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FURTHER INVESTIGATIONS ON SOME ELECTROCHEMICAL AND THERMAL PROPERTIES OF STABILIZED AND SINTERED ZIRCONIA REFRACTORIES

M.M. ABOU SEKKINA *[†] and T.M. ABD EL-HALIM *

Department of Chemistry, Faculty of Science, Tanta University (Egypt)

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ABSTRACT

Pure zirconia was doped with various amounts of CaO, La_2O_3 and UO_3 using the high temperature ceramic procedure and sintering technique. Several measurements were carried out on these doped refractory bodies comprising true and bulk densities, X-ray diffraction (XRD), and the temperature dependence of DC electrical conductivity. Results obtained were all in conformity, and are explained and discussed on the basis of the interaction of dopants with the zirconia lattice and their effects on phase constitution, degree of crystallinity, electrical conductivity and activation energy for electric conduction of doped zirconia bodies.

INTRODUCTION

The interest of the present investigation is due to the fact that stabilized zirconia bodies have successful applications where a high degree of reliability and dimensional stability are required at high temperatures. It is important to note that by the addition of certain oxides, zirconia can be stabilized in a cubic form free from inversion. A small amount of inversion in incompletely stabilized zirconia bodies has been shown however to reduce the overall thermal expansion and to increase thermal shock resistance. Wolten [1] deduced that the zirconia phase change possesses many of the characteristics associated with a diffusionless phase transformation of the type observed in several pure metals and metal alloy systems. Wolten [1] from high temperature X-ray diffractometry XRD suggested that zirconia inversion is very similar to the Fe–Ni martensitic class of displacive transformations. Barrett [2] found that displacive transformations are described as distortions of atom or lattice networks in which the atomic linkages are

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* Present address: Faculty of Science, The United Arab Emirates University, Al-Ain, P.O Box 15551, U.A.E.

[†] Author to whom correspondence should be addressed.

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maintained intact in their new crystal phase configuration. Thus, the displacive transformation is produced by a diffusionless, shearing mechanism involving the cooperative translation of planes and/or groups of atoms or ions. Hund [3] proposed the oxygen vacancy model by comparing XRD patterns and pyknometric densities. For the $CaO-ZrO_2$ system, Tien and Subbarao [4], and Johansen and Cleary [5] found that the maximum electrical conductivity occurs in those compositions where the structure is close to the monoclinic–cubic solid solution phase boundary. Also, the maximum conductivity was found to change with the additive cation. For, the $M_2O_3-ZrO_2$ system, Bray and Merten [6] found the same results as for the $CaO-ZrO_2$ system. Dixon et al. [7] suggested that the conductivity increased as the ionic radius of the substituted cation decreased; however, complete evidence of this trend was not presented. Strickler and Carlson [8] noticed that all $M_2O_3-ZrO_2$ systems, except for $M = La$, formed cubic solid solutions of fluorite type structure.

The present investigation reports the influence of doping on the temperature dependence of electrochemical properties of zirconia refractories.

EXPERIMENTAL TECHNIQUES

Material synthesis and sample preparation

The starting materials were: ZrO_2, $CaCO_3$, La_2O_3 and UO_3 of extra pure grade (purity > 99.98%). Several doped, sintered $CaO-ZrO_2$, $La_2O_3-ZrO_2$ and UO_3-ZrO_2 ceramic systems were carefully prepared with chosen molar ratios and firing conditions. The two components, zirconium dioxide (host) with different molar ratios of the dopants (guest), were first mixed intimately and ground in an agate mortar for 1 h. The mixes were then fired and sintered at 1350°C for 3 h in air. In all cases, the amount of dopants ranged from 2 to 6 mol%. In some cases a relatively low sintering temperature, down to 500°C, was deduced to be interesting, depending on the origin of the zirconia used.

The products were compressed in the form of pellets (thickness 3 mm, diameter 1.0 cm) using a hydraulic pressing machine at 500 kg cm^{-2}. The prepared disks were sintered at 500–1350°C for 3 h which, after many trials, were chosen to be the most suitable conditions. The establishment of doping and good sintering were followed by careful XRD analysis and bulk density measurements.

Density measurements

Pyknometer density measurements

A known weight (W_1) of very finely ground sample was introduced into the pyknometer of (W_2). The bottle was filled to the mark with distilled water. The pyknometer was subjected to a moderate vacuum pump (10^{-2} mm Hg) to remove the trapped air. After the liquid had completely penetrated all the sample pores, the pyknometer was gently thermostated at 30°C and weighed (W_3). The solid was removed and the pyknometer was filled lately to the mark, under same thermostating temperature (30°C), with liquid alone and weighed (W_4). Thus, the density (true) of the test sample ρ was $(W_1\rho')/(W_4 - W_3 + W_1)$ g cm^{-3} at 30°C, where ρ' is the density of distilled water at 30°C.

Bulk density measurements

The density of the test sample was measured in the solid state without its destruction, by calculating the sample volume, taking its dimensions, and weighing. This method is very similar to that previously used by Atkin and Fulrath [9] as it implies no destruction of the well-sintered zirconia bodies and directly relates to the degree of sintering and thus could be used as a sintering parameter of the present ferrite samples.

