High-temperature Materials and SHS Products

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ABSTRACT Self propagating High temperature Synthesised (SHS) ceramics have been widely used for various electronic applications. The investigation on SHS materials has been reported. The purposes of this study were as follows: fabricating the high temperature functional materials, and evaluating crystal structure and electrical properties. The regularities and peculiarities in SHS structures of high temperature materials as a result of the molecular interactions during burning process are considered.

Introduction

Ceramics for heating elements, including $LaCrO_3$, stabilized ZrO_2 produced by conventional methods, such as sintering and hot-pressing; require expensive high-temperature process steps and machining, which add significant cost to the material. The use of exothermic, self-propagating reactions has been of interest for forming high-purity refractory compounds. SHS defined as material synthesis by combustion is therefore an interdisciplinary research subject in the material science. Energy for the transformation primarily comes from the reaction enthalpy. The cost-effective production of hard, strong, and dense refractory materials has been claimed. Lanthanide orthochromites ($LaCrO_3$) used

for manufacturing various constructional ceramics and high-temperature heaters owing to its excellent oxidation resistance, reasonable strength, good thermal and electro conductivity at high temperatures. The stabilized ZrO_2-base solid solutions possess rather unique electrical properties, and as a result have considerable potential as solid electrolytes in galvanic and fuel cells and, possibly, as heating elements in high-temperature furnaces [1-2].

In the present work effects of the addition of di-or trivalent cations for Zr dioxide upon oxide ionic conductivity were investigated for compounds prepared by SHS. We investigated the influence of the sample diameter, preheating, post-combustion cooling rate on the formation of a homogeneous product and in situ stability

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of the for $LaCrO_3$ system properties.

Experimental Part

a) Samples

All reagents (La_2O_3 and chromium metal), Y-ZrO_2 (YZ), and Ca -ZrO_2 (CZ) compositions were prepared by SHS method from a mixture of solid powders pressed to 50-60% of the theoretical density into cylindrical pellet. The pellets were supported on a ceramic boat and the reaction ignited by an electrically heated Ni -Cr wire filament at one end. This produces a solid flame that moves out from point of initiation through the whole material. Oxygen was admitted through the tube (10 l/min). The combustion temperatures were measured using an optical pyrometer and B-type (Pt30%Rh-Pt6%Rh) thermocouple, which was more suitable than a tungsten one due to the highly oxidizing environment. Specimen densities were calculated from weight and geometric measurements and the apparent densities of all specimens were in the range 90 to 95% of theoretical density. Electrodes were applied to the circular faces of the specimens by spraying on a platinum-organic mixture and heating the coated

specimens at 1100°C for 1 hour. Rectangular samples (0.25 by 0.25cm in cross section and 1.5cm long) were cut from the sintered $LaCrO_3$ for electron conductivity measurement.

b) Conductivity measurements

The standard dc four-probe method was used. Current was applied through probes consisting of several turns (2mm wide) of Pt wire wound tightly around the sample at each end. Voltages were measured between two single turns of Pt wire 4.5mm from the ends and 6mm apart. To avoid the electrochemical effect the potentials across the voltage measuring electrodes was always < 10mV. The sample was connected in series with a standard resistor and a variable resistor. The sample current was measured from the Ohm drop across a standard resistor (either $100\,\Omega$ or $1k\,\Omega$) and the potential across the sample was controlled by the variable resistor. Voltage was measured with a high impedance digital voltmeter. The sample was placed horizontally in a vertical Mo-wound tube furnace. Ar/O_2 or CO/CO_2 gas mixtures were used to control the $P(O_2)$ in the ambient atmosphere. The $P(O_2)$ was measured by a zirconia cell (at 800°C down

stream from the furnace) The difference between log $P(O_2)$ obtained from the zirconia cell and that calculated from the CO/CO_2 relations was less than 0.1. The temperature of the furnace was controlled within 2°C and the measurements were made at 1000°C to 1300°C.

Results and Discussion

a) LaCrO₃

In the experiments we did not independently fix the La and Cr activity, but instead kept the La/Cr ratio fixed for all experiments. If volatilization of these cations is insignificant, then the variation of the defects with the change in oxygen activity is defined. It was established, that electronic conductivity, ♦, at each temperature is independent of $P(O_2)$ in the highest $P(O_2)$ range. In the middle range ♦ decreases with decreasing $P(O_2)$. In the lowest range ♦ increases with decreasing $P(O_2)$. The conductivity passes through a minimum value, ♦ min, at the $P(O_2, \text{♦min})$. These values are listed in Table 1. Conductivity measurements could not be continued below the $P(O_2)$ due to the erratic fluctuations in the dc conductivity, which presumably indicated decomposition

of $LaCrO_3$ according to the reaction: 2 $LaCrO_3$ (s) = La_2O_3 (s) + 2 Cr(s) + 3/2 O_2. In a perovskite type oxide represented by ABO_3, the BO_3 portion is a stochiometric ReO_3 structure, whereas the A site may easily be deficient [2-3].

b) $(CaO)x(ZrO_2)_{1-x}$ and $(Y_2O_3)x (ZrO_2)_{1-x}$

Yttria-zirconia compositions were prepared to span the range 5 to 50mole・% Y_2O_3. Nominal compositional increments were 5mole・% Y_2O_3 except in the region of the lower solid-solution limit. X-ray powder patterns showed the presence of two phases at 7.0mole・% Y_2O_3 and a single phase cubic solid solution at 9mole・% Y_2O_3. The high cubic solid-solution phase boundary falls between 45 and 50mole・% Y_2O_3.

