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Periclase Solid Solutions Containing Li^{+1} and R^{+3} Ions

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Recent work on phase equilibria diagrams has shown that periclase can take R^{+3} (Cr^{+3}, Al^{+3}, and Fe^{+3}) in solid solution at elevated temperatures. In order to retain electrical neutrality, $2R^{+3}$ and a vacancy replaces $3Mg^{+2}$ in the periclase lattices. When Li^{+1} is added to MgO/R_2O_3 compositions, one Li^{+1} and one R^{+3} replaces 2 Mg^{+2} to form a solid solution which is stable at room temperature. These periclase solid solutions are more stable under conditions of temperature fluctuations and hydration than periclase/R_2O_3 solid solutions without lithia.

1. Introduction

In the past few years it has been shown that periclase can take R^{+3} (Cr^{+3}, Al^{+3} and Fe^{+3}) [1] in solid solution at elevated temperatures. In 1964, Kordes and Petzoldt [2] pointed out that $LiCrO_2$ could enter the periclase lattice in solid solution. In an earlier publication, Kordes [3] showed that $Li_2Fe_2O_4$ could also enter the periclase lattice in solid solution.

In the present work, mixtures of 55% MgO: 45% Transvaal chrome ore* were melted with various additions of Li_2CO_3. Chrome ore was selected because of its use in basic refractories. Some work was also done with Li_2CO_3 additions to the MgO/Al_2O_3 and MgO/Cr_2O_3 systems.

2. Experimental Procedure

All melting of the specimens was done in MgO containers in an induction furnace under a nitrogen atmosphere. The procedures were similar to those listed in [1].

Varying proportions of Li_2CO_3 were added to 55% U-99 MgO: 45% TCO. Table I lists the various raw materials employed in this study. These compositions were mixed and ball-milled in preparation for pressing into specimens suitable for melting in crucibles.

Specimens were then prepared for examination of polished sections and X-ray diffractograms. Unit-cell dimensions were calculated from high-angle peaks collected from a GE XRD-5 diffractometer.

TABLE I Raw materials.

(1) Transvaal chrome ore (typical analysis)

11.8% MgO	43.8% Cr_2O_3
17.4% FeO	15.0% Al_2O_3
8.9% Fe_2O_3	3.2% SiO_2

(2) International U-99 MgO
0.65% Maximum impurities
(3) ALCOA A-2 Al_2O_3
0.5% Maximum impurities
(4) J. T. Baker Company CP Cr_2O_3
(5) J. T. Baker Company Purified Powder Li_2CO_3

3. Periclase Solid Solutions

Five per cent Li_2CO_3 (2.02% Li_2O), 10% Li_2CO_3 (4.04% Li_2O), and 20% Li_2CO_3 (8.09% Li_2O) were added to 55% MgO : 45% TCO batches. After fusion at approximately 2550° C, these bodies were found to retain 1.19, 2.40, and 4.48% Li_2O, respectively, indicating 42% average volatilisation of Li_2O. Marked changes were observed in the microstructures of these bodies with increasing Li_2O (fig. 1). Specimens prepared without the Li_2O additions contained periclase solid-solution crystals with a considerable amount of exsolved spinel blebs. Minor amounts of primary spinel, metal, and olivine were also detected.

As the Li_2O content increased, the amount of spinel decreased. At the 4.48% Li_2O level, no

