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Terminal solid solubilities at 900–1000 ° C in the magnesium oxide–zinc oxide system measured using a magnesium fluoride solid-electrolyte galvanic cell

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Abstract

The terminal solid solubilities of the periclase (MgO-rich) and zincite (ZnO-rich) solid solutions in the MgO–ZnO system have been determined by measuring the activity of MgO using a solid-state galvanic cell of the type $O_2(g)$, Pt/MgO, $MgF_2//MgF_2//\{x\text{MgO}+(1-x)\text{ZnO}\}$(s, sln), MgF_2/Pt, $O_2(g)$ in the temperature range 900–1050 ° C. The ZnO activity was calculated by graphical Gibbs–Duhem integration. The activity–composition plots of both components exhibit a strong positive deviation from ideality and are characterised by a miscibility gap. The terminal solid solubilities of the periclase and zincite solid solutions obtained from the activity–composition plots are found to be in reasonable agreement with those reported in the literature.

INTRODUCTION

According to the phase diagram shown in Fig. 1 [1], the MgO–ZnO system is a eutectic type characterised by an extensive solid solubility of ZnO in the periclase phase (MgO-rich) and a restricted solubility of MgO in the zincite phase. Segnit and Holland [1], Rigamonti [2], Kondrashev and Omelchenko [3] and Sarver et al. [4] determined the solid solubility limits of these terminal solid solutions by the X-ray method. According to Segnit and Holland [1], the solid solubility of ZnO in MgO is 39 mol.% at 1600 ° C. This value is consistent with the result of Sarver et al. [4] who determined the solubility limits of ZnO in MgO and MgO in ZnO at 1300 ° C as 32 mol.% and 4 mol.%, respectively. These values for the solubility limit of ZnO in MgO are also consistent with the corresponding value of 35 mol.% at 1300 ° C given by Kondrashev and Omelchenko [3]. However, the value of 16 mol.% for the solid solubility of MgO in ZnO at 1300 ° C reported by Kondrashev and Omelchenko [3] is not in agreement with the phase diagram [1], nor with the corresponding value of 4 mol.% given by Sarver et al. [4].

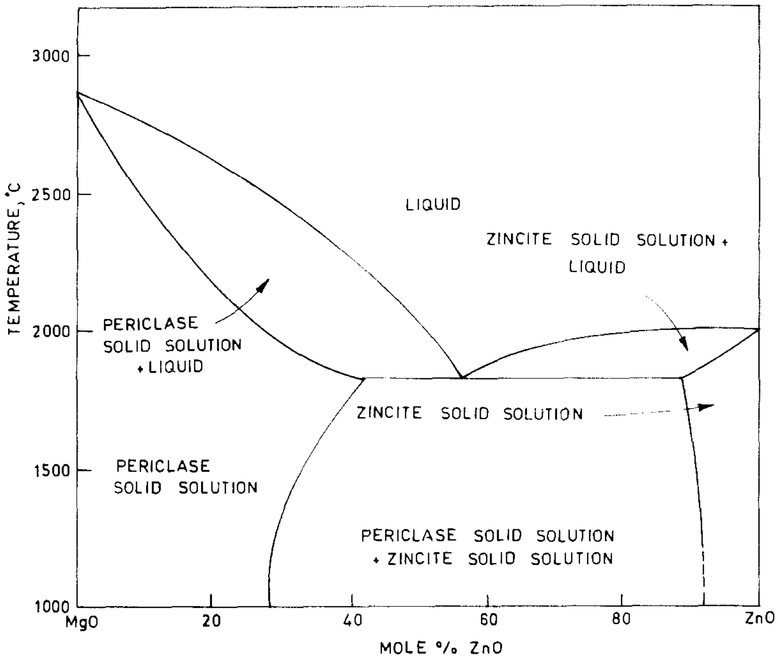

Fig. 1. Phase diagram of the system ZnO–MgO.

