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Lattice defect and oxygen self-diffusion in MgO-stabilized ZrO_2

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Electrical conductivity of various stabilized ZrO_2 has been determined by many investigators. In contrast, direct determination of oxygen self-diffusion by the tractor technique has been performed for only CaO-stabilized ZrO_2 by Kingery *et al.* [1] at 680 to 890° C and by Simpson and Carter [2] at 800 to 1100° C. Since these temperature ranges are within two-phase regions, according to the recent CaO–ZrO_2 phase diagram [3], those oxygen self-diffusion coefficients are interpreted to have been determined at a metastable state.

The present work was undertaken to determine the oxygen self-diffusion in MgO–ZrO_2 solid solution to clarify the diffusion mechanism by comparing the results with those of CaO-stabilized ZrO_2. The determination was extended from two-phase regions to the single-cubic phase region toward high temperatures. Since the phase transition rate on cooling is known to be higher in the MgO–ZrO_2 system than in the CaO–ZrO_2 system [4], the effect of phase transition from the cubic form to the two-phase state on the oxygen self-diffusion is expected to be elucidated better for the MgO–ZrO_2 solid solution.

Two types of lattice defect, oxygen vacancy and cation interstitial, were reported for a cubic CaO–ZrO_2 solid solution [5]. To confirm the lattice defect type for the employed MgO–ZrO_2 solid solutions, a density measurement was conducted.

Samples were prepared from mixed powders of and ZrO_2 (99.6% pure). Mixed powder for a designed composition was pressed into a disc shape and sintered at 2200° C for 3 h in an argon atmosphere. The sintered pellet was annealed in air at 1800° C for 4 h and subsequently quenched by dropping into an ice and water bath. The quenched sample was crushed and ground using an agate mortar and subjected to the pycnometric density measurement and X-ray diffraction.

Samples were prepared from mixed powders of MgO and ZrO_2 for the designed compositions. The mixed powders were isostatically pressed under a pressure of 7 ton cm^{-2}, subsequently ground into a spherical shape and sintered at 1750° C for 3 h in air. Densities of sintered samples for four compositions ranged from 93 to 95% of the theoretical densities calculated for the lattice defect type which was determined later. The samples were heat-treated again at 1580° C for 2 h to stabilize the microstructure of the fluorite-cubic phase. After quenching to room temperature, samples were ground and finished into spheres of 6 to 7 mm diameter using SiC paper and subjected to the oxygen self-diffusion coefficient determination. Three compositions (12.0, 14.0, and 16.0 mol % MgO) and temperatures employed for the determination are plotted on Grain's phase diagram [6] as shown in Fig. 1.

The oxygen self-diffusion coefficient was determined by the isotope exchange technique using ^{18}O as the tracer. Before the diffusion experiment the sphere sample was pre-annealed in a natural oxygen atmosphere for 20 min at the same temperature under the same O_2 pressure (180 torr) as in the diffusion anneal. Diffusion annealing was conducted using a high-frequency induction furnace with a Pt–Rh susceptor. The ^{18}O concentrations decreasing in the gas phase were determined at scheduled intervals during the diffusion anneal by means of a mass-spectrometer. The diffusion coefficient was calculated from the ^{18}O diffusion amount using a diffusion equation for the boundary condition where diffusion from a well-stirred fluid of a fixed volume into a sphere was controlled by the surface exchange rate [7].

In Fig. 2 are shown the densities determined for samples of the four compositions quenched from 1800° C in air into an ice-water bath, where the results are compared with theoretical densities (solid lines) calculated with the assumption of the

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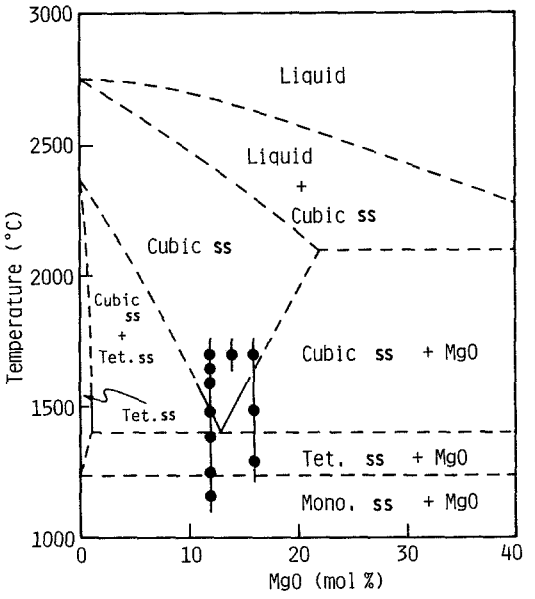

Figure 1 Compositions and temperatures for determination of oxygen self-diffusion coefficient plotted on Grain's $MgO–ZrO_2$ phase diagram [6].

