The oxidation of zirconium diboride has been studied more fully than that of TiB₂ and HfB₂ [1-7]. An investigation into the oxidation of ZrB₂ specimens in oxygen and dry air at temperatures of 649-1315°C has shown that zirconium diboride oxidizes more rapidly in dry oxygen than in dry air [1]. The effects of oxygen partial pressure have been studied at temperatures of 1218-1529°C and pressures of 100-700 mm Hg. It has been established that, with rise in oxygen pressure, the rate of the process grows [2], while, according to [3], B₂O₃ losses during the oxidation of ZrB₂ produced by the zone melting process are negligible at temperatures below 1060°C. The oxidation resistance of HfB₂ has so far received less study [8, 9]. In [8], it is reported that HfB₂ oxidizes vigorously at 600-700°C, total disintegration of specimens taking place at 1000-1200°C. In later studies, oxidation experiments were carried out on HfB₂ specimens produced by the zone melting technique at temperatures of 1480-1870°C [3].

In the above-mentioned investigations, materials of different purities and porosities were tested in different atmospheres and temperature ranges, and the experimental results are therefore not directly comparable. No attempt has been made as yet to study the structural characteristics of the diffusion zone forming during the dissolution of oxygen in the initial and later stages of the process, and no data are available concerning the effects of the properties of the resultant scale layer upon the dissolution of oxygen in the borides. The full phase composition of the scale has not been determined, and it has thus been impossible to elucidate the role of the nitrogen in the air in the formation of the nitride phases of the relevant metals and boron nitride and determine the effects of the protective properties of the scale layer upon this process.

The microhardness of oxidized ZrB₂ and HfB₂ specimens depends on the concentration of dissolved oxygen, which is determined by the temperature and the protective properties of the scale forming on the specimens. At low temperatures (700°C), when the oxygen concentration is negligible, the process probably involves no more than the filling of vacant sites in the anionic sublattices of the borides, which is accompanied by some increase in their microhardness. With rise in temperature (800-1000°C), the microhardness sharply falls over the whole depth of oxidized specimens. This may be a result of an increase in the concentration of dissolved oxygen, which of course not only fills vacancies in the anionic sublattices, but also replaces a substantial proportion of the boron (Fig. 1a and b). The latter has been detected in scale layers during the oxidation of ZrB₂ and HfB₂ for 4 min at 600-1000°C (Table 1). With further rise in temperature (1100-1200°C), the intensity of the dissolution of oxygen markedly decreases owing to the formation of borates, which possess good protective properties, bringing about changes in microhardness affecting only wide surface zones of oxidized specimens. At still higher temperatures (1300, 1400, and 1600°C), the scale layer experiences pronounced sintering, which impedes the diffusion and dissolution of oxygen, so that the microhardness of ZrB₂ remains unchanged during oxidation. In the case of HfB₂, the same is observed during oxidation in the temperature range 1300-1500°C. Some dissolution of oxygen, in a very thin surface layer, occurs only at 1200°C.

**Oxidation of ZrB₂**

Zirconium diboride is distinguished by its high resistance to oxidation (Fig. 2a). At 600-800°C, it is

*For Part I, see Poroshkovaya Met., No. 2, 57 (1975). - Translator.*

virtually immune against oxidation, no significant changes being observed in the appearance of specimens. Barely perceptible oxidation begins at temperatures of 900–1000°C, and at 1100–1200°C the rate of the process grows a little. Raising the temperature to 1400°C brings about a marked increase in the intensity of oxidation in the initial stage of the process, although the character of kinetic oxidation curves shows that, in the later stages, the scale layer undergoes sintering and subsequently protects the basis material. At 1600°C, the intensity of sintering grows appreciably, resulting in a sharp fall in the rate of the process. ZrB₂ differs from TiB₂ in that the porosity of its specimens plays an important part in its oxidation.

Because of appreciable dissolution of oxygen, at 800°C a change takes place in the actual structure of specimens: their central portions are coarse-grained, but toward the scale/boride interface the grain size decreases to less than one-sixth that in the core. At 900°C, evaporation of B₂O₃ slightly increases the porosity of specimens, and the structure becomes fine-grained. At all temperatures up to 1100°C, the scale contains several phases, namely, ZrO₂cub., ZrO₂mon., ZrN, and B₂O₃. Starting from a temperature of 1000°C, the nitride ZrN (microhardness $H_\mu = 1496$ kg/mm²) and formations of a gray color and high microhardness (zirconium borate) are found in the scale; the density of distribution of the latter phase grows with rise in temperature.