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Ceramics International 33 (2007) 147–150

CERAMICS
INTERNATIONAL

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Nitrogen incorporation into pure and doped zirconia

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Received 18 April 2005; received in revised form 6 July 2005; accepted 5 August 2005
Available online 9 November 2005

Abstract

The defect chemistry of the nitrogen incorporation into pure and cation (Y^{3+}, Eu^{3+}, Ce^{4+}, Mg^{2+}, Ca^{2+})-doped ziconia is quantitatively described using simple thermodynamic considerations, allowing the calculation of the anion vacancy concentration as a function of the nitrogen and oxygen pressure in the surrounding atmosphere. The effective equilibrium constants for the nitrogen incorporation into pure and cation-doped zirconia (K) can be expressed by $KP_{O_2}^{-3/2}P_{N_2} = 4[V_O^{oo}]_N^3/(1-3[V_O^{oo}]_N)^3$ and $KP_{O_2}^{-3/2}P_{N_2} = (4[V_O^{oo}]_N^2([V_O^{oo}]_N + [V_O^{oo}]_Y))/(1-3[V_O^{oo}]_N - [V_O^{oo}]_Y)^3$, respectively, and are in the order of 10^{-25} at 1900 °C. Sievert's and Henry's law for gas solubility at high temperatures in melts and alloys were applied to model the results with only partial success.

Keywords: D: ZrO_2; D: Nitrides; Oxynitrides

1. Introduction

The nitridation of zirconia occurs at temperatures between 1400 and 2200 °C in nitrogen atmosphere leading to the formation of zirconium oxynitrides (nitrogen-containing zirconia) [1,2]. Theoretical and experimental investigations show that the nitridation of zirconia is to be explained as a grain-size dependent reaction, equilibrium conditions after 2 h of nitridation are observed at temperatures of 1900 °C and higher [1–4].

Nitrogen-containing zirconia exhibits exceptional mechanical, electrical and optical properties compared to undoped zirconia [3–7]. A combination of doping in the cation and the anion sublattice allows controlled synthesis of anion-deficient fluorite-type materials with ordered (β-type phases, etc. [2]) or randomly distributed anion vacancies [1–4].

At ambient pressure, ZrO_2 exists in three polymorphs: monoclinic (m-ZrO_2), tetragonal (t-ZrO_2) and cubic zirconia (c-ZrO_2) [8]. The high temperature t-ZrO_2 and c-ZrO_2 phases are stabilized at room temperature by the presence of oxygen vacancies. In this way the nitridation is a very useful approach to prepare metastable zirconia phases and to affect their physical properties.

This paper presents a quantitative physicochemical model for nitrogen incorporation into the zirconia lattice and clarifies the thermodynamics of incorporation. The nitridation of pure and cation-doped zirconia is of interest because of the promising optical properties of ZrO_2:Eu, ZrO_2:Ho, ZrO_2:Sm and ZrO_2:Tb materials [9–13]. According to our previous papers, even small amounts of nitrogen lead to an improvement of the luminescence properties of ZrO_2:Eu and may be used for coloration of ZrO_2 and ZrO_2–CeO_2 ceramic materials [5–7].

2. Results and discussion

The incorporation of N_2 in the zirconia lattice may be described as follows:

$$N_2 + 3O_O^x = 2N_O^{/} + V_O^{oo} + 1.5O_2 \qquad (1)$$

Aliovalent cationic dopants like Y^{3+} also lead to anionic vacancy formation:

$$Y_2O_3 + 2Zr_{Zr}^x + O_O^x = 2Y_{Zr}^{/} + V_O^{oo} + 2ZrO_2 \qquad (2)$$

In Eqs. (1) and (2), O_O^x, Zr_{Zr}^x, $N_O^{/}$, $Y_{Zr}^{/}$ and V_O^{oo} denote oxygen anion on a regular oxygen site, zirconium cation on a regular zirconium site, nitrogen anion replacing an oxygen anion,

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0272-8842/$32.00
doi:10.1016/j.ceramint.2005.08.007

yttrium cation replacing a zirconium cation, and oxygen vacancy in the anionic sublattice, respectively. The relative positive (o) or negative (/) electric charges are given as superscripts.