Kondrashev and Omelchenko [3] reported the solubility limits for ZnO in MgO and MgO in ZnO at 1100 °C as 26.5 mol.% and 12 mol.%, respectively. While the results of these authors on the MgO-rich side appear to be in fair agreement with the phase diagram, the agreement on the ZnO-rich side is not satisfactory. In addition, Rigamonti [2] determined the solubility limits of ZnO in MgO and MgO in ZnO at 900 °C as 33 mol.% and 5 mol.%, respectively. Apparently, the solubility limit of ZnO in MgO at 900 °C reported by Rigamonti [2] is not in agreement with the value of Kondrashev and Omelchenko [3] at 1100 °C, nor with that which can be derived by extrapolation of the solvus line in the phase diagram. However, on the ZnO-rich side, there appears to be reasonable agreement.

Kenny and Navrotsky [5] derived the activity–composition relations in the MgO–ZnO system from the direction of the conjugation lines between oxide and spinel phases in the ternary system ZnO–MgO–Al_2O_3 at 1205 °C in air, assuming that the spinel phase behaves ideally. These authors reported the solubility of ZnO in MgO and MgO in ZnO as 29 mol.% and 3 mol.%, respectively, at 1205 °C. Thus, the solubility results of Kenny and Navrotsky [5] are not in agreement with the phase diagram on the ZnO-rich side; but on the MgO-rich side, there appears to be good agreement. Moreover, there is reasonable agreement on the MgO-rich side between the results of Kenny and Navrotsky [5], Kondrashev and Omelchenko [3] and Sarver et al. [4].

Thus, on the MgO-rich side, with the exception of the work of Rigamonti [2], the solid solubility limits reported by the different authors [3–5] are in reasonable agreement with the phase diagram due to Segnit and Holland [1]. On the ZnO-rich side, the solubility limits reported are not in agreement with the phase diagram. Also, barring the work of Rigamonti [2], no information is currently available on the solid solubility limits of the periclase and zincite phases below 1100 ° C.

In the present work, an MgF_2 solid-electrolyte galvanic cell was employed to measure MgO activities and, hence, the terminal solid solubilities of periclase and zincite solid solutions in the temperature range 900–1000 ° C. The suitability and reliability of this technique for the determination of the thermodynamic properties of solid solutions and compounds involving MgO are well documented [6–8].

EXPERIMENTAL

Materials

Magnesium fluoride, for the solid electrolyte and electrode pellets, was synthesised according to the method of Taylor and Schmalzried [6]. The electrolyte was prepared by pressing the powder at 235 MPa in a cylindrical die. The green pellet was then sintered in an atmosphere of CO_2-free dry argon gas at 1050 ° C for 4 hours. The MgO–ZnO solid solutions of fixed compositions were synthesised from fine powders of dry reagent grade MgO and ZnO. These starting materials were mixed in the correct ratio under acetone. The oxide mixtures were pressed at 235 MPa and sintered in a stream of dry, CO_2-free oxygen gas at 1000 ° C for 24 hours, followed by quenching in air. The product was finely ground and sintered again at 1000 ° C for 24 hours. For compositions with more than 50 mol.% MgO, a third heat treatment at 1000 ° C for 24 hours was given. Samples with MgO mole fractions of 0.025, 0.05, 0.114, 0.3, 0.7, 0.75, 0.85 and 0.95 were prepared by the above procedure. Formation of true equilibrium phases was confirmed by the X-ray method. Control experiments on the sample with the highest ZnO content showed negligible loss in weight after sintering in a stream of oxygen at 1000 ° C for 24 hours. The sintered samples in this system were powdered, mixed with MgF_2 (about 10–15 wt.%), pressed and sintered at about 1000 ° C in a stream of dry CO_2-free oxygen.

Cell operation

EMF measurements were carried out using a modified form of the cell assembly employed by Vecher and Vecher [9]. EMF values were measured with a vernier potentiometer correct to ±0.2 mV. The performance of the polycrystalline MgF_2 solid electrolyte was checked by operating the cell

$$O_2(g), Pt/MgO, MgF_2//MgF_2//MgO \cdot 2TiO_2, TiO_2, MgF_2/Pt, O_2(g)$$

in the temperature range 900–1000 °C. The objective of these measurements was to check the suitability of MgF_2 as a solid electrolyte with $t(F^-)$ close to unity, for obtaining reliable thermodynamic results on metal oxide systems. Shah et al. [10] used the above cell to measure the Gibbs energies of formation of the various magnesium titanates. The EMFs obtained in the present work for the above cell agreed with those reported by Shah et al. [10]. The Gibbs energies of formation of $MgO \cdot 2TiO_2$ from the pure oxides calculated from the EMFs are in good agreement with the results of Elliott et al. [11] when the reported error limits are taken into account.