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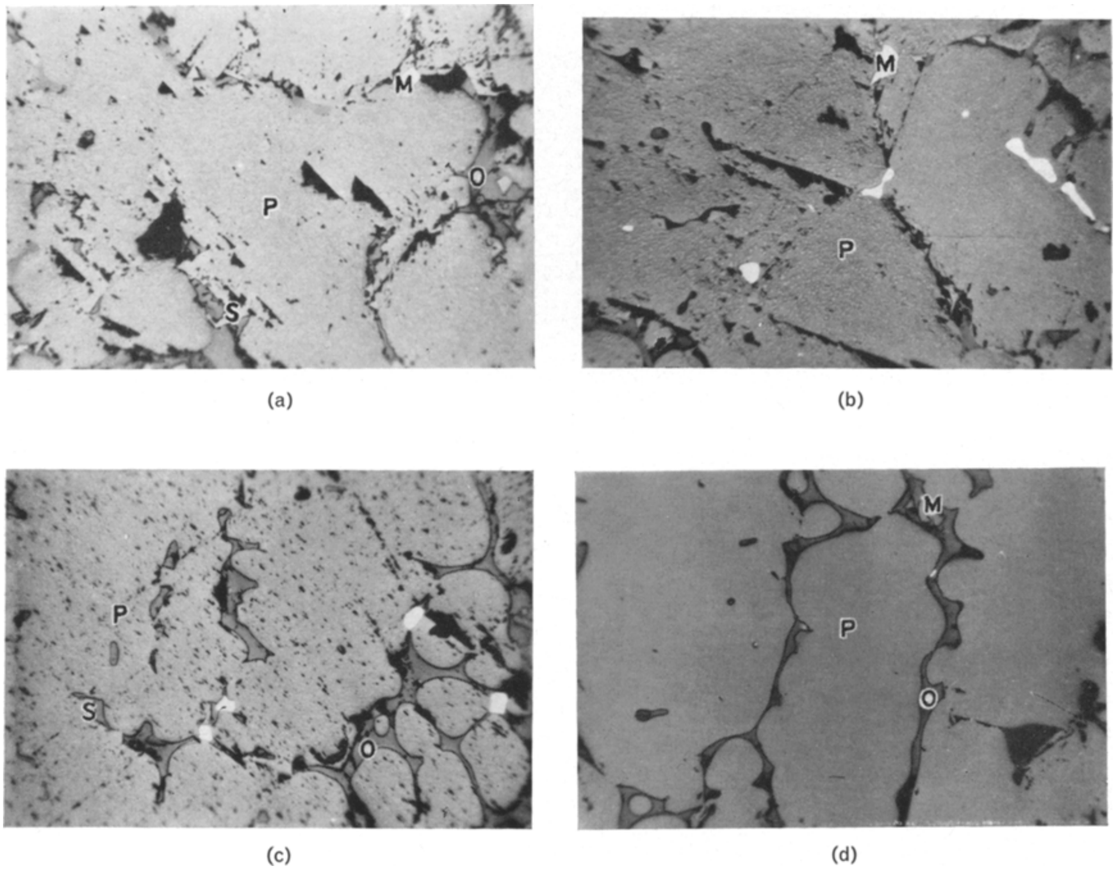
*Transvaal chrome ore will be abbreviated hereafter to TCO spinel could be detected. The photomicrograph of this melt in fig. 1 shows only the periclase solid-solution phase with minor amounts of olivine and metal. The periclase of this specimen contains Li^{+1}, Cr^{+3}, Al^{+3}, Fe^{+2}, and probably a minor amount of Fe^{+3} in solid solution. It is believed that a monophased periclase solid-solution body could be prepared if high-purity chrome ore was employed.

4. Crystallography

The periclase lattice has the same structure as the NaCl lattice (face-centred cubic). In this structure the Mg-ions are octahedrally co-ordinated by the surrounding oxygen-ions. The periclase solid-solution phase of the 55% MgO : 45% TCO specimen contains Fe^{+2} and probably some R^{+3} (Al^{+3}, Cr^{+3}, and Fe^{+3}). In these periclase solid solutions 3 Mg^{+2} are probably replaced by 2 R^{+3} and a vacancy in order to maintain a neutral charge. When lithium-ions are added to the periclase solid-solution phase, 1 R^{+3} and 1 Li^{+1} replace 2 Mg^{+2}; fewer vacancies should occur (see fig. 2).