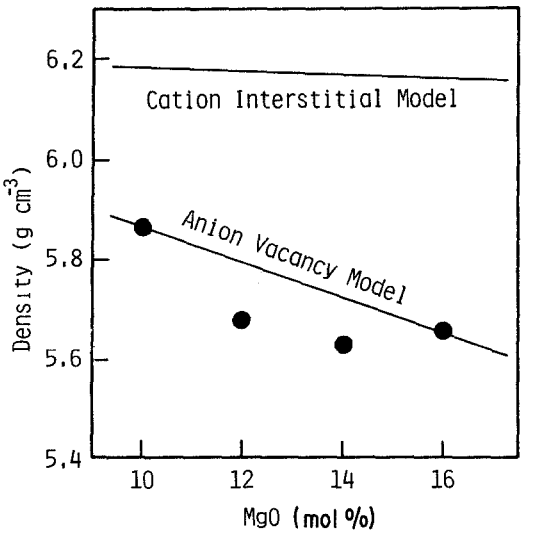

Figure 2 Pycnometric densities in comparison with theoretical densities for two defect types of $MgO–ZrO_2$ solid solutions.

anion-vacancy type and cation-interstitial type solid solutions, respectively. The results indicate that oxygen vacancies are the predominant lattice defect in the present cubic $MgO–ZrO_2$ solid solutions at 1800° C.

Oxygen self-diffusion coefficients determined for $12MgO·88ZrO_2$ are shown by closed circles as a function of temperature in Fig. 3, where phase boundary temperatures read from the phase diagram [6] are indicated by dashed lines. The whole diffusion coefficients can not be properly represented by a single Arrhenius equation, but the four data in the single-cubic phase region can be represented by

$$D = 1.02 \times 10^{-8} \times \exp\left[-62.8(\mathrm{kJ\,mol^{-1}})/RT\right] \mathrm{m^2\,sec^{-1}} \quad (1)$$

In comparison with the extrapolation of those results (dotted line), as the temperature decreases, oxygen self-diffusion coefficients tend to deviate toward the lower side with increasing apparent activation energy.

Oxygen self-diffusion coefficients determined for $14MgO·86ZrO_2$ and $16MgO·84ZrO_2$ are similarly shown by squares and triangles, respectively in Fig. 4 where the solid line represents the results for $12MgO·88ZrO_2$ in Fig. 3. As compared at 1697° C, the three different samples do not reveal significant composition dependence of the oxygen self-diffusion coefficient. Although the number of determinations is limited for $16MgO·84ZrO_2$, the temperature dependence of the oxygen diffusion with respect to phase transition is understood to be similar to the $12MgO·88ZrO_2$ case.

Regarding the lattice defect type in the fluorite-cubic $CaO–ZrO_2$ solid solution, according to Diness and Roy [5], and Carter and Roth [8], oxygen vacancies are the predominant defect in the low temperature range, while interstitial cations are predominant in the relatively high temperature range. Since the ionic radius of the magnesium ion is smaller than that of the calcium ion, one may expect the possibility of interstitial cations to occur more in the $MgO–ZrO_2$ system than in the $CaO–ZrO_2$ system. However, as shown in Fig. 2, the predominance of the oxygen vacancy type was confirmed at 1800° C for the composition range of 10 to 16 mol % MgO. At temperatures lower than 1800° C, the oxygen vacancy type is expected to remain predominant by analogy with CaO-stabilized ZrO_2 in which occurrence of the interstitial cation types is limited to only relatively high temperatures [5]. Consequently, formation of a lattice defect in $MgO–ZrO_2$ solid solution is primarily described by Equation 2 in the Kroger–Vink notation.