The cell employed in this investigation is of the type

$$O_2(g), Pt/MgO, MgF_2//MgF_2//[xMgO + (1-x)ZnO](s, sln),$$
$$MgF_2/Pt, O_2(g)$$

The EMF is due to the reaction

$$MgO(s) = MgO(s, sln) \tag{1}$$

where MgO(s, sln) represents MgO in the equilibrium phase assemblage at the temperature of interest. The reactions at the two electrodes can be represented as follows, in accordance with Benz and Wagner [12] for a similar cell: at the reference electrode where pure MgO is in contact with MgF_2 electrolyte

$$MgO(s) + 2F^- = MgF_2 + 1/2O_2(g) + 2e^- \tag{2}$$

and at the working electrode where $[xMgO + (1-x)ZnO](s, sln)$ is in contact with the MgF_2 electrolyte

$$MgF_2 + 1/2O_2(g) + 2e^- = MgO(s, sln) + 2F^- \tag{3}$$

Therefore the measured EMF E is related to the activity of MgO, $a(MgO)$, in the equilibrium phase assemblage according to the expression

$$-2EF = RT \ln a(MgO) \tag{4}$$

where F is Faraday's constant. These cell reactions indicate clearly that oxygen is necessary for the operation of the cell. If the same oxygen pressure prevails at both electrodes, the overall reaction is as given by eqn. (1). An atmosphere of CO_2-free dry oxygen was provided throughout the working period of the cell.

The in situ temperature of the cell was measured with a Pt–PtRh(13%Rh) thermocouple in contact with the reference electrode of the cells. The temperature of the furnace was controlled by another thermocouple to within ±3 K. The reversible EMF of the cell was measured as a function of

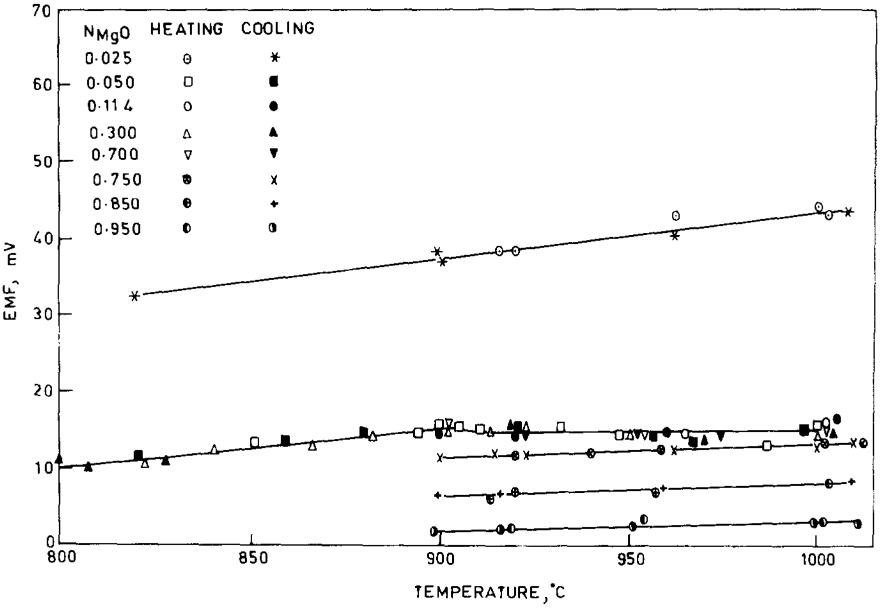

Fig. 2. EMF vs. temperature for the system ZnO–MgO.

temperature during both heating and cooling. The EMFs were reproducible on temperature cycling. The cell attained equilibrium at 1000 ° C within 2 h in most cases. For compositions with less than 50 mol.% MgO, EMF measurements could be extended down to 800 ° C. The times of equilibration varied from 2 to 4 h depending on the temperature. Although the cell EMF could be maintained for long hours at any temperature, in general a temperature change was made when the cell EMF had remained constant within ±0.5 mV for at least 2 h, at any temperature between 800 and 1050 ° C. The reproducibility of the cell EMF was about ±1 mV.