From Eqs. (1) and (2) it follows that:

$$[V_O^{oo}] = [V_O^{oo}]_N + [V_O^{oo}]_Y \tag{3}$$

In Eq. (3), $[V_O^{oo}]_N$ and $[V_O^{oo}]_Y$ are the concentrations (anion fractions) of oxygen vacancies created by nitrogen and yttrium incorporation, respectively. For nitridation of pure zirconia $[O_O^x] = [O_O^x]^* - 3[V_O^{oo}]_N$, where the asterisk (*) represents the concentration at the beginning of the nitridation, which is 1. From Eq. (1) it follows that $2[V_O^{oo}]_N = [N_O]^/$. In the case of nitriding yttria containing zirconia the following results: $[O_O^x] = [O_O^x]^* - 3[V_O^{oo}]_N - [V_O^{oo}]_Y$.

Using Eqs. (1–4), the effective equilibrium constant K of nitrogen incorporation into pure ZrO_2 may be expressed as follows:

$$KP_{O_2}^{-3/2}P_{N_2} = \frac{[N_O^/]^2[V_O^{oo}]_N}{[O_O^x]^3} = \frac{4[V_O^{oo}]_N^3}{[O_O^x]^3} \tag{4}$$

A combination of Eqs. (1–3) leads to Eq. (5) for the nitridation of zirconia:

$$KP_{O_2}^{-3/2}P_{N_2} = \frac{4[V_O^{oo}]_N^3}{(1-3[V_O^{oo}]_N)^3} \tag{5}$$

For the nitridation of zirconia doped with Y^{3+} or trivalent rare earth ions, a combination of Eqs. (3) and (5) gives:

$$KP_{O_2}^{-3/2}P_{N_2} = \frac{4[V_O^{oo}]_N^2([V_O^{oo}]_N + [V_O^{oo}]_Y)}{(1-3[V_O^{oo}]_N - [V_O^{oo}]_Y)^3} \tag{6}$$

In Eqs. (4–6), P_{O_2} and P_{N_2} are the partial pressures of oxygen and nitrogen. If an oxygen getter material like a graphite-heated resistance furnace is used, P_{O_2} is controlled by the reaction $2C + O_2 = 2CO$ and can be calculated from the reliable data [4]. The nitrogen content of samples with 10 mol% dopant oxide, equilibrated for 2 h in nitrogen atmosphere (1 bar) is in the range of ~7 anion%. This compares with ~15% for pure zirconia. Both are well described in Eq. (6) (e.g., [3,6,7]). Eqs. (5) and (6) can be used for the calculation of both K and the standard change of the Gibbs free energy $\Delta G^\circ_{\mathrm{react}}$ of nitrogen incorporation for different materials. Furthermore, P_{O_2} can be calculated from the fitting process of the experimental data [4]. In Table 1 the values of K and $\Delta G^\circ_{\mathrm{react}}$ are given which have been calculated by using the nitrogen analyses in [2–5]. The data in Table 1 show that nitrogen incorporation is facilitated by the absence of aliovalent cationic dopants, according to Eq. (3). The activation energy of the nitrogen incorporation is about 500 kJ/mol, where the activation energy of the oxidation of nitrogen-containing zirconia was determined to 84 kJ/mol [9]. In this way the low temperature stability (up to 400–600 °C) of nitrogen-doped zirconia in air may be explained. Wrba and Lerch [3] pointed out that the controlling process for the nitridation of zirconia is not the diffusion of nitrogen but an interface process. The dissociation enthalpy, ΔH°, of N_2 is 945 kJ/mol [14], comparable with the values of ΔG° in Table 1. If the standard enthalpy of nitrogen incorporation coincides with the dissociation enthalpy, ΔH°, of N_2, the standard entropy, ΔS°, of the nitrogen incorporation is about −185 J/mol K (Table 1).

Table 1
$K \times 10^{25}$ and $\Delta G^\circ_{\mathrm{react}}$ for different nitrogen-containing zirconia materials

Material	References	$K \times 10^{25}$	$\Delta G^\circ_{\mathrm{react}}$ (kJ/mol)	T (°C)
Zr–Eu(III)–O–N	[6]	1.03	1039	1900
Zr–Y(III)–O–N	[3]	1.00	1040	1900
Zr–Ce(IV)–O–N	[7]	11.00	997	1900
Zr–Ca(II)–O–N	[3]	1.50	1032	1900
Zr–Mg(II)–O–N	[3]	1.23	1036	1900
Zr–O–N	[4]	8.08	1071	2050

The error of K is about 0.01×10^{-25} which leads to an error of about 20 kJ/mol in $\Delta G^\circ_{\mathrm{react}}$.