$$MgO \xrightarrow{ZrO_2} Mg''_{Zr} + V_O^{\cdot\cdot} + O_O^x \quad (2)$$

The diffusion samples were equilibrated at

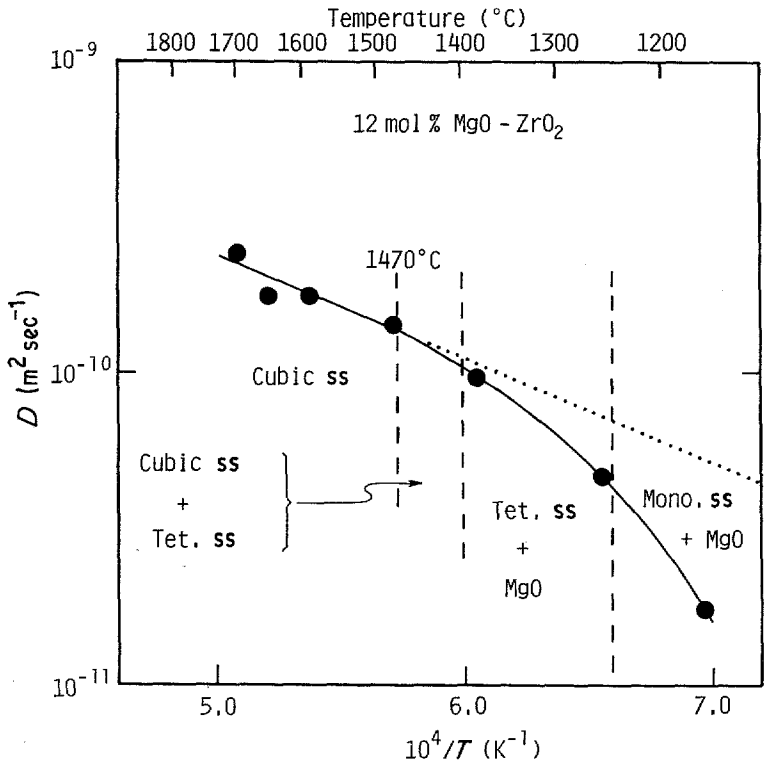

Figure 3 Oxygen self-diffusion coefficients for $12MgO \cdot 88ZrO_2$ as a function of temperature.

1580° C prior to the diffusion experiments. No appreciable phase transition is expected to proceed from the single-cubic phase state during the pre-annealing and diffusion anneal, since cationic inter-diffusions required for those phase transitions are slow [9]. However, deviations of the temperature dependences of oxygen self-diffusion coefficients in low temperature ranges shown in Figs. 3 and 4 appear to be corresponding to phase transitions indicated in the phase diagram.

With respect to the composition $12MgO \cdot 88ZrO_2$, as seen in Figs. 1 and 3, the fluorite cubic phase is stable at temperatures higher than 1470° C; the temperature range 1470 to 1400° C is a two-phase region for fluorite-cubic and tetragonal solid solutions; the temperature range 1400 to 1240° C is a two-phase region for the tetragonal solid solution and MgO; the temperature range lower than that is a two-phase region for the monoclinic solid solution and MgO.

As shown in Fig. 3, the oxygen self-diffusion coefficient exhibits a break in its temperature dependence at 1400° C where the fluorite-cubic phase with high MgO content disappears and the tetragonal phase with reduced MgO content and the MgO phase are formed. If this transition takes place, it should result in a substantial decrease of oxygen vacancy concentration and consequently, in low oxygen diffusivity.

In the higher temperature range 1470 to 1400° C, the tetragonal phase occurs in the host cubic phase. However, as seen in Fig. 1, the substantial fraction in the phase composition here is the cubic phase, which is the continuous phase and primarily determines the oxygen diffusivity of the overall system. Thus, even if that phase transition takes place, the normally expected oxygen diffusivity is not necessarily pronounced in this temperature range, which appears to be the case in Fig. 3. The pronounced decrease in oxygen diffusion from the tetragonal phase plus MgO region to the monoclinic phase plus MgO region, shown in Fig. 3, is interpreted to be due to the higher oxygen diffusivity in the tetragonal solid solution than in the monoclinic solid solution which has lower MgO solubility than the tetragonal phase.

As mentioned earlier, the oxygen self-diffusion in the single fluorite-cubic phase region above 1470° C is described by Equation 1. Its comparison with the $16MgO \cdot 84ZrO_2$ data in Fig. 4 does not seem to indicate a pronounced difference in the magnitude of the activation energy in this single-cubic phase region. The activation energy, 62.8 kJ mol^{-1}, is interpreted to be the migration energy of