Calcia-zirconia compositions were prepared to span the range 10 to 25mole・% CaO in 3mole・% increments. The deviation from exponential behavior for the higher CaO compositions is similar to observed by other investigators and is attributed to an order-disorder transition of the oxygen vacancies which occurs at about 1100°C [5].

In this paper we want to determine the evidence for a reversible order-disorder

transition in Y_2O_3-ZrO_2 compositions containing 15 to 35mole·% Y_2O_3 which were annealed at 900℃ for 2 weeks. Conductivity temperature data were obtained for these specimens during heating from 600℃ to 1350℃ and during cooling to 800℃. Only those compositions containing 20 and 25mole·% Y_2O_3 exhibited a conductivity anomaly at about 1100℃, which is indicative of a transition from an ordered to a disordered state. In low yttria compositions (10 to 15mole·% Y_2O_3) the degree of ordering is very low whereas for high yttria compositions (>30 mole % Y_2O_3) the degree of ordering is high. A conductivity temperature anomaly would not be detected for these extremes in ordering. Intermediate compositions hence would show the conductivity anomaly since the degree of ordering can be varied by annealing. The existence of an ordered phase, the degree of which is composition dependent, would explain why the activation energy increases as the cubic solid solution becomes richer in either Y_2O_3 or CaO.

c) Conductivity measurements at low oxygen partial pressure

Conductivity measurements were made by passing a constant current through the specimen and measuring the resistance with a bridge-type circuit. A specimen of composition $(Y_2O_3)_{0.09}(ZrO_2)_{0.91}$ was tested at constant current levels of 0.50, 0.75, 1.0 and 10mA dc. To eliminate thermoelectric effects, two measurements were made at each current level with the polarity being reserved in the second measurement. The specimen was re-oxidized in air for 5 to 10 minutes at 1000℃ after each test run. In each case, the original resistance value (″12 Ω) was obtained. Extending the measurement period to 3 hours showed a continuously increasing resistance for a test current of 0.5mA but a definite leveling of resistance for test currents of 0.75mA or larger. The higher conductivities obtained with the larger currents are believed to be caused by reduction of Zr^{4+} to Zr^{3+}, which would give rise to a mixed valence conduction mode. The oxidation potentials of Y^{3+} and Zr^{4+} indicate that Zr^{4+} would be more easily reduced than Y^{3+}. Partial reduction of the specimen occurred in those tests which exhibited a resistance leveling and the degree of reduction in some manner associated with the impressed voltage which increases with increasing resistance to maintain a constant current level [5]. The

threshold voltage for reduction appears to be about 2.0V. Thus, the resistance-time data for a constant current of 0.5mA represents the case of negligible reduction. These data also suggest that the specimen had not attained equilibrium with surrounding atmosphere, since a static resistance level was not observed after a 4-hour test. However, a conservative estimate of the transference number for the oxygen ion can be obtained from the original specimen resistance (''12Ω) and the specimen resistance after a 1-hour test period (''3600Ω). Using these values equation (*) gives an oxygen ion transference number (to 2-) greater than 0.99. If reduction occurs in the high-current tests, it will manifest itself as both a weight loss and a change in specimen color. To have specimens show these changes, several specimens were subjected to extreme reducing conditions of 50mA in a depleted-oxygen atmosphere for a period of 2 hours. After this test, specimens were gray and on re-oxidation exhibited a weight gain of approximately 0.2%. This is too great a weight loss to be attributed to reduction of impurities in the specimens and consequently must represent reduction of Zr^{4+} to Zr^{3+}. Conductivity-temperature

measurements were made in an inert atmosphere on a specimen which had attained a constant conductivity level after subjected to a direct current of 10mA for a period of 2 hours.

Conclusion

1. The ionic conductivity of cubic solid solutions in the system CaO-ZrO_2 and Y_2O_3-ZrO_2 prepared by SHS was examined. For these systems, the composition of highest conductivity was found to lie in the Y_2O_3-ZrO_2 binary at 9mole・% Y_2O_3 near the low yttria cubic solid solution limit. The higher conductivity appears to be related to the lower activation energy rather than to the number of oxygen vacancies dictated by composition. Annealed specimens of Y_2O_3-ZrO_2 compositions containing 20 and 25mole・% Y_2O_3 exhibited an anomaly in conductivity temperature data at ''1100℃ which is indicative of a reversible order-disorder transition analogous to that observed for CaO-ZrO_2 cubic solid solutions.

2. Electronic conductivity of $LaCrO_3$ were measured as a function of temperature (1000 to 1300℃) and $P(O_2)$ (10^5 to 10^{13}).

The carrier concentrations were calculated as a function of $P(O_2)$ and defect structure was described. It was found that the electrical properties of $LaCrO_3$ are determined not only by the concentration of oxygen vacancies, but also the La/Cr ratio.

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