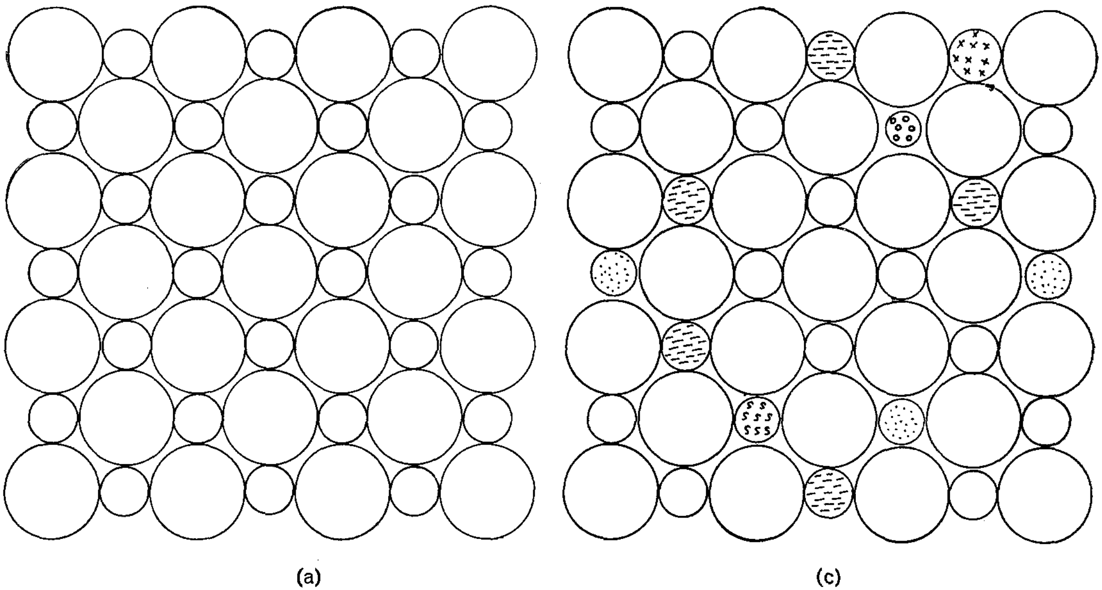
5. Unit Cell-Dimensions

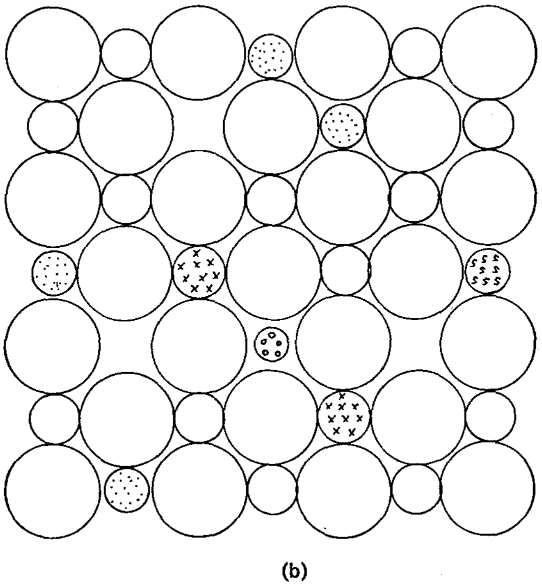
In addition to the petrographic observations, the changes in the amount of solid solution in the periclase lattice were also reflected by measurements of the refractive indices and unit-cell dimensions. The periclase solid-solution phase is quite complex. Even though a neutral atmosphere was employed (nitrogen), a slight amount of reduction was evident from the examination of the polished sections; that is, iron-rich metal was observed. The periclase solid-solution phase contains Li^{+1}, Fe^{+2}, Al^{+3}, Cr^{+3}, and possibly minor amounts of Fe^{+3}. Even without lithia, the



(a) (b) (c) (d)

Figure 1 Photomicrographs of (55% MgO : 45% TCO) with Li_2O additions. Periclase solid solution (P), spinel (S), metal (M), and olivine (O). (a) 0.0% Li_2O; (b) 1.19% Li_2O; (c) 2.40% Li_2O; (d) 4.48% Li_2O.





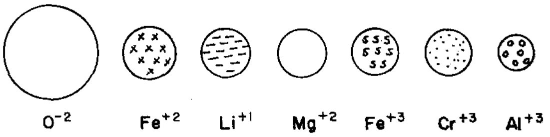


Figure 2 Schematic representation of (a) periclase lattice compared to (b) periclase solid-solution lattice and (c) lithium-containing periclase solid-solution lattice.

periclase phase formed by melting 55% MgO : 45% TCO contains Fe^{+2} in solid solution. A unit-cell dimension of 4.218 Å was measured on specimens without lithia; much higher than the unit-cell size of pure periclase, 4.212 Å.

Fig. 3 is a plot of unit-cell dimensions against the amount of Li_2O retained. A more realistic plot would have been the mole ratio of R_2O_3/Li_2O in the specimens, since the change in unit-cell size is related to the amounts of Li_2O and various R_2O_3 cations. Because complete chemical analyses are not available, the data had to be plotted against the percentage of Li_2O retained. However, the plot is considered reliable because of the close relationship of R_2O_3 to Li_2O in solid solution in the periclase lattice.

