BRIEF COMMUNICATIONS

THERMAL DIFFUSIVITY OF PYROLYTIC ZIRCONIUM DIBORIDE AT HIGH TEMPERATURES

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The results of measurements of the thermal diffusivity of ZrB_2 plates are given. The specimens were obtained by the method of chemical gas-phase deposition from a mixture of Zr and B halide vapors with H_2 at 1200°C.

Zirconium diboride is a solid refractory compound with a melting point of 3040°C [1] and high metal-type electrical conductivity up to a temperature of more than 2000°C [2]. This substance is used as a heat-resistant and relatively fireproof material or in the form of protective coatings [3-5]. In view of this it is of interest to investigate its thermophysical properties, particularly the thermal diffusivity and conductivity at high temperatures. A promising method of fabricating articles and coatings of zirconium diboride is chemical gas-phase deposition from a mixture of zirconium and boron halides with hydrogen [6], which provides monolithic pore-free material of high purity.

In the present work we investigated the thermal diffusivity of zirconium diboride specimens obtained by this method at 1200°C in the same way as in [7]. Chemical analysis showed that the obtained zirconium diboride contained 81.18 wt.% Zr and 19.10 wt.% B. X-ray analysis showed that the specimen contained only hexagonal ZrB_2 with lattice constants $a = 3.161$ and $c = 3.525$ kX. The relative intensity of the lines on the x-ray diagrams indicated considerable growth texture in which the crystal plane [00l] was oriented parallel to the deposition surface (i.e., normal to the direction of measurement of the thermal diffusivity). The measured density of the specimens was 6.12 g/cm^3; this is very close to the theoretical density of ZrB_2 [1] and indicates the absence of pores in the specimens, which was confirmed by an investigation of their microstructure (Fig. 1). The electrical resistivity of the obtained zirconium diboride specimens at room temperature was 6.1-6.5 $\mu\Omega \cdot$ cm, which is significantly lower than published values [1, 8, 9] for ZrB_2 specimens obtained by powder metallurgy techniques (16.6-35 $\mu\Omega \cdot$ cm), but a little higher than the figure given in [10] for ZrB_2 single crystals (2.9-3.4 $\mu\Omega \cdot$ cm). This indicates that the purity and structure of the investigated ZrB_2 specimens were satisfactory.

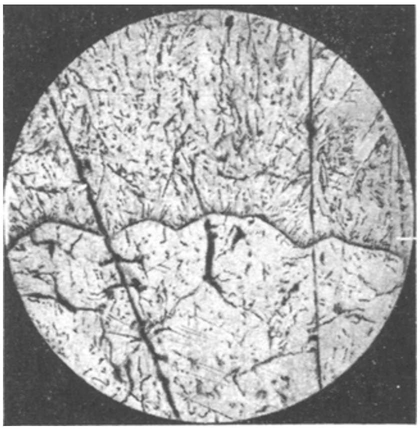

Fig. 1. Microstructure of pyrolytic zirconium diboride specimens (× 500) (etched in an alcoholic HF solution with the addition of NH_4SiF_6).

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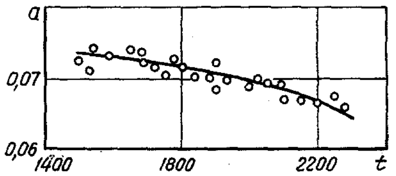

Fig. 2

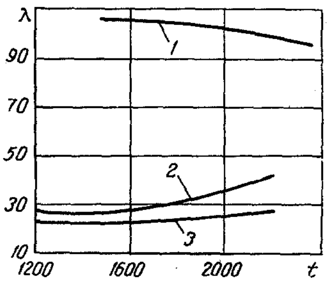

Fig. 3

Fig. 2. Thermal diffusivity a, m^2/h of zirconium diboride as function of temperature t, °C.

Fig. 3. Thermal conductivity λ, W/m·deg of zirconium diboride as function of temperature t, °C: 1) present work (pyrolytic ZrB_2 specimens); 2 and 3) data of [14] and [13] (powder-metallurgy ZrB_2 specimens).