A correlation between nitrogen pressure and anion vacancy concentration can be expressed with the following equation:

$$P_{N_2} = \frac{P_{O_2}^{3/2}}{K}\gamma[V_O^{oo}]_N^2 = \frac{P_{O_2}^{3/2}}{4K}\gamma[N_O^/]^2 \tag{7}$$

Eq. (7) is similar to Sievert's law for gas solubility at high temperatures in melts and alloys.

Sievert's law describing the dissolution of nitrogen into melts [15] can be written as follows:

$$P^{1/2} = \frac{1}{K_S}\gamma[N] \tag{8}$$

Eq. (8) predicts a quadratic parabolic dependence of the pressure, p, upon the concentration of the dissolved nitrogen [N] and may be used for calculation of the activity coefficient, γ, of nitrogen and the solubility equilibrium constant K_S. On the other hand, Henry's law predicts a linear dependence between P_{N_2} and [N] for γ = const [14].

According to Sievert's law, γ from Eq. (7) is related to the activity of the incorporated nitrogen which depends on $[V_O^{oo}]$. For zirconia nitridation, γ is defined as:

$$\gamma = \frac{4[V_O^{oo}]_N}{(1-3[V_O^{oo}]_N)^3} \tag{9}$$

For the case of nitridation of zirconia doped with yttrium or trivalent rare earth ions the coefficient γ can be expressed as:

$$\gamma_Y = \frac{4([V_O^{oo}]_N + [V_O^{oo}]_Y)}{(1-3[V_O^{oo}]_N - [V_O^{oo}]_Y)^3} \tag{10}$$

Eqs. (9) and (10) display an asymptotical behavior for $[V_O^{oo}]_N = 0.33$ and $3[V_O^{oo}]_N + [V_O^{oo}]_Y = 1$, where a Taylor expansion of γ may be applied. The exact physical significance of γ and its relation to the vacancy formation phenomena accompanying the preparation of nitrogen-containing zirconia needs additional measurements and will be clarified in a subsequent contribution. For low nitrogen contents the term $(1 - 3[V_O^{oo}]_N)$ can be neglected.

The nitridation of ZrO_2 doped with divalent ions like Ca^{2+}, Mg^{2+} or divalent rare earth ions also can be described with Eqs. (6), (7) and (9), but $[V_O^{oo}]_Y$ must be replaced by $[V_O^{oo}]_{Ca}$, the concentration of oxygen vacancies created by calcia incorporation.

Fig. 1 displays the calculated nitrogen pressure versus the concentration of oxygen vacancies. The positions of the different curves depend on the values of K and P_{O_2} which are a function of the experimental conditions like temperature, nitrogen pressure and oxygen pressure. All curves are calculated with a constant $K = 8 \times 10^{-25}$ and $P_{O_2} = 8 \times 10^{-15}$ bar, and are compared to an ideal Henryan or Sievertian behavior.

Fig. 2 presents a comparison between the theoretical calculated nitridation behavior and some experimental data for different ceramic materials where the $[V_O^{oo}]_N$ values have been determined using hot-gas extraction analysis [2–7]. It should be remarked that the calculated p versus $[V_O^{oo}]_N$ curves are in good agreement to our previous experimental data. For example, we obtained an experimental value $K = 8.08 \times 10^{-25}$ for the nitridation of pure zirconia between 1 and 6 bar nitrogen pressure. The nitridation behavior cannot be reproduced by Henry's or Sievert's law.

At this time, experiments investigating the pressure dependence of nitrogen incorporation into zirconia have only carried out for undoped zirconia [4]. Nevertheless, many nitridations are performed at a nitrogen pressure of 1 or 1.5 bar, which do agree with the model for cation-doped zirconia proposed in this work [1–4]. Extended investigations at various nitrogen pressures may help to understand the nitrogen incorporation into zirconia in more detail.

