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SOLUBILITY LIMITS IN THE MgO-Fe₂O₃ SYSTEM
AS DETERMINED BY DIFFUSION

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Diffusion studies on the MgO-Fe₂O₃ couple provided information on the solubility limits in air. Of particular interest is the solubility of iron oxide in MgO.

A diffusion profile for Fe obtained with an electron microprobe (no differentiation between different valences of the element) at 1300°C in air for 43 hours is shown in Fig. 1. The profile shows an atomic fraction of 0.063 Fe in MgO and 0.286 in magnesioferrite (subsequently referred to as ferrite) at the MgO-ferrite interface, and 0.354 Fe in ferrite and 0.400 in Fe₂O₃ at the ferrite-Fe₂O₃ interface (indicating no detectable solubility of MgO in Fe₂O₃). These are equilibrium compositions of total Fe as indicated by a number of anneals for different times at 1300°C.

The 1300°C isothermal section for the MgO-FeO-Fe₂O₃ system determined by Speidel is shown in Fig. 2. The diagram indicates the following

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At the time this work was done, the writers were, respectively, research assistant and professor of ceramic engineering, Department of Materials Science and Engineering, and Inorganic Materials Research Division, Lawrence Radiation Laboratory, University of California.

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equilibrium compositions in $10^{-0.68}$ atm oxygen (air) for ferrite:
in presence of magnesiofusite--20.0 w/o MgO, 0.2 w/o FeO, and 79.8 w/o
Fe$_2$O$_3$; in presence of Fe$_2$O$_3$--7.9 w/o MgO, 16.2 w/o FeO, and 75.9 w/o
Fe$_2$O$_3$. These compositions correspond to the following molar quantities:
0.994 MgO, 0.006 FeO, 1.000 Fe$_2$O$_3$ and 0.465 MgO, 0.535 FeO, 1.130 Fe$_2$O$_3$,
respectively. This indicates a stoichiometric spinel composition (with
a small amount of Mg$^{+2}$ replaced by Fe$^{+2}$) in equilibrium with MgO. The
spinel in the presence of excess Fe$_2$O$_3$, however, has more than half of
the Mg$^{+2}$ replaced by Fe$^{+2}$ and some Fe$_2$O$_3$ in solid solution. The cal-
culated atomic fraction of Fe, from these values, in the ferrite in
equilibrium with MgO is 0.287 and with Fe$_2$O$_3$, 0.365. The corresponding
values shown by the diffusion profile in Fig. 1 agree well. Consequently,
the diffusion studies have supported the results for 1300°C in air re­
ported by Speidel, Willshee and White, and within experimental limits
by Reijnen who showed a very small solubility of MgO in the spinel
phase, but not by Paladino.

It then can be assumed that the 0.063 atomic fraction of Fe in the
MgO at the ferrite interface, shown by the diffusion profile, is the
equilibrium solubility limit at 1300°C. The solubility in MgO was not
determined by Speidel, but Fig. 2 does indicate that approximately 0.2
w/o FeO would be present in the MgO under these conditions. Taking this
value and calculating the balance of the total Fe as Fe$_2$O$_3$ results in the
following composition for the MgO phase in equilibrium with ferrite:
77.2 w/o MgO, 0.2 w/o FeO, and 22.6 w/o Fe$_2$O$_3$, or 93.0 mole % MgO, 0.14
FeO, and 6.86 Fe$_2$O$_3$. This agrees well with the value of 21.8 w/o Fe$_2$O$_3$,
shown on the quasi-binary isobaric temperature-composition diagram for MgO-Fe₂O₃ reported by Phillips et al.⁶ Using our diffusion composition as a point on the 10⁻⁰.⁶⁸ isobar allows the estimation of a new boundary line indicating solubility limits in MgO at varying oxygen pressures, which is shown as the lower short-dash line in Fig. 2. The upper long-dash line appeared in Speidel's original figure.

The diffusion study also provided data for solubility limits of Fe in MgO of 0.070 atomic fraction at 1330°C, 0.086 at 1370°C, and 0.155 at 1460°C. The diffusion couples were analyzed only for diffusivities of total Fe;¹ information was not available to differentiate between relative amounts of ferrous and ferric iron.
REFERENCES


Fig. 1 Diffusion profile in the Fe$_2$O$_3$ system in air at 1300°C for 43 hours
Fig. 2 The 1300°C isothermal section for the MgO-FeO-Fe₂O₃ system, from Speidel,² with addition of lower short-dash line as discussed in text.
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