THE INFLUENCE OF ZrO_2 ADDITIVES ON HIGH-TEMPERATURE OXIDATION OF Si_3N_4 CERAMICS

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The oxidation behaviour of high-density Si_3N_3-Al_2O_3-Y_2O_3-ZrO_2 materials has been studied at the temperature up to 1600 °C in air. Technological features of materials manufacturing from powders of plasma-chemical synthesis are given in [1]. It was found that ZrO_2 additives notably effect on the oxidation kinetics of silicon nitride ceramics. Small amount of ZrO_2 improved the oxidation resistance of Si_3N_3-2% Al_2O_3-5% Y_2O_3 material (below indicated as Si_3N_4), whereas its increase up to 10 % considerably decreases the resistance to oxidation (indicated % by mass).

XRD analysis of the surfaces of Si_3N_4-ZrO_2 samples oxidized at the temperature up to 1380 °C showed the presence of β-cristobalite (SiO_2), yttrium disilicate ($Y_2Si_2O_7$), tetragonal ZrO_2. Samples heated up to 1520 °C and 1600 °C do not reveal of β-cristobalite phase.

With rise of oxidation time the amount of $Y_2Si_2O_7$ and $ZrSiO_4$ is increasing and after 20 h of oxidation weakly change. On the contrary, the amount of ZrO_2 decreases with increase of oxidation time. After grounding of the oxide film the XRD analysis of the substrate under the scale showed Si_2N_2O.

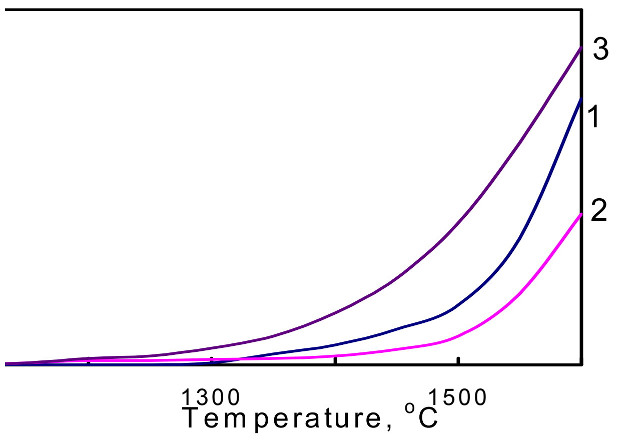

Fig. Weight gain as a function of temperature. Rate of heating is 20 grad/min: 1 – Si_3N_4; 2 – Si_3N_4-5ZrO_2; 3 – Si_3N_4-10ZrO_2.

The results of the present investigation show that ZrO_2 additives effect on the oxidation kinetics of Si_3N_4-materials. ZrO_2 additives to Si_3N_4 form additional quantity of silicon oxynitride in starting material during sintering. XRD analysis confirms higher content of Si_2N_2O in Si_3N_4-ZrO_2-materials.

Apparently higher content of intergranular glass phase explains the different oxidation behavior of Si_3N_4 and Si_3N_4-ZrO_2. For Si_3N_4 increase of gain mass is observed only at 1300 °C, whereas for Si_3N_4-ZrO_2 it starts at 1100 °C (Fig.). First 3 hours of isothermal oxidation at 1380 °C of Si_3N_4 proceeds with loss mass. The surface of the scale was covered with grate number of pores formed by removal of N_2. High content of silicon oxynitride in intergranular phase, which is a barrier for oxygen permeation, results in that oxidation of Si_3N_4-ZrO_2 from the beginning closely followed parabolic kinetics. Whereas its low content in Si_3N_4 results in its oxidation with loss mass due to intensive removal of N_2 until SiO_2 film of sufficient thickness is formed. Further the gain mass is observed and its rate follows parabolic low.

Composition of silicon nitride ceramics is one of the decisive factors determining its oxidation behavior. ZrO_2 additives to Si_3N_4 promote the formation of intergranular glass phase and its quantity finally determines the oxidation behaviour of Si_3N_4-ZrO_2-ceramics.

In oxidized Si_3N_4-5ZrO_2-ceramics a continuous cristobalite layer forms on the glassy scale-ceramics interface providing a barrier to oxygen diffusion. Elevated content of Si_2N_2O in Si_3N_4-5ZrO_2 ceramics promotes the formation of silicon oxynitride enriched layer on cristobalite-ceramics interface that decreases the rate of its oxidation in comparison with that of Si_3N_4.

In Si_3N_4-10ZrO_2 ceramics the formation of cristobalite continuous layer is not observed apparently due to high rate of Zr and Y migration from intergranular glass phase into the scale. Fast permeation of oxygen through the glassy scale controls high rate of Si_3N_4-10ZrO_2 oxidation.

1. Kaidash O.N., Danilenko N.V., Vereshchaka V.M. The influence of ZrO_2 on the formation of structure and properies of materials prepared from nanodispersed Si_3N_4-Al_2O_3-Y_2O_3 composites // J. Superhard Mater. – 1999. – 21, No. 6. – P. 63-70.