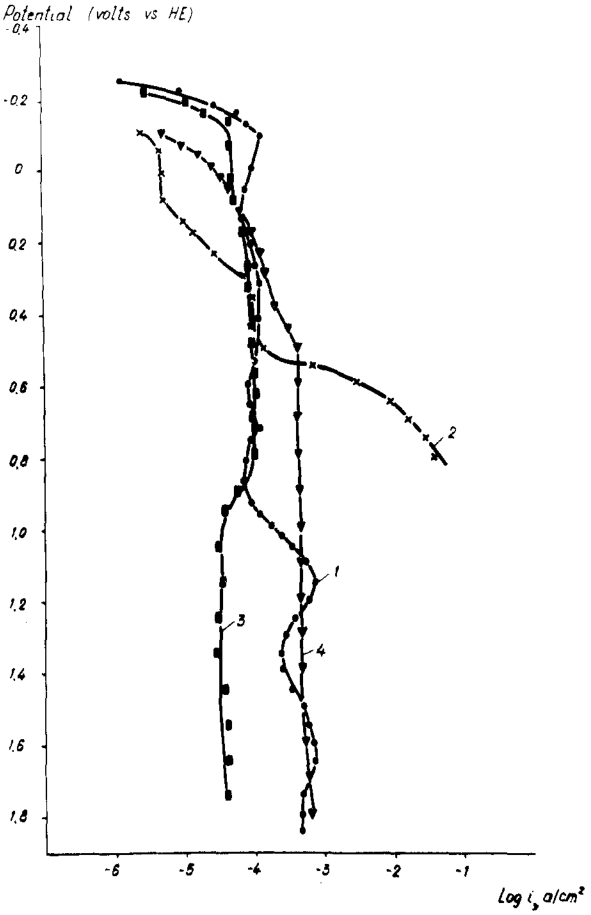

Fig. 2. Anodic polarization curves of (1) ZrB_2, (2) W_2B_5, (3) NbB_2, and (4) TaB_2 in 1 *N* H_2SO_4 at 25°C.

to be in the following order:

$$W_2B_5 > TaB_2, ZrB_2 > NbB_2$$

Therefore, in both the gas phase and in H_2SO_4, tungsten boride was the most active from the standpoint of corrosion.

The composition of the surface compounds was examined during the oxidation of borides in a gas medium and in an electrolyte to characterize the corrosion processes. Tables I and II provide the data from the petrographic analysis and the electron diffraction reflection picture.

Table I. Composition of Oxide Film on Metal Borides

	Petrographic analysis				Electron diffraction analysis
Medium	W_2B_5	TaB_2	NbB_2	ZrB_2	ZrB_2
Oxidation in atomic-molecular oxygen	B_2O_3, WO_3, black nontransparent phase (presumably W_3O)	Small quantity of B_2O_3, main phase black nontransparent (presumably TaO and Ta_2O)	B_2O_3, black nontransparent phase (presumably NbO and Nb_2O)	B_2O_3, ZrO_2, black nontransparent phase (presumably ZrB)	ZrO_2
Oxidation in electrolyte	B_2O_3, black nontransparent phase	Attempt to scrape off film failed	Attempt to scrape off *film failed*	B_2O_3 and single black grains (ZrB)	ZrB, B_2O_3

Table II. Interplanar Distances and Intensities of Electron Diffraction Lines from Oxidized ZrB_2[a]

Starting material		Anodic oxidation in 1 N H_2SO_4 at $\varphi = 0.4$ V for 50 min				Oxidation in gas phase at 1000°C and 0.1 Torr for 3 h	
ZrB_2		B_2O_3		ZrB		ZrO_2	
d	I	d	I	d	I	d	I
2.75	m	2.06	s	2.34	m	2.93	s
2.18	s	1.23	w	1.46	m	2.58	m
1.57	m	1.19	m			1.81	s
		1.06	m			1.53	m
						1.27	w
						1.16	vw
						1.05	w

[a] Notation: s, strong; m, medium; w, weak; vw, very weak.

On the basis of the data presented, we conclude that a complex multiphase scale forms during oxidation of refractory borides in oxygen atoms. This scale possesses good protective properties and contains virtually no metal superoxides. High resistance to oxidation is explained by the B_2O_3 oxide enveloping either the particles of the metal suboxides formed or the surface protections formed. At the same time the defectiveness and the electrical conductivity of the scale decrease, and, accordingly, the rate of diffusion of the reaction components drops. The described picture is observed during the oxidation of tantalum and niobium borides. The descending line of the oxidation curves at 1000°C under low-pressure conditions in the gas phase is explained by the evaporation of volatile oxides (primarily B_2O_3). In the case of W_2B_5 oxidation, WO_3 forms, although in a considerably lesser quantity than the suboxide, W_3O. The latter, in the form of a black nontransparent phase, also prevails over B_2O_3, which determines the course of the corresponding kinetics curve (Fig. 1). During the anodic oxidation of tungsten boride, the formation of W_3O evidently results in the loss of passivation properties in sulfuric acid (Fig. 2). The oxidation of ZrB_2 was characterized by the formation of a multilayer scale; moreover, a phase of zirconium subboride, ZrB, was observed, by both petrographic and electron diffraction analyses, beneath the layer of ZrO_2. During anodic oxidation the zirconium oxides were not observed on the surface, evidently as a result of their rapid dissolution in sulfuric acid. The morphological similarity between the scale of ZrB–B_2O_3 during the anodic process and subscale during oxidation in the gas phase indicates that the layers are formed by oxygen diffusion. At the same time, the conditions were created for direct oxidation of boron atoms as a result of the crystallochemical properties of the atomic arrangement of Zr and B in the lattice of ZrB_2.[7] The difference in composition between the scale on ZrB_2 in gas and in the electrolyte (Table I) explains the change of its corrosion properties and arrangement in the orders indicated previously.

The following conclusion is drawn on the basis of this investigation. Oxidation of borides in both atomic oxygen and in the electrolyte takes place at comparable rates, the corrosion resistance in the two media being similar. In both cases we observed the formation of both B_2O_3 and the corresponding transition metal oxide (Table I). This indicates that the primary stage of anodic passivation in acid electrolytes involves atomic oxygen. However, compounds formed in contact with various physical and chemical media change as a result of concomitant processes, such as the evaporation of volatile oxides in low-pressure gas and the dissolution of certain components in the liquid electrolyte.

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