The thermal diffusivity of the 0.30 mm thick zirconium diboride plates was measured in a vacuum (10^{-5} mm Hg) in the temperature range 1500-2300°C by a phase method, similar to that described in [11], in which the specimen is heated by electron bombardment. The temperature of the specimen was measured with an OMP-043 microoptical pyrometer. For conversion of the brightness temperature of the specimen to its true temperature we used the emission coefficient $\varepsilon = 0.75$ for wavelength 0.65 mμ.

The obtained results of the thermal diffusivity measurements are shown in Fig. 2. The figure shows that the thermal diffusivity of zirconium diboride decreases with temperature increase, which is characteristic of metal conductors with relatively low residual electrical resistivity, where the main contribution to the thermal conductivity and thermal diffusivity of the material is made by free electrons, and scattering on impurities and other defects is of minor importance [12]. Using the data given in [13] for the specific heat of ZrB_2 we calculated the thermal conductivity λ of pyrolytic zirconium diboride from the obtained experimental thermal diffusivity data, using the well-known relationship $\lambda = ac\gamma$, where γ is the density of the material and c is the specific heat.

Figure 3 shows a plot of the obtained values against temperature. The figure shows that the thermal conductivity of ZrB_2 decreases with temperature increase in the investigated temperature range, which is also characteristic of metal conductors with low residual resistance.

For comparison Fig. 3 shows the data of Neel et al. [13, 14] for the thermal conductivity of ZrB_2 specimens obtained by powder-metallurgy techniques. The lower values of the thermal conductivity of the powder-metallurgy specimens of zirconium diboride in comparison with specimens obtained by gas-phase chemical deposition, and the different nature of the temperature dependence of the thermal conductivity of these specimens in the investigated temperature range, can probably be attributed to the lower electrical conductivity of the power-metallurgy specimens. The low conductivity is probably due to the presence of

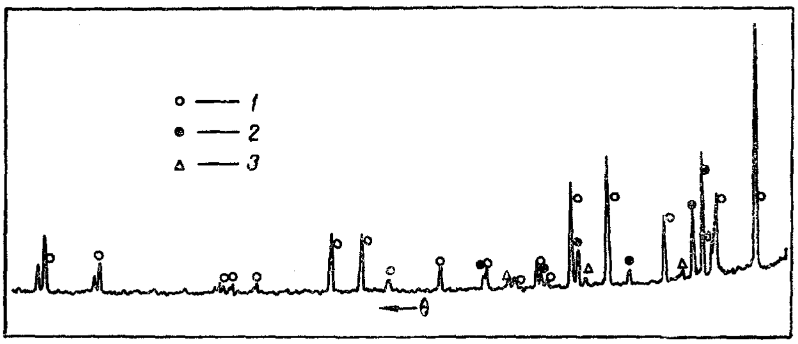

Fig. 4. X-ray diagram of zirconium diboride specimen, heated by electron bombardment in vacuum (10^{-5} mm) at 2200°C, during measurement of the thermal diffusivity [1) ZrB_2; 2) Zr; 3) ZrB].

impurities and residual porosity, and also to the less perfect microstructure of powder-metallurgy specimens in comparison with the crystal-oriented specimens obtained by chemical gas-phase deposition.

Thermal diffusivity measurements at temperatures above 2300°C with our apparatus were impossible owing to the interaction of the ZrB_2 specimens with the tungsten holder.

An x-ray analysis of the zirconium diboride specimens after measurement showed that the ZrB_2 lattice constants were practically the same (α = 3.101; c = 3.531 kX), but the x-ray diagrams of specimens heated to temperatures above 2150°C showed, in addition to the ZrB_2 lines, weak lines of the cubic phase of zirconium monoboride (ZrB) with lattice constant 4.68 kX and metallic zirconium (Fig. 4), which indicates the onset of dissociation of zirconium diboride in vacuum at these temperatures and the loss of boron by evaporation.

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