X-ray diffraction measurements

The CuK_α XRD patterns of doped and stabilized zirconia refractories were carried out using a Shimadzu X-ray diffractometer Model XD-3 (Japan). The ground sample was pressed on the standard sample holder to get better briquetting and the holder was fixed in the automatic sample changer. A Geiger Müller tube was adjusted at a rate of 2° min^{-1}. The amplifier counter output was recorded simultaneously on a chart, set at a speed of 10 mm min^{-1}. The diffraction peak was taken to be the average of the position of the positive and negative halves of the Debye–Scherrer ring.

DC electrical conductivity measurements

These were undertaken by using the two-probe method under vacuum. The circuit and mode of measurement used are very similar to those described previously [10] with some modification. Silver electrodes were made on the surfaces of the test specimen by vacuum evaporation. Measurements were taken at both room and elevated temperatures up to ca. 550 K and the readings were taken three times at 15 min intervals for each temperature equilibration. The circuit used was well shielded with copper to prevent current leakage and to attain stable and reliable electrometer readings. In all of the above measurements, the readings were checked three times and in each case reliable data were obtained.

RESULTS AND DISCUSSION

Figure 1 represents the variation of true density (specific gravity) and bulk (apparent) density of various doped zirconia moeities as functions of

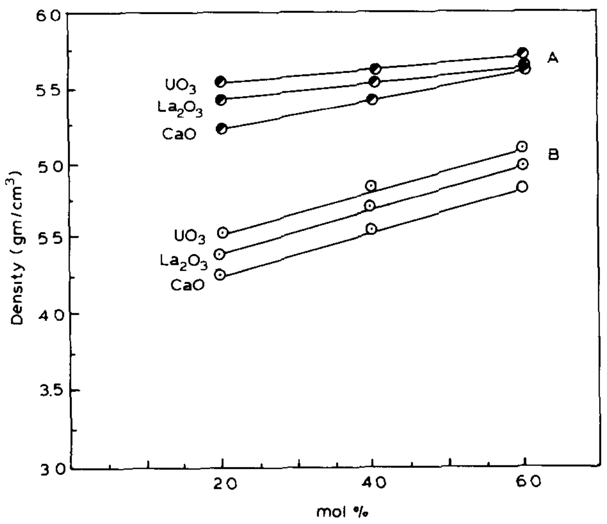

Fig. 1. A diagrammatic representation of the variations of (A) true density and (B) bulk density as functions of mol% of dopant in zirconia refractories.

mol% of the dopants. It was clearly shown that the straight line relationships obtained have a general trend in common, namely the true (curves A) and bulk (curves B) densities increase with increasing mol% of dopant in straight line relationships. This behaviour could be ascribed to the increased sintering parameter and/or propagation of solid solution formation in the same direction. Furthermore, both true and bulk densities increase with increasing molecular weight of the dopant oxide. The high bulk density obtained for the test sample of 6 mol% dopant, reaching 90% of the corresponding true density, indicates the attainment of well sintered (doped zirconia) bodies.

Figure 2 shows the CuK_α XRD patterns of: (a) zirconia doped with 6 mol% UO_3 fired at 500°C for 3 h where $ZrOCl_2$ was used instead of ZrO_2; (b) zirconia doped with 6 mol% UO_3 fired at 1350°C for 3 h. Analysis of the XRD patterns obtained and comparison of these with those of the ASTM X-ray card, indicate that: (i) pattern (a) belongs to a purely cubic zirconia solid solution phase; and (ii) pattern (b) belongs to a mixture of zirconia cubic solid solution and monoclinic zirconia phases. Thus, it was deduced that the UO_3–ZrO_2 cubic solid solution formed (at relatively low temperature, 500°C) undergoes thermal destabilization partially at high temperature (1350°C, pattern b) to a mixture of cubic and monoclinic zirconia phases.

For the results of the temperature dependence of electrical conductivity, it was found that the conductivity varies exponentially with temperature according to the well known relation [11]