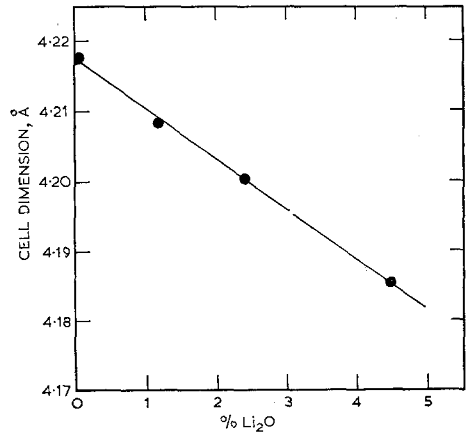


Figure 3 Unit-cell dimension of periclase solid-solution phase plotted against % Li_2O retained.

TABLE II Ionic radii of cations in periclase solid-solution phase.

(1) Mg^{+2} 0.66 Å	(4) Cr^{+3} 0.63 Å
(2) Fe^{+2} 0.74 Å	(5) Al^{+3} 0.51 Å
(3) Fe^{+3} 0.64 Å	(6) Li^{+1} 0.68 Å

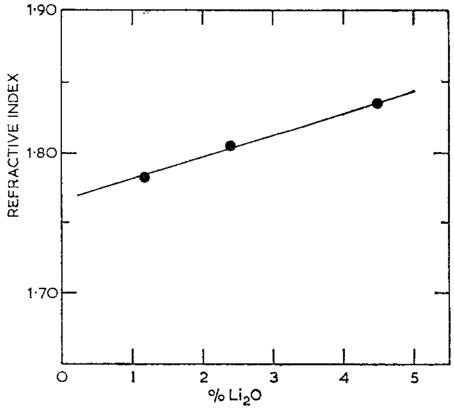


Figure 4 Refractive indices of the periclase solid-solution phase plotted against % Li_2O retained.

In table II it can be seen that Cr^{+3}, Fe^{+3}, and Al^{+3} are smaller than the magnesium ion. Thus, the decrease in unit-cell dimension is related to these smaller cations, mainly Cr^{+3} and Al^{+3}, in the periclase solid-solution lattice.

A few experiments were also done on the $MgO/Al_2O_3/Li_2O$ and $MgO/Cr_2O_3/Li_2O$ systems. Small amounts of Li_2O were added to the 55% MgO : 45% Al_2O_3 composition, and the unit-cell dimensions of the periclase solid-solution phase decreased to 4.171 Å when approximately 1% Li_2O* was retained. A composition of 46.94% MgO/44.31% Cr_2O_3/8.75% Li_2O (estimated 5% Li_2O retained) was also melted, and the unit-cell dimension of 4.161 Å was obtained, much lower than pure periclase.

It should be pointed out that it was not necessary to quench the specimens containing lithium-ions in order to retain the periclase solid-solution phase. On the other hand, to obtain periclase solid-solution phases without lithia, it is necessary to quench the specimens rapidly from eutectic temperatures to room temperature [1]. In other words, the lithium-containing periclase solid-solution phase is stable even when the melt is slowly cooled (~ 19° C/min) to room temperature.

6. Refractive Indices

Refractive index values were determined for the periclase solid-solution phases containing Li_2O, and they were found to increase with increasing amounts of solid solution in the periclase lattice (fig. 4). This increase is probably due to the iron- and chromium-ions in the periclase lattice.

7. Phase Stability

Specimens with dimensions of $1\frac{1}{2} \times \frac{1}{2} \times \frac{1}{4}$ in. (1.0 in. = 2.5 cm) were heated in an air atmosphere to 1250° C, and then thermally cycled between 1250 and 1650° C for twelve cycles at the rate of two cycles per day. The dimensions of the specimens were measured before and after the test to determine per cent linear growth. The per cent linear growth decreased from 1.55, when no Li_2O was present in the 55% MgO : 45% TCO composition, to no measurable growth when 4.48% Li_2O was retained with the same MgO : TCO ratio (fig. 5).

Another test of thermal stability consisted of heating the samples at 1400° C in a Globar furnace for three days and comparing the X-ray diffraction patterns. It was suspected that the Li_2O could prevent the spinel from unmixing during the heat-treatments. As evidenced from the X-ray diffractograms (fig. 6), there was some unmixing of spinel from all of the 55% MgO : 45% TCO samples. It can be seen that the intensities of the spinel peaks of the heated specimens decreased with increasing Li_2O. An $MgO/Cr_2O_3/Li_2O$ specimen was also examined in the same test. It can be noticed in fig. 6 that no spinel was detected in the X-ray diffractogram after heat-treatment. The lithium prevents much of the R^{+3} ions from unmixing and re-entering the periclase lattice during thermal cycling. It is believed that much of the spinel which exsolved in the 55% MgO : 45% TCO samples containing Li_2O is due to the oxidation of FeO in the periclase lattice and subsequent formation of $MgFe_2O_4$. There is a possibility that vaporisation of Li_2O will occur if longer hold times or higher temperatures are employed and more spinel exsolution may occur.