RESULTS

EMF versus temperature plots for all the compositions are shown in Fig. 2; it can be seen that the EMFs for compositions in the range 5–70 mol.% MgO lie within a band fixed by ±1 mV in the temperature range 800–1050 ° C. The EMF versus temperature relations for the compositions 2.5, 75, 85, and 95 mol.%MgO were found to be approximately linear in the temperature range studied. There is an uncertainty of ±3 ° C in the temperature measurements but this is not likely to introduce any serious error in the activity data as the variation of EMF with temperature was quite small, less than 10 mV for 100 ° C for most of the compositions. The ±1 mV deviation in the EMF measurements would lead to an error of 193 J mol^{-1} in the chemical potential of the metal oxide. This deviation gives an uncertainty of

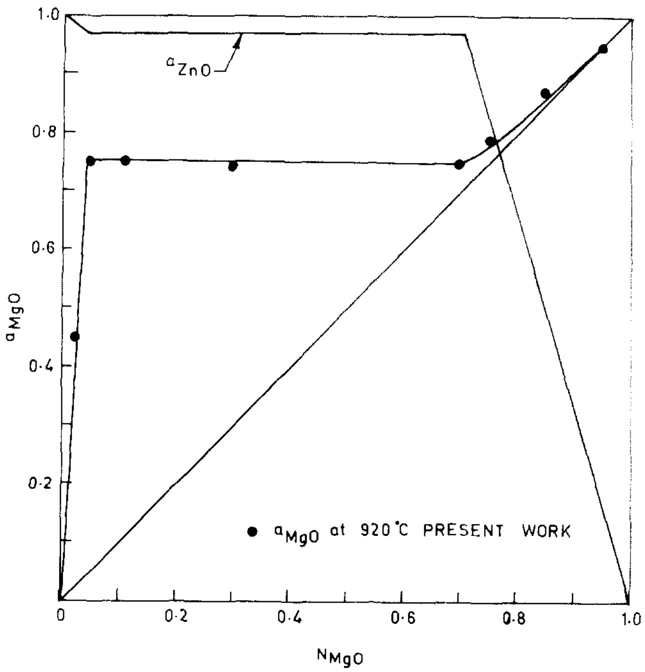

Fig. 3. Activities at 920 °C in the system ZnO–MgO.

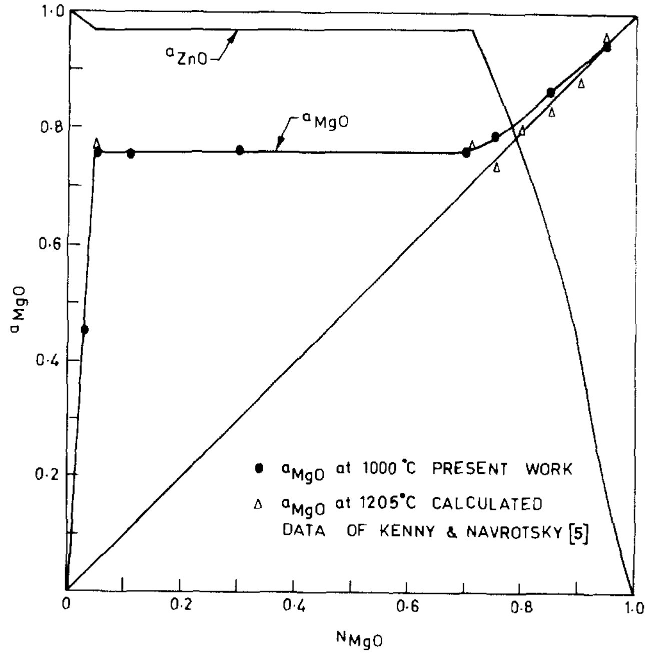

Fig. 4. Activities at 1000 °C in the system ZnO–MgO.