$$\sigma = \sigma_0 \exp(-\Delta E/kT)$$

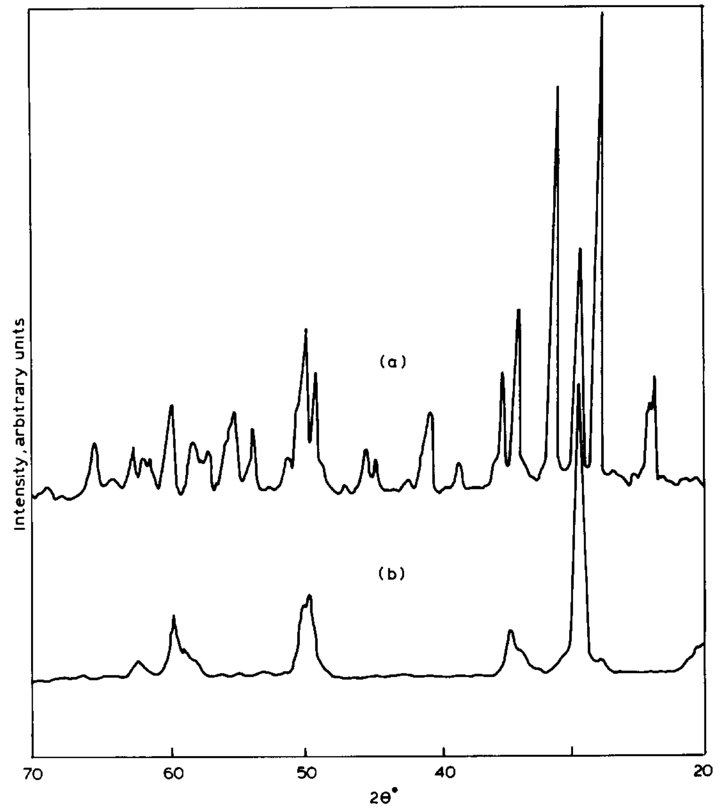

Fig. 2. The CuK_α XRD patterns of: (a) UO_3 (6 mol%) doped zirconia fired at 1350°C for 3 h; (b) UO_3 (6 mol%) doped zirconyl chloride fired at 500°C for 3 h.

The relatively slight response of σ with temperature involves ΔE values which can be interpreted by a simple single-band model in most cases. The ΔE values were calculated and assumed to correspond to the activation energies of defect mobilities. Thus, Fig. 3 shows the variation of activation energy (eV) for conduction as a function of the cationic radii of the dopants in the zirconia lattice. It can easily be seen from Fig. 3 that the activation energy for conduction gets higher as the ionic radius of the substituted cation rises. This was in conformity with the previous observation of Dixon et al. [7] that "the conductivity increased as the ionic radius of the substituted cation increases". In our view this could be explained on the basis that as the ionic radius of the dopant cation decreases the mobility increases, resulting in an increased electrical conductivity and a decrease in its attendent activation energy for conduction. Alternatively, our conductivity data were in conformity with Wagner's suggestion [12] that the stabilization of zirconia is accompanied by direct substitution of di- or trivalent cations of appropriate size for the host cation, Zr^{4+}, thus forming a cubic solid

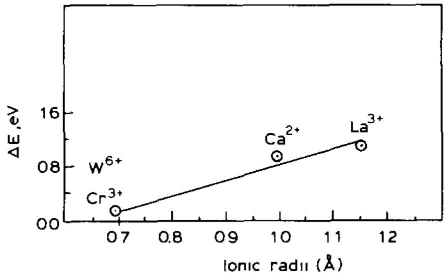

Fig. 3. The variation of activation energy for conduction (eV) as a function of ionic radius of dopant cation in the zirconia refractories.

solution of fluorite-type structure. Because the substituted cation is of lower valence than the host cation, oxygen vacancies are thus created that preserve lattice neutrality; this is reflected in the increased electrical conductivity on doping (see Fig. 3). Furthermore, our present results support the idea that the aforementioned high oxygen vacancy concentration formed should also give rise to a high oxygen ion mobility. This illustrates why the electrical conductivity increases and the corresponding activation energy for conduction decreases as a function of doping. The electrical conductivity is governed by the point defects in zirconia which can serve as donors or acceptors, thus the electrical conductivity data can be very helpful in elucidating the defect structure of the oxide refractory because the defect concentration depends on the partial pressure of O_2 and on the temperature. Therefore, the electronic conduction of fabricated oxide refractories should be insignificant compared with their ionic conduction since certain impurities affect the onset of electronic conduction [13].

REFERENCES

1 G.M. Wolten, J. Am. Ceram. Soc., 46 (1963) 418; Acta Crystallogr., 17 (1964) 763.
2 C.S. Barrett Structure of Metals, 2nd edn., McGraw-Hill, New York, 1952, p. 538.
3 F. Hund, Z. Phys. Chem., 199 (1952) 142.
4 T.Y. Tien and E.C. Subbarao, J. Chem. Phys., 39 (1963) 1041.
5 H.A. Johansen and J.G. Cleary, J. Electrochem. Soc., 111 (1964) 1041.
6 D.T. Bray and U. Merten, J. Electrochem. Soc., 111 (1964) 447.
7 J.M. Dixon, L.D. LaGrange, V. Merten, C.F. Miller and J.T. Proter, J. Electrochem. Soc., 110 (1963) 276.
8 D.W. Strickler and W.G. Carlson, J. Am. Ceram. Soc., 48 (1965) 286.
9 R.B. Atkin and R.M.F. Fulrath, J. Am. Ceram. Soc., 54 (1971) 265.
10 M.K. El-Nimr, M.M. Abou Sekkina and A. Tawfik, Ind. Ceram., 21 (1978) 147.
11 M.M. Abou Sekkina, J.P. Bonnet, J.C. Grenier, M. Onillon, M. Pouchard and P. Hagenmüller, Rev. Chim. Mineral., 17 (1980) 431.
12 C. Wagner, Naturwissenschaften, 31 (1943) 285.
13 A. Kumer, D. Rajdev and D.L. Douglass, J. Am. Ceram. Soc., 55 (1972) 439.