Vapor Phase Growth of Monoclinic ZrO_2 Whiskers

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Growth of ZrO_2 whiskers by the reaction of $ZrCl_4$ and O_2 or H_2O was examined at 1100°-1300°C. Only powder products were obtained at temperatures below 1200°C in both reaction systems. At 1250°-1300°C, however, monoclinic whiskers or needle crystals were produced. In $ZrCl_4$-O_2 system, the whiskers were grown on a mullite substrate together with flaky materials, bricky crystals and powder. Optimum conditions for the whisker growth were $ZrCl_4$ 1-3%, O_2 0.25-0.35%, and total flow rate of the reactant gas 40-60 cm³/min. The size of the whiskers was 0.1-2 μm in width and 10-100 μm in length. The growth axis was the <010> direction or perpendicular to the (104) plane. In $ZrCl_4$-H_2O system, no whiskers were formed on the substrate, but needle crystals (whisker-like) and powder were obtained at the outlet of the reaction tube. The monoclinic needles were very minute, their dimension being 0.05-0.5 μm in width and 0.5-3 μm in length. The growth axis was the <010> direction or perpendicular to the (104), (11$\bar{3}$) or (211) plane. Optimum conditions were $ZrCl_4$ 2-5%, H_2O 3-4%, and total flow rate of the reactant 30-60 cm³/min. Electron microscopic observation revealed that the whiskers and the needles had no particles on the tops, suggesting that both of them grew by a VS mechanism.

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ZrO_2 Transformation of Glass-Ceramics in the System ZrO_2-SiO_2 Prepared by the Sol-Gel Process from Metal Alkoxides

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Crystal growth of ZrO_2 and crystallite size dependence of tetragonal to monoclinic ZrO_2 transformation were investigated in relation to the fracture toughness of glass-ceramics. Glasses of 2 ZrO_2·3 SiO_2, ZrO_2·SiO_2 and 3 ZrO_2·2 SiO_2 in molar ratio, prepared by the sol-gel process from metal alkoxides, were heat-treated to precipitate tetragonal (t-) ZrO_2 crystals. Tetragonal-ZrO_2 crystals grew in proportion to the cube-root of heat-treatment time, and the growth rate increased with increasing ZrO_2 content. Crystals of t-ZrO_2 larger than a critical size transformed into monoclinic (m-) ZrO_2 during cooling. Transmission electron microscopy revealed that the m-ZrO_2 particles showed twinning associated with t- to m-ZrO_2 transformation. Tetragonal to m-ZrO_2 transformation temperature was found proportional to the reciprocal ZrO_2 crystal size, which was consistent with Garvie's transformation equation. The critical sizes corresponding to the transformation temperature of 273 K were estimated to be 90, 56 and 40 nm for 2 ZrO_2·3 SiO_2, ZrO_2·SiO_2 and 3 ZrO_2·2 SiO_2 glass-ceramics, respectively. The interfacial and strain energies for the transformation calculated from Garvie's equation increased with decreasing ZrO_2 content. The fracture toughness (K_{Ic}) of these glass-ceramics increased in proportion to the cube of t-ZrO_2 crystal size. From the critical crystal size of t-ZrO_2 in the glass-ceramics, the maximum K_{Ic} was estimated to be 4.7, 4.7 and 5.0 $MN/m^{3/2}$ for 2 ZrO_2·3 SiO_2, ZrO_2·SiO_2 and 3 ZrO_2·2 SiO_2, respectively. After reaching the maximum, K_{Ic} decreased abruptly on further heating, which was attributed to the occurrence of m-ZrO_2 crystals in the glass-ceramics.

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Preparation of Cordierite Ceramics from Metal Alkoxides (Part 1) Preparation and Characterization of the Powder

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A new method for preparing homogeneous cordierite ceramics by a sol-gel process is described. Reactive and fine cordierite-type amorphous powder with high homogeneity was prepared by the sol-gel method. The hydrolysis of metal alkoxides used as starting materials was controlled. Namely, $Si(OC_2H_5)_4$, with a hydrolysis rate lower than that of $Mg(OC_2H_5)_2$ or $Al(OC_2H_7^i)_3$, was partially hydrolyzed and then mixed or reacted with Mg and Al alkoxides which had been reacted in butyl-alcohol. The cordierite powders prepared by the sol-gel method were characterized by infrared spectroscopy, X-ray diffraction study, differential thermal analysis (DTA) and transmission electron microscopy (TEM) with an energy dispersion X-ray microprobe analyzer (EDX). Homogeneous cordierite powders were obtained from $Mg(OC_2H_5)_2$, $Al(OC_2H_7^i)_3$, and $Si(OC_2H_5)_4$. The homogeneity of resultant oxides depended upon the hydrolysis method of alkoxides.

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