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Corrosion behaviour of hafnium diboride in aqueous solutions

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Abstract

A dense HfB_2 ceramic material was prepared by hot pressing in the presence of 2.5 wt.% Si_3N_4, as a sintering aid. The microstructure consisted of a fine HfB_2 matrix with refractory secondary phases (BN, HfO_2, Hf(C,N,O)) and Si, mainly located at the triple points. The material corrosion behaviour in acid and alkaline solutions of chlorides and sulphates was investigated by means of several experimental techniques, that is potentiodynamic polarization curve recording and potentiostatic tests coupled to solution chemical analysis, scanning electron microscope (SEM) observations and X-ray photoelectron spectroscopy (XPS) surface chemical characterization. Sintered HfB_2 undergoes an electrochemical corrosion attack of the HfB_2 phase and a chemical corrosion attack, mainly localized on the secondary phases. In acid sulphate solution a strong corrosion attack on the diboride phase occurs which leaves a secondary phase skeleton. In acid chloride solution and in alkaline chloride and sulphate solutions, the rate of secondary phase dissolution is quicker than the dissolution rate of the primary diboride phase and an intergranular corrosion attack morphology occurs. The Si phase dissolves relatively fast only in alkaline solutions. In analogy with the corrosion behaviour of ZrB_2, corrosion of HfB_2 phase is thought to produce both soluble and insoluble (hafnium and boron oxides) corrosion products. In acid sulphate solution the soluble corrosion products are mainly boric acid and a sulphate complex of Hf(IV). In the other solutions they are mainly constituted by boric acid (or borates, depending on the solution pH). The high corrosion rates detected in acid sulphate solution are due to the marked stability of the soluble sulphate complex of Hf(IV).

Keywords: Hafnium diboride; Corrosion; Aqueous solutions; XPS; Solution analysis

1. Introduction

Refractory diborides (HfB_2 and ZrB_2) are candidate materials for a variety of industrial applications due to their high melting point, high electrical and thermal conductivity, stability against complex gaseous and thermal environments, superb thermal shock resistance and wear resistance [1].

The relatively low strength and fracture toughness are still, however, an obstacle to a wider application of these ceramics, and the strong covalent bonding which gives them a very high melting point also makes their densification very difficult [2]. The addition of sintering aids represents a possibility of overcoming the intrinsic low sinterability [1–6], and high-density materials could be obtained through liquid phase sintering. However, the secondary or grain boundary phases deriving from sintering aids affect the physical, chemical and mechanical properties, especially when metal sintering aids are used [2,6–11]. The hafnium diboride material used in this study was obtained by hot pressing HfB_2 powder with the addition of 2.5 wt.% of Si_3N_4. Full density was reached, since boron oxide, constituting the external shell around hafnium diboride powder particles, reacted with silicon nitride to form secondary phases. Good mechanical properties were, thus, achieved [12].

Literature information mainly involves high temperature corrosion behaviour of diborides in view of high temperature applications [13–16]. However, an understanding of low temperature corrosion mechanisms in aqueous solutions containing quite common anions also constitutes a key factor for the optimization of the material performances. Chemical and elec-

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trochemical properties of hafnium and zirconium are known to be similar [17], because they have the same valence electronic configuration and the hafnium atom or ion size is similar to that of the zirconium atom or ion, due to the lanthanide contraction. For this reason, previous results obtained with monolithic ZrB_2 densified with Si_3N_4 addition [18] may be taken into account when interpreting the results obtained with monolithic HfB_2 produced with the same sintering aid. In particular, it has been found that, during the corrosion process of ZrB_2 in aqueous acid solutions containing different aggressive anions such as chlorides, perchlorates, sulphates, oxalates and fluorides, this material is converted into both soluble (boric acid and complexes of the different anions with Zr(IV)) and insoluble (mainly ZrO_2) corrosion products. It has also been reported that the higher the stability of the Zr(IV) soluble complex formed by a particular anion, the higher the corresponding solution aggressiveness and consequently the lower the protectiveness of the surface oxide film [18]. The solution aggressiveness in the presence of different anions has been found to increase in the following order: perchlorates $\cong$ chlorides $\ll$ sulphates $\cong$ oxalates $<$ fluorides.

