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Solid solution studies in the MgO-LiAlO$_2$ system

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Experimental data in the MgO-LiAlO$_2$ system indicates that about 53 wt % LiAlO$_2$ can enter the MgO lattice in solid solution at 1600°C, an increase of 7.5 wt % over the solid solution phase at 1500°C. The data also indicates that the periclase lattice retains about 41% LiAlO$_2$ at temperatures lower than 1400°C. Data indicates that there is probably no solid solution of MgO in LiAlO$_2$. The proposed phase diagram for the MgO-LiAlO$_2$ system is presented with an estimated eutectic composition of 17 wt % MgO-83 wt % LiAlO$_2$ and a melting point of $\sim$ 1625°C.

1. Introduction

In the past it was shown that stable periclase solid solutions could be produced by adding Li$_2$O to MgO-chrome ore mixtures [1]. Previously Kordes [2], reported that LiFeO$_2$, and Kordes and Petzoldt [3] showed that LiCrO$_2$, could enter the periclase lattice to form solid solutions. Doman, Alper, and McNally [1] reported that the addition of Li$_2$O to MgO-Al$_2$O$_3$ compositions produced stable periclase solid solutions. Previous studies in the MgO-MgAl$_2$O$_4$ system [4] indicated that 18% Al$_2$O$_3$ could enter the periclase lattice in solid solution at 1995°C ± 15°C. However, upon heating at lower temperatures, the solid solutions were not stable and unmixing occurred in the form of small spinel spheres in the periclase. When adding Al$_2$O$_3$ in the form of the compound LiAlO$_2$, the maximum amount of alumina that can enter the periclase lattice increases to about 41%. These periclase solid solutions are more stable than those produced in the MgO-MgAl$_2$O$_4$ system. The present study defines the limits of solid solution of LiAlO$_2$ in MgO. A tentative phase equilibria diagram is proposed for the MgO-LiAlO$_2$ system based on the solid solution studies and data available from the literature.

2. Experimental procedures

Raw materials employed for this study are 99.0% or better in purity and are listed in Table I. Lithium aluminate spinel was prepared by reacting the correct amounts of Li$_2$CO$_3$ with the Al$_2$O$_3$. Chemical analyses and X-ray diffraction revealed that the LiAlO$_2$ structure was produced at the correct stoichiometry.

TABLE I Raw materials

Material	Supplier
Reagent Grade MgO	J. T. Baker Co
Alucer Al$_2$O$_3$	Compagnie General D'Electro Ceramique
Purified Powder Li$_2$CO$_3$	J. T. Baker Co

Mixtures of MgO and LiAlO$_2$ were heated by two methods; induction furnaces for temperatures above 1500°C, and platinum-wound tubular furnaces for temperatures at 1500°C and lower. For the specimens fired in the induction furnaces, an argon atmosphere was maintained by flowing 10 litres per min of argon over the specimen. This procedure has been described in a previous paper [5]. Temperature measurements in this furnace were obtained with an optical pyrometer, whereas the temperatures in the platinum tubular furnaces were measured with Pt/10 Rh thermocouples.

During the initial experiments, it was evident that with prolonged heating at ≥ 1500°C lithia was being lost by vaporization. To eliminate this problem, mixtures of MgO and LiAlO$_2$ were compacted in $\frac{1}{4}$ in. diameter platinum tubes, and the tubes were hermetically sealed by welding the ends. Because of the platinum tubes, the solid solution studies were limited to a maximum temperature of 1600°C. Experimental difficulty (vaporization of Li$_2$O) was encountered above

TABLE II Solid solution specimens

Wt %		Temperature (°C)	Hours	Phases	Unit cell (Å) MgO s.s.
MgO	$LiAlO_2$				
100.0	—	—	—	MgO	4.212[4]
89.7	10.3*	1500	15	MgO s.s.	4.191
79.8	20.2*	1500	15	MgO s.s.	4.165
64.0	32.0*	1500	15	MgO s.s.	4.141
58.4	41.6*	1500	15	MgO s.s.	4.118
53.6	46.4*	1500	15	MgO s.s., $LiAlO_2$	4.110
48.6	51.4*	1500	15	MgO s.s., $LiAlO_2$	4.110
40.0	60.0	1500	15	MgO s.s., $LiAlO_2$	4.108
40.0	60.0	1600	15	MgO s.s., $LiAlO_2$	4.092
40.0	60.0	1400	15	MgO s.s., $LiAlO_2$	4.119
40.0	60.0	1300	21	MgO s.s., $LiAlO_2$	4.119
40.0	60.0	1000	15	MgO s.s., $LiAlO_2$	4.120
40.0	60.0	800	16	MgO s.s., $LiAlO_2$	4.121

*Actual values from wet chemical analyses. Other listed values are batched compositions.

that temperature which prevented complete liquidus and solidus studies.

Unit-cell dimensions were calculated from high-angle diffraction peaks with a G.E. XRD-5 diffractometer. All of the compositions in this article are listed as percentages by wt.

3. Solid solution studies

Mixtures of MgO and $LiAlO_2$ were prepared in the proportions listed in Table II. After the powders were compacted and sealed in the platinum tubes, they were placed in the platinum-wound tubular furnaces at the temperatures listed in Table II. Following the heat-treatments for the designated times, the specimens were air-quenched.

