# OXIDATION BEHAVIOUR AND ELECTROCONDUCTIVE PROPERTIES OF $S_3N_4$ DOPED $ZrB_2$

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Zirconium diboride-based ceramic are interesting materials owing to unique properties like high melting point, high electrical and thermal conductivity, coupled with resistance to chemical attack, high wear resistance and hardness [1,2].

A limit in the application of zirconium boride as a structural material arises from the low fracture toughness and strength it possesses, combined with a poor sinterability.

An effort in improving both sinterability and strength of zirconium diboride was made by using ceramic like additives (i. e. $Si_3N_4$) as sintering aid [3].

Furthermore, with the addition of components such as SiC the oxidation resistance was improved by modifying the oxidation kinetics with the formation of a protective silica glassy layer [4].

The oxidation of an electroconductive ceramic composite of composition $ZrB_2$ 5vol% $Si_3N_4$ was studied in order to evaluate the change in the electrical properties after oxidation.

The oxidation behaviour was characterised by thermogravimetric analysis (TGA) recording mass change, x-ray diffraction (XRD) and scanning electron microscopy (SEM).

The material was oxidised in a pure oxygen atmosphere in the temperature range 850-1100°C. As reported by other authors[5] the oxidation kinetics were found to follow a parabolic behaviour up to 1000°C. The weight gain versus time and the squared weight gain versus time are reported in Figs. 1 and 2 respectively.

The parabolic constants for the oxidation process were evaluated from the slopes of the linear fit and the activation energy was estimated which correspond to 134kJ/mol (Fig.3).

The temperatures selected for the analysis of the oxidation behaviour fall in the range 900-1100°C in which a porous $ZrO_2$ scale forms according to the following reaction:

$$ZrB_2(s) + 5/2O_2(g) \rightarrow ZrO_2(m) + B_2O_3(l,g)$$

The surface oxidation product is largely monoclinic $ZrO_2$ under all conditions. $B_2O_3$ could be fluid or gaseous depending on the temperature.

At temperatures up to 1000°C, the oxidation process of the material seems to be controlled by a diffusion mechanism of the oxygen through a porous zirconia layer sealed by liquid boria that provide partial oxidation protection. At lower temperature $B_2O_3$ has a low oxygen diffusivity value and presents an effective barrier to the transport of oxygen.

Above 1100°C $B_2O_3$ starts to volatilise and the zirconia layer alone is not able to prevent further oxidation.

Electrical resistivity measurements were performed on the sample before and after the oxidation experiments in order to evaluate the effects of corrosion on electroconductive properties.

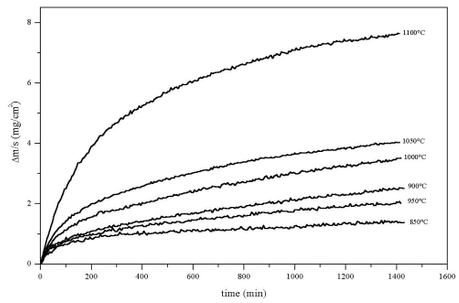


Figure 1: TG curves of the investigated material treated for 24h at each temperature in a pure oxygen atmosphere

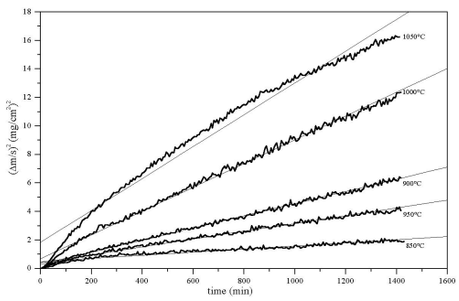


Figure 2: Plot of (weight gain)$^2$ vs time for the 24h isothermal treatments in pure oxygen atmosphere showing calculated linear fits

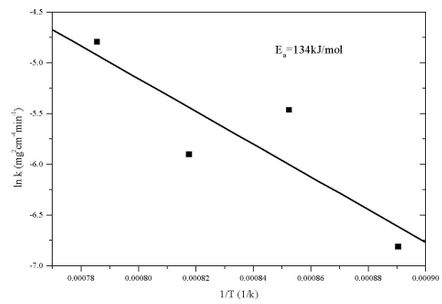


Figure 3: Arrhenius plot of the oxidation rate constants in the range 850-1000°C

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