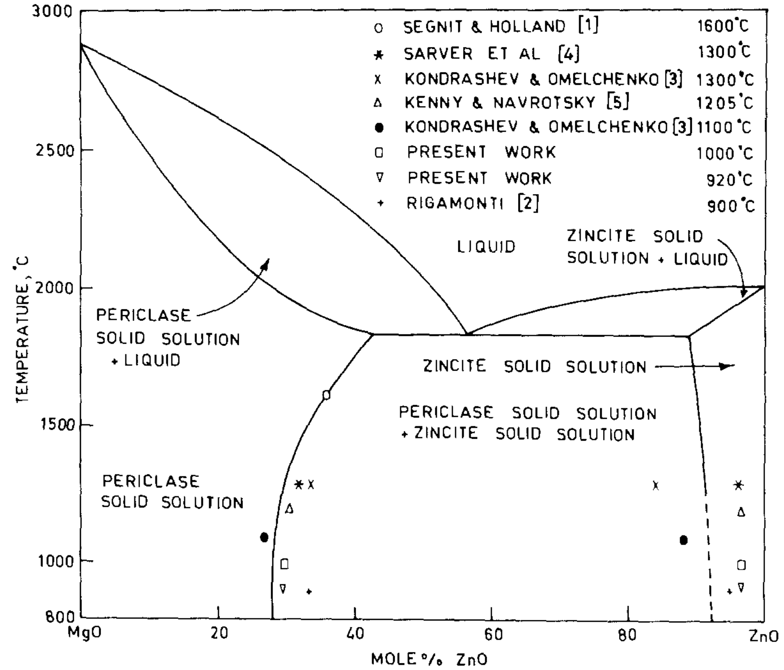

Fig. 5. Terminal solid solubilities in the system ZnO–MgO.

±0.01 for the activity at low-metal-oxide contents and ±0.019 at high-metal-oxide contents.

DISCUSSION

The activities of MgO for all compositions at 920 and 1000 °C are shown in Figs. 3 and 4. The ZnO activities were calculated from the MgO activities by the graphical Gibbs–Duhem integration. The activities of both components show a strong positive deviation from ideality characterised by a miscibility gap. The isoactivity region which extends over a wide range of composition is identified as a two-phase region from phase rule considerations. It can be seen from Figs. 3 and 4 that the two-phase region extends from 3.5 ± 1.1 to 71.0 ± 1.5 mol.% MgO and from 3.5 ± 1.1 to 70.5 ± 1.5 mol.% MgO at 920 and 1000 °C, respectively. This is further substantiated by X-ray analyses of samples quenched from 1000 and 920 °C. X-ray diffraction analysis of the samples containing 2.5 and 75 mol.% MgO confirmed that they were single-phase solid solutions, the former being hexagonal and the latter cubic; those of 5.0 and 70.0 mol.% MgO showed two phases of hexagonal (ZnO-rich) and cubic (MgO-rich) solid solutions. The results obtained in the present work have been superimposed on the phase diagram of Segnit and Holland [1] in Fig. 5. The other results reported in the literature are also shown for comparison.

The solid solubility limits of ZnO in MgO derived from the results of the present work at 1000 and 920 ° C appear to be in reasonable agreement with the phase diagram due to Segnit and Holland [1]. The present results on the solubility limit of MgO in ZnO are not in agreement with the extrapolated value derived from the phase diagram. The present results at 920 ° C appear to be in reasonable agreement with the values reported by Rigamonti [2] at 900 ° C. However, there is disagreement between the present work and the extrapolated values which can be obtained from the work of Kondrashev and Omelchenko [3] on the mutual solid solubilities of MgO and ZnO.

The results of Segnit and Holland [1] at 1600 ° C and of Sarver et al. [4] at 1300 ° C on the MgO-rich side, may be considered to be consistent with the lower temperature values obtained in the present work.

The present results are consistent with those at 1205 ° C reported by Kenny and Navrotsky [5], whose calculated activities of MgO at 1205 ° C are shown in Fig. 4. It can be seen that in the two-phase region the $a(\mathrm{MgO})$ values are in reasonable agreement with the present work while in the single phase (cubic) region, the $a(\mathrm{MgO})$ values of these authors show a slight negative deviation from ideality. Considering the lower temperature in the present work, the higher $a(\mathrm{MgO})$ values shown in Fig. 4 may be considered to be consistent with those of Kenny and Navrotsky [5].

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