8. Hydration Resistance

A very interesting result of the Li_2O addition to the 55% MgO : 45% TCO composition was the increase in hydration resistance. Atlas [4]

*Spectrographically analysed

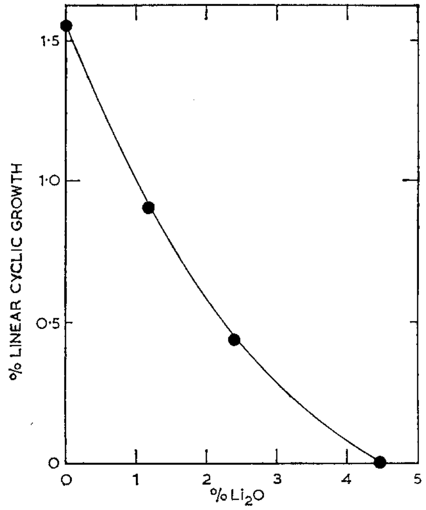


Figure 5 Percentage linear cyclic growth versus % Li_2O retained in the 55% MgO : 45% TCO specimen.

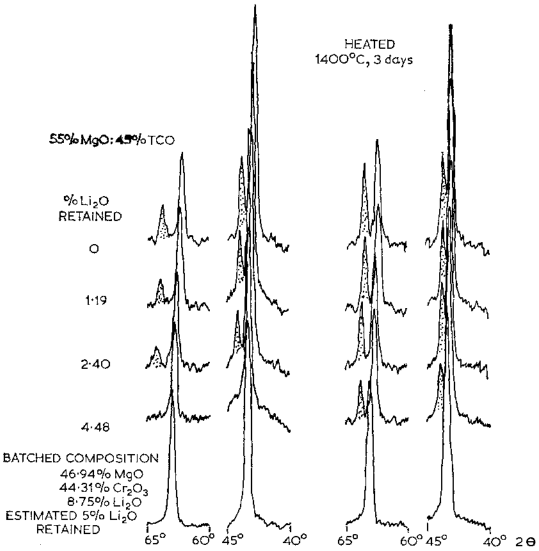


Figure 6 Portions of X-ray diffraction patterns before and after heat-treatment.

reported increased hydration resistance when minor additions of lithium compounds were made to magnesia for densification purposes. Although he reported that minor additions of lithium ferrite, lithium chromate, and lithium aluminate could be used for the densification of MgO, it was pointed out that superior results were obtained using lithium compounds which do not contain any other metallic atoms or ions, or lithium compounds which are lithium salts of non-metallic anions. No relation was reported for the addition of Li_2O and R_2O_3 for the increased hydration resistance of magnesium oxide.

Several tests were employed to determine the rate of hydration of the specimens. One-inch cubes were immersed in boiling water, and the time required for disintegration was recorded. The 55% MgO : 45% TCO cubes without Li_2O disintegrated within 3 to 6 h. The bodies with Li_2O additions were boiled for 400 h and no complete failures were recorded. One cube with 1.19% Li_2O (retained) cracked after 217 h in boiling water, but it did not disintegrate with continued boiling.

In a second test, polished sections of the same materials were immersed in water and checked periodically for hydration. The bodies without Li_2O hydrated quite rapidly (fig. 7). A noticeable change could be seen in the polished sections after soaking for only 16 h, and a drastic change took place after being immersed 5 days in water. It was also observed that the lithium-containing periclase solid-solution bodies were much more resistant to hydration than fused MgO. When lithium-ions were added to the 55% MgO : 45% TCO materials, only a slight discoloration could be detected in the specimen which retained 1.19% Li_2O. The polished sections of the periclase solid-solution phases containing 2.40% Li_2O and 4.48% Li_2O showed no change after soaking in water for 5 days. Thus, both tests indicated that, even with small additions of Li_2O, 1.19% Li_2O retained, the hydration resistance was significantly improved.