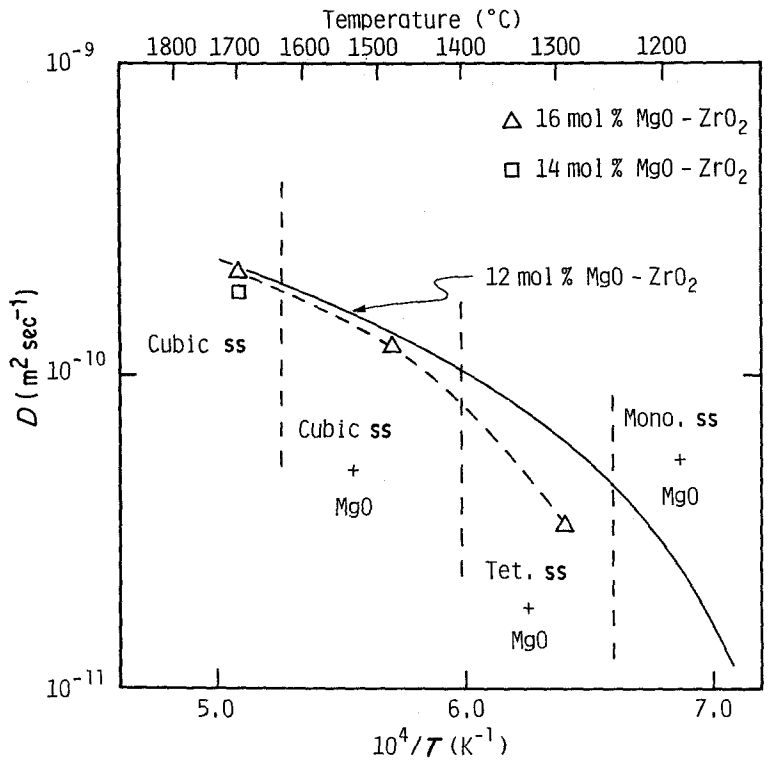

Figure 4 Oxygen self-diffusion coefficients for $16MgO \cdot 84ZrO_2$ as a function of temperature.

the oxygen ion typical of the fluorite-cubic MgO–ZrO_2 solid solution. (Defect association which might be relevant to the problem is not discussed here.)

The temperature dependence of the diffusion coefficients below 1400° C for $12MgO \cdot 88ZrO_2$, shown in Fig. 3, may be expressed as an activation energy of approximately 150 kJ mol^{-1}. As discussed above, however, this activation energy has no physical meaning for a simple self-diffusion but varies depending on the thermal history of the samples.

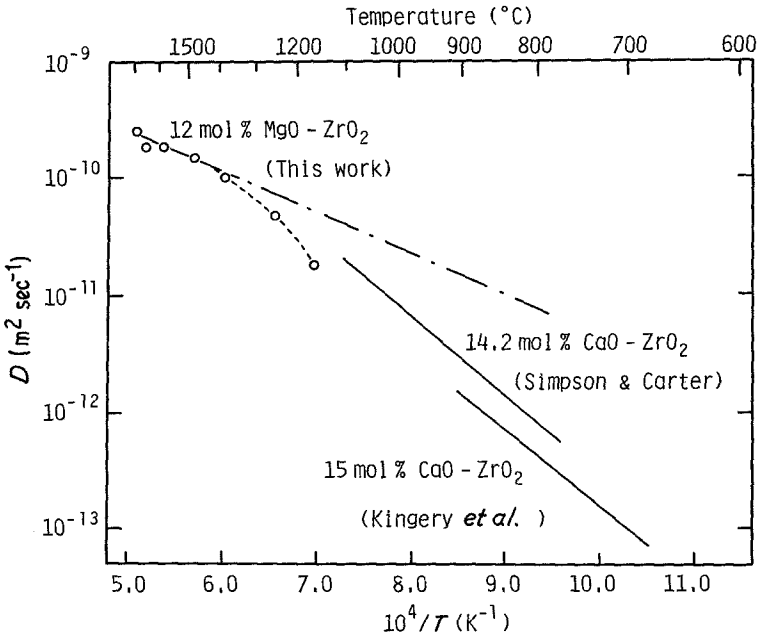

Figure 5 Comparison of oxygen self-diffusion coefficients in systems MgO–ZrO_2 and CaO–ZrO_2.

With respect to the composition 16MgO·84ZrO_2, the oxygen self-diffusion coefficient exhibits no significant change from the single-cubic phase region to the two-phase region of the cubic and MgO phases, as compared with 12MgO·88ZrO_2 in Fig. 4. This can be explained in a similar manner to the cubic plus tetragonal region of 12MgO·88ZrO_2, that is, as seen in the phase diagram, the substantial fraction in the phase composition here is the cubic solid solution, which is the continuous phase and primarily determines the oxygen diffusivity of the overall system; the MgO phase with low diffusivity [10] is an isolated phase in the host cubic solution. The pronounced decrease of the oxygen diffusion coefficient from the cubic solid solution plus MgO region to the tetragonal solid solution plus MgO region was already explained for 12MgO·88ZrO_2, except that this phase transition effect appears to be more pronounced in the solid solution with higher MgO content.

The oxygen self-diffusion coefficients determined for 12MgO·88ZrO_2 are compared in Fig. 5 with those for CaO-stabilized ZrO_2 in the literature. The activation energy for the single-cubic phase region of 12MgO·88ZrO_2, 62.8 kJ mol^{-1}, is similar in magnitude to the migration energy of the oxygen vacancy for ZrO_2-based crystals, 66 kJ mol^{-1}, reported in a review by Kilner and Brook [11]. The magnitudes of these activation energies are approximately one half of those determined for the oxygen diffusion in 15CaO·85ZrO_2 (127 kJ mol^{-1}) [1] and 14.2CaO·85.8ZrO_2 (131 kJ mol^{-1}) [2]. The migration energy of the oxygen vacancy in a fluorite-cubic oxide is primarily determined by the host cation and is not sensitive to dopant cations [11]. Those high activation energies determined for CaO-stabilized ZrO_2 are understood to involve energy other than the migration energy of the single oxygen vacancy.

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