Phase Transformation of Zirconium Oxide

Influence of Pressure and Temperature

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MONOCLINIC ZIRCONIA received from Wah Chang Corp. (99.9+% with 82 p.p.m. hafnium and < 100 p.p.m. iron as the major impurities) was prepressed at room temperature at 1500 atm., placed in a cylindrical high pressure device, and pressed to about 20,000 atm. at > 1800° C., using a Pt, Pt-10% Rh thermocouple which failed at the maximum temperature. The device was then rapidly quenched to room temperature by the cutoff of the DC power supply and by water cooling the die. The high pressure cell consisted of a cylindrical silicon carbide-carbon heating element, boron nitride insulation, Pyrophyllite top and bottom pieces, and a platinum foil sample holder. Spectrographic analysis of the zirconia indicated that only a small amount of impurities were picked up during the experiment. The only significant concentration changes were an increase in aluminum content from 25 to 100 p.p.m. (from the Pyrophyllite), and an increase in the boron content from 0.2 p.p.m. to < 500 p.p.m. (from the boron nitride).

Samples obtained in this manner were hard, lusterless white, and close to the theoretical density for the monoclinic phase of zirconia (5.68 g./cc.) (*5*). Specimen size was about ¼ inch in diameter by ¼ inch in height. The zirconia was then fired in a platinum boat inside an alumina tube furnace to 1350° C. in air for 1 hour and water quenched. The specimens did not crack as usually happens in quenching unstabilized zirconia which goes through the monoclinic-tetragonal phase transformation at 1100° to 1250° C. (*1, 3*) with substantial transformation at 1193° to 1200° C. (*2*). The quenching experiments were repeated several times on the same specimens and no cracking was observed. Subsequently, high temperature x-ray diffraction patterns were obtained while scanning several times through the phase transformation temperature range from 800° to 1240° C., using Cu Kα radiation. The new monoclinic-tetragonal phase transformation had shifted to a lower temperature, that is from 900° to 1020° C., with the region of substantial transformation between about 950° and 1000° C. On cooling the transformation was sluggish, as is usually the case (*7*), with the tetragonal phase partially retained to 800° C. The region of transformation during cooling is considerably less, however, than in the normal case where it is from 1200° to 800° C.

Sense (*6*) recently reported that a dense zirconia body, prepared by a low-temperature, hot-pressing operation followed by sintering above 2250° C., retained its integrity on quenching, and proposed a skip transformation such as has been observed for plutonium (*4*). Yavorsky (*8*) has proposed the alternative that the impurities in that dense body (which appeared black with a semimetallic luster) have increased the thermal conductivity to permit rapid traversing of the transformation zone.

Pressure applied during the transformation thermodynamically would be expected to lower the temperature of formation of the more dense tetragonal phase. On cooling under pressure this more dense phase should also be retained to a lower temperature. Here we have observed the same effects after the pressure has been removed. Lowering the transition temperature has apparently increased stability, perhaps decreasing the rate of transformation and thus decreasing the amount of cracking. Further work will be needed to clarify the nature of this shift in the transformation temperature.

In the past it has been necessary to stabilize zirconia (using CaO, MgO and Y_2O_3) for high temperature applications. Unfortunately the stabilized cubic phase is not as stable as the monoclinic phase and reverts back during thermal cycling, and the zirconia again cracks up. Stabilization also increases the thermal expansion of zirconia, which decreases the thermal shock resistance (*7*). Another approach is to use small amounts of metal additions, but this is not useful in oxidizing environments. This high purity, dense, pseudo-monoclinic zirconia looks very promising for future applications at high temperatures.

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