2. Experimental

2.1. Material production

The ceramic material of selected composition HfB_2 + 2.5 wt.% Si_3N_4 was produced starting from the following commercial powders:

- HfB_2 Cerac Incorporated, Milwaukee, WI; Fisher size: 2.08 μm; impurities: Al (0.07 wt.%), Fe (0.01 wt.%), Zr (0.47 wt.%).
- Si_3N_4 Baysinid, Bayer, Germany; specific surface area: 12.2 m^2/g; impurities: O (1.5 wt.%).

The powders were mixed through ball milling using Si_3N_4 balls for 24 h in ethyl alcohol. Then the slurry was dried using a rotary evaporator and the dry powder mixture was sieved through a metallic sieve at 75 μm. Sintering was performed by hot pressing at 1800 °C in an induction heated graphite die, with an applied pressure of 30 MPa and a holding time of 30 min, in vacuum (0.5 mbar).

Microstructural characteristics of the ceramic material were analyzed by X-ray diffraction (XRD), scanning electron microscopy (SEM) and microanalysis (energy dispersion spectroscopy, EDS). In particular, the mirror-polished surface and the fracture surface were examined.

2.2. Corrosion tests and characterization methodologies

The electrodes were prepared according to the procedures described elsewhere [19], with a surface area of 1 cm^2. After polishing down to 1 μm by diamond paste, degreasing by acetone and drying, they were exposed to the following aqueous solutions at 45 ± 1 °C, under natural aeration conditions:

(a)	0.5 N NaCl + 0.1 N HCl	(pH 1)
(b)	0.5 N Na_2SO_4 + 0.1 N H_2SO_4	(pH 1)
(c)	0.6 N NaCl + 0.1 N NaOH	(pH 13)
(d)	0.6 N Na_2SO_4 + 0.1 N NaOH	(pH 13)

For the electrochemical experiments a three-electrode cell was used, equipped with a Pt auxiliary electrode and a saturated calomel reference electrode (SCE). All the potentials quoted in the text refer to this reference electrode.

To avoid glass degradation and solution contamination induced by contact with alkaline solutions, during all the tests carried out in types (c) and (d) solutions, polypropylene cells were adopted and the glass-mounted auxiliary and reference electrodes were properly wrapped in Teflon tape. Freshly prepared alkaline solutions were always used to avoid variation in the initial pH value, due to dissolution of atmospheric carbon dioxide. On the contrary, during the tests no procedure was adopted to avoid carbon dioxide dissolution. The highest pH decrease was measured after 15 days of exposure and values of about 10.5 were reached.

Anodic and cathodic polarization curves were recorded at a potential scan rate of 1 mV s^{-1}, after 1 h, 3 and 15 days of immersion, starting from the corrosion potential. Potentiostatic tests consisted of 5-day immersions in a constant solution volume (0.08 dm^3), at an applied potential of 0 V (in acid solutions) or 0.1 V (in alkaline solutions). These potential values were chosen after analysis of the polarization curves, in order to keep the electrodes anodic during all the immersion period. After each test, the anodic charge passed was calculated from the current integration upon time. Moreover, the chemical analysis of the solutions was performed by means of inductively coupled plasma-optical emission spectrometry (ICP-OES) in order to determine the amounts of hafnium, boron and silicon elements present in the solutions as dissolved species. The instrument used in this work was a Perkin-Elmer Optima 3100 XL ICP-OES with an axially viewed plasma. The design of this spectrometer includes a 40 MHz free-running generator, an echelle grating polychromator combined with a solid state detector, a pneumatic Low-Flow Gem Cone nebulizer and a cyclonic spray chamber. The instrument was equipped with a Perkin-Elmer peristaltic pump and an autosampler model AS91. Blank data, measured from solutions kept under the same experimental conditions of the actual tests, but in the absence of the working electrode, were also obtained and subtracted from the species amounts detected at the end of the potentiostatic tests, to correctly quantify the ceramic material dissolution. All tests were carried out in duplicate.

HfB_2 specimens (surface area 2.5 cm^2) were also exposed to the aggressive solutions under free corrosion conditions for 3 or 15 days, after which the morphology of the corrosion attack (by SEM) and the surface chemical composition of the exposed specimens (by X-ray photoelectron spectroscopy, XPS) were properly investigated. On these specimens gravimetric analysis was carried out with a resolution of ±0.01 mg. The calculated corrosion rates were expressed in mg dm^{-2} day^{-1} (mdd).