Two possible explanations for the increase in hydration resistance of the specimens containing Li_2O are: (i) the addition of lithium ions enables more R^{+3} ions to enter the periclase lattice in solid solution, thereby forming a more chemically resistant phase; or (ii) the periclase lattice without lithium ions is under much strain due to the combined R^{+3} solid solution and the vacant octahedral sites. With the addition of lithium-ions, one Li^{+1} and one R^{+3} replaces the 2 Mg^{+2}, and fewer vacancies should occur. Therefore, the residual strain on the lattice may be much lower. The lower strain on the periclase lattice may eliminate the strain factor in crystals which Davies *et al* [5] shows is necessary for the hydration of MgO compacts.

9. Summary

It has been shown that compositions of 55% MgO : 45% TCO with Li_2O additions can form

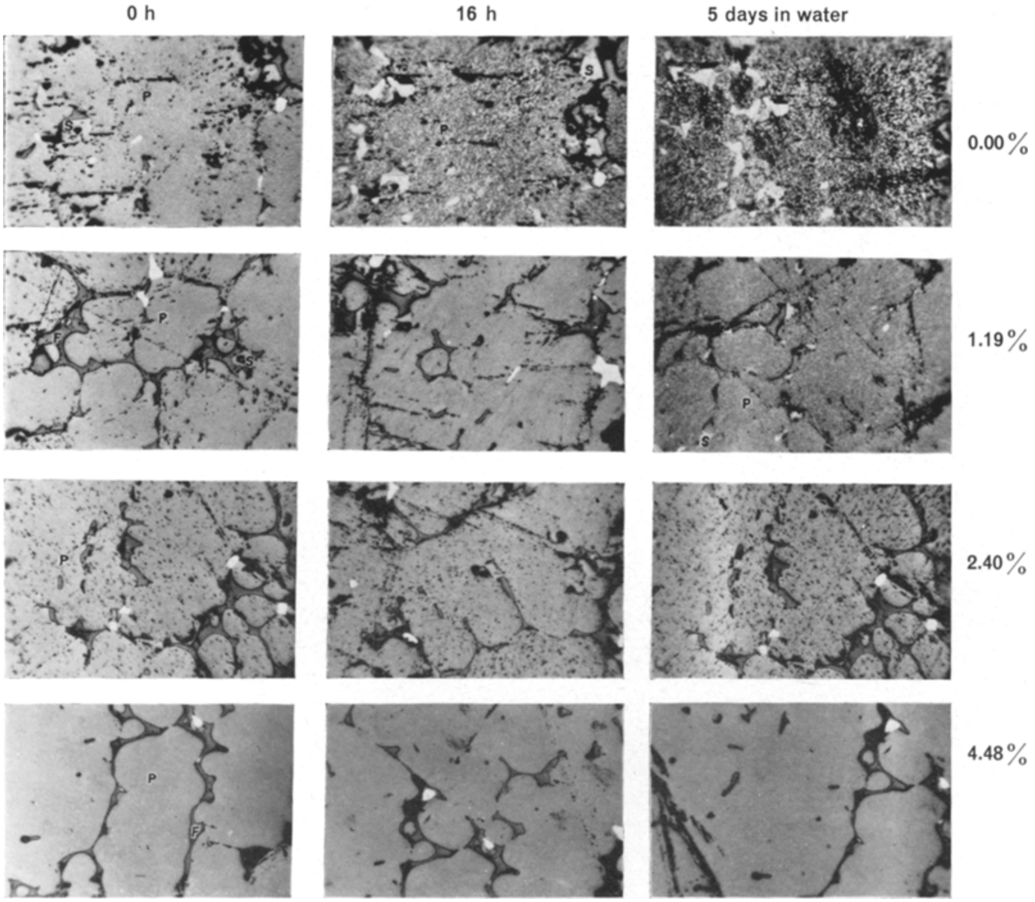


Figure 7 Photomicrographs of 55% MgO : 45% TCO polished sections with varying per cent of retained Li_2O which were immersed in water. Compare Li_2O containing specimens with the sample without Li_2O.

periclase solid solutions which are stable at room temperature.

In addition, solid-solution phases were prepared for $MgO/Cr_2O_3/Li_2O$ compositions, and initial data were collected to show $MgO/Al_2O_3/Li_2O$ solid solutions can be formed which are stable at room temperature.

The periclase solid-solution materials containing lithium are more stable than bodies without lithium when thermally cycled between 1250 to 1650° C or heated at 1400° C for 3 days.

The hydration resistance of the 55% MgO : 45% TCO bodies was increased when lithium-ions were retained in the periclase solid-solution lattice. Additional information on stabilised periclase solid solutions can be found in a recent US Patent [6].

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