The relationship of unit-cell dimensions, Table II, to the amount of $LiAlO_2$ in solid solution in the periclase lattice was established with various mixtures heated to 1500°C for 15 h. From the curve in Fig. 1, it is evident that the maximum amount of $LiAlO_2$ observed in solid solution at 1500°C is 45.5%. Specimens containing higher amounts of $LiAlO_2$ resulted in essentially equivalent unit-cell dimensions (~ 4.109Å) for the MgO solid solution phase and, in addition, contained the $LiAlO_2$ phase.

One specimen, 40% MgO-60% $LiAlO_2$, was heated in a sealed platinum container at 1600°C to determine whether the periclase could take even more $LiAlO_2$ into solid solution at higher temperatures. This point is also plotted in Fig. 1, and it indicates that about 53% $LiAlO_2$ can enter the periclase lattice in solid solution at 1600°C, an increase of 7.5% over the 1500°C solid solution phase. Because of the temperature limitations of the platinum containers and the rapid volatilization of Li_2O at higher temperatures in the furnace atmosphere, no attempt was made to study the solid solution phase above 1600°C.

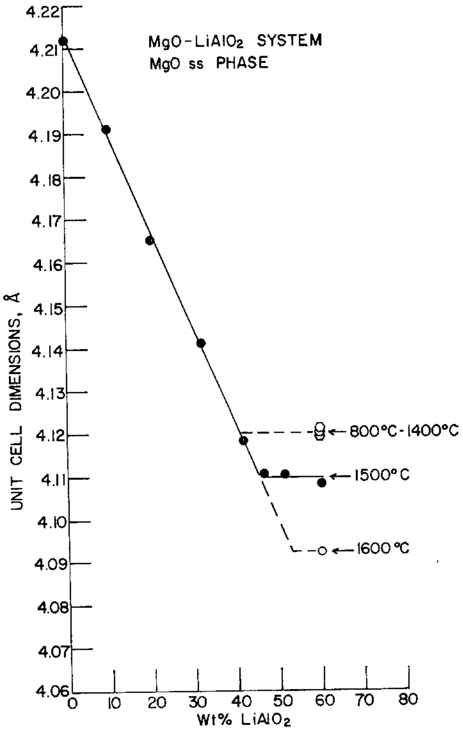

Figure 1 Unit cell dimensions of MgO-$LiAlO_2$ solid solutions.

Studies were also done at lower temperatures, 1400 to 800°C, to determine the stability of the periclase solid solution phase. For these studies a 40% MgO-60% $LiAlO_2$ mixture was first heated at 1500°C to produce the periclase solid solution phase. The specimens were then heated to lower temperatures listed in Table II. Unit-cell dimensions for those specimens were essentially equivalent, 4.120Å, and indicated that 41.0% $LiAlO_2$ remained in solid solution at temperatures ranging from 800 to 1400°C.

4. Proposed MgO-$LiAlO_2$ phase equilibria diagram

Attempts were made to define the liquidus of the MgO-$LiAlO_2$ system, but X-ray diffraction patterns obtained from the specimens fused in the induction furnaces indicated severe loss of Li_2O. Even though the melting temperatures were not valid, there was an indication that the eutectic is located in proximity to the 17% MgO-83% $LiAlO_2$ composition. Values for the melting points of MgO, 2825°C [5], and $LiAlO_2$, 1700°C [6], were obtained from the literature. Since no melting was observed in the specimen prepared at 1600°C for the solid solution study, and since the melting point of $LiAlO_2$ is reported at 1700°C, the eutectic melting point was estimated to be near 1625°C.

The subsolidus was defined for the periclase solid solution phase in the studies reported in the above section. Since the major effort was to define the limits of the $LiAlO_2$ solid solution in the periclase lattice, limited time was spent to determine whether MgO entered the $LiAlO_2$ lattice in solid solution. One specimen (90% $LiAlO_2$-10% MgO) was heated at 1500°C for 15 h and the X-ray diffraction pattern of the air-quenched specimen gave the same peak positions as those of the pure $LiAlO_2$. In addition the MgO solid solution phase was easily detectable in the diffraction pattern. Thus, this one experiment suggested that there is probably no solid solution of MgO in $LiAlO_2$.

The tentative phase diagram for the MgO-$LiAlO_2$ system presented in Fig. 2 was constructed from the solid solution data and the speculations made with the available information.

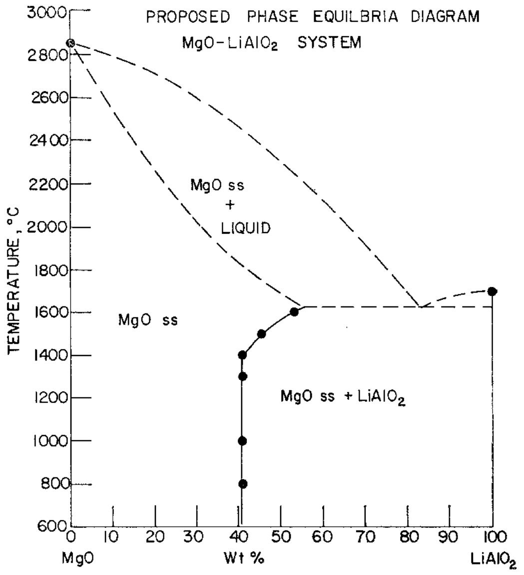

Figure 2

5. Summary

It has been shown that up to 53% of $LiAlO_2$ can enter the periclase lattice in solid solution. A tentative phase equilibria diagram was constructed, based on the solid solution studies and data available from the literature.

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