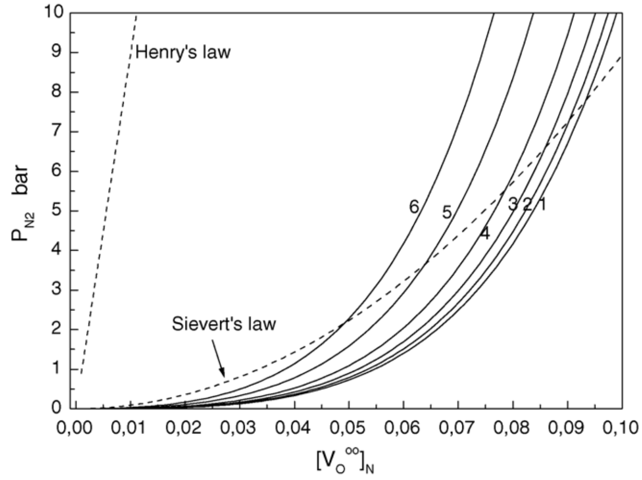

Fig. 1. Calculated nitridation behavior of pure and cation-doped zirconia, $K = 8 \times 10^{-25}$ and $P_{O_2} = 8 \times 10^{-15}$ bar. The concentrations (anion fractions) of anion vacancies created by cation doping $[V_O^{oo}]_{cat}$ of the samples are 1-0, 2-0.01, 3-0.025, 4-0.05, 5-0.1 and 6-0.15, respectively. The calculated curves are compared to an ideal Henryan or Sievertian behavior ($\gamma = 1$) with $K = 8 \times 10^{-25}$ and $P_{O_2} = 8 \times 10^{-15}$ bar (dashed lines).

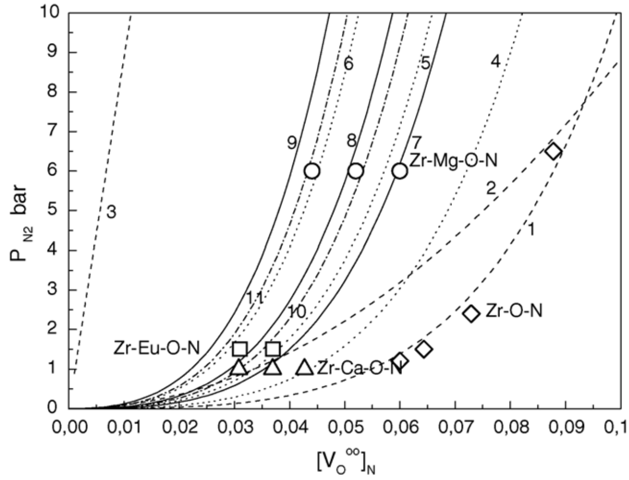

Fig. 2. Comparison between theoretical (lines) and experimental obtained (symbols) p vs. $[V_O^{oo}]_N$ data for some zirconia ceramics. (1) Zr–O–N, $P_{O_2} = 8 \times 10^{-15}$ bar; (2 and 3) Sievert's and Henry's law for Zr–O–N, dashed lines and diamonds; (4, 5 and 6) Zr–Ca–O–N, $P_{O_2} = 4.5 \times 10^{-15}$ bar, $P_{N_2} = 1.0$ bar, dotted lines and triangles; (7, 8 and 9) Zr–Mg–O–N, $P_{O_2} = 5 \times 10^{-15}$ bar, $P_{N_2} = 6$ bar, solid lines and circles; (10 and 11) Zr–Eu–O–N, $P_{O_2} = 4.5 \times 10^{-15}$ bar, dot-dashed line and squares, $P_{N_2} = 1.5$ bar.

From a physicochemical point of view, the equilibrium condition for gas solubility is $\mu_{N_2}^{(g)} = \mu_{N_2}^{(s)}$ where $\mu_{N_2}^{(g)}$ and $\mu_{N_2}^{(s)}$ are the chemical potentials of nitrogen in the gas and the solid phase. For the case of nitrogen incorporation into zirconia the equilibrium condition is $\Delta\mu_{react} = 0$, where $\Delta\mu_{react}$ is the change of the chemical potential of Reaction (1). Furthermore, the ideal gas approximation for nitrogen is used.

Some factors, however, must be taken into account by calculating the nitrogen incorporation at different pressures. It is known that the solubility of nitrogen in pure zirconia has a limit of about 4 wt% at 2050 °C. At 1 bar nitrogen pressure, a limit of ~2 wt% has been observed [4]. High nitrogen pressure (>4 bar) leads to the dominant formation of ZrN, but the solubility of nitrogen in zirconia has not yet been experimentally investigated in detail at other temperatures.

There are phenomena like formation of surface sites [7], secondary phases like ZrN, electronic defects (e.g., Zr^{3+}), and defect interactions which are not in the range of the proposed thermodynamic model. First experimental results (single crystal diffuse neutron-scattering experiments) concerning defect interaction in Y–Zr–O–N materials as a function of temperature have been published by Boysen et al. [16]. Theoretical calculations on defect interactions and electronic defects by Bredow [17] will be presented in the near future. All these results have to be taken into consideration for more improved models in the future.

Acknowledgement

S.G. thanks the Hertie Stiftung (Germany) for financial support.

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