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SOLUBILITY LIMITS IN THE $MgO-Fe_2O_3$ SYSTEM AS DETERMINED BY DIFFUSION

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Diffusion studies on the $MgO-Fe_2O_3$ 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.[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 Fe_2O_3 at the ferrite-Fe_2O_3 interface (indicating no detectable solubility of MgO in Fe_2O_3). 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 $MgO-FeO-Fe_2O_3$ system determined by Speidel is shown in Fig. 2.[2] The diagram indicates the following

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equilibrium compositions in $10^{-0.68}$ atm oxygen (air) for ferrite: in presence of magnesiowüstite--20.0 w/o MgO, 0.2 w/o FeO, and 79.8 w/o Fe_2O_3; in presence of Fe_2O_3--7.9 w/o MgO, 16.2 w/o FeO, and 75.9 w/o Fe_2O_3. These compositions correspond to the following molar quantities: 0.994 MgO, 0.006 FeO, 1.000 Fe_2O_3 and 0.465 MgO, 0.535 FeO, 1.130 Fe_2O_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_2O_3, however, has more than half of the Mg^{+2} replaced by Fe^{+2} and some Fe_2O_3 in solid solution. The calculated atomic fraction of Fe, from these values, in the ferrite in equilibrium with MgO is 0.287 and with Fe_2O_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 reported by Speidel,[2] Willshee and White,[3] and within experimental limits by Reijnen[4] who showed a very small solubility of MgO in the spinel phase, but not by Paladino.[5]

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_2O_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_2O_3, or 93.0 mole % MgO, 0.14 FeO, and 6.86 Fe_2O_3. This agrees well with the value of 21.8 w/o Fe_2O_3

shown on the quasi-binary isobaric temperature-composition diagram for $MgO-Fe_2O_3$ 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.

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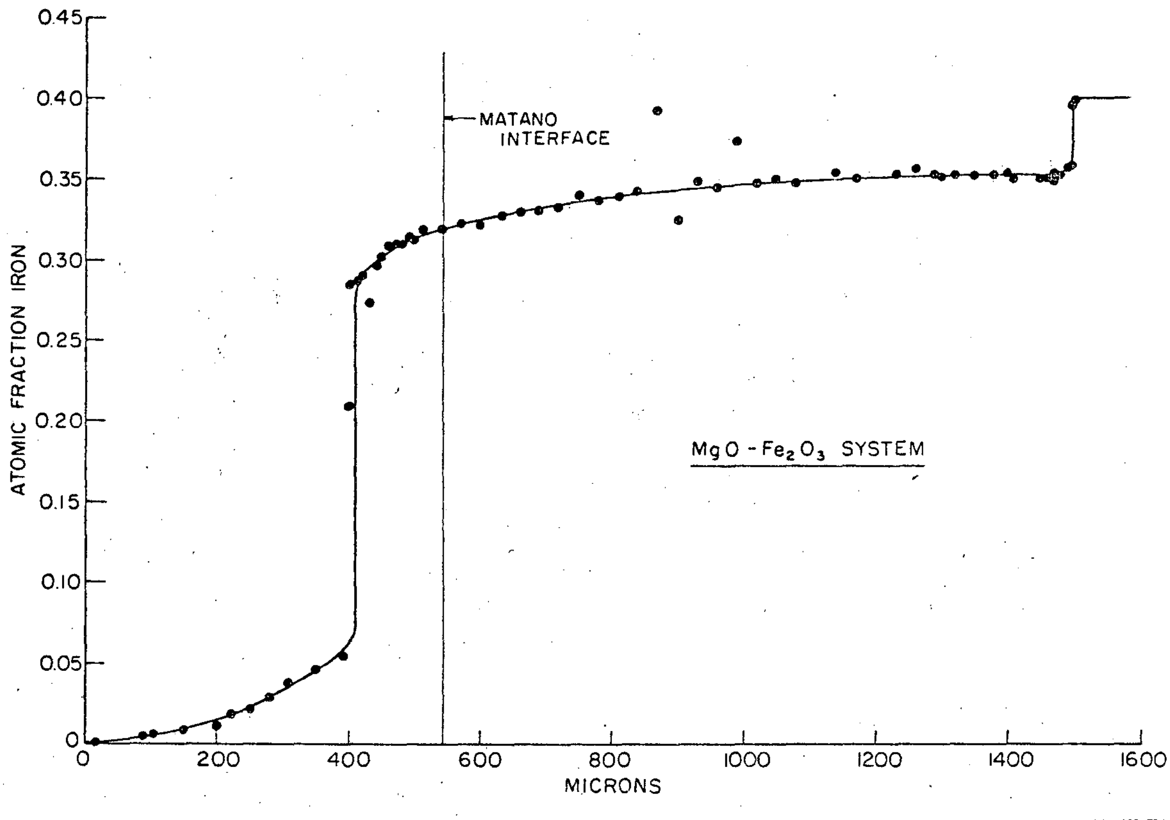

Fig. 1 Diffusion profile in the Fe_2O_3 system in air at 1300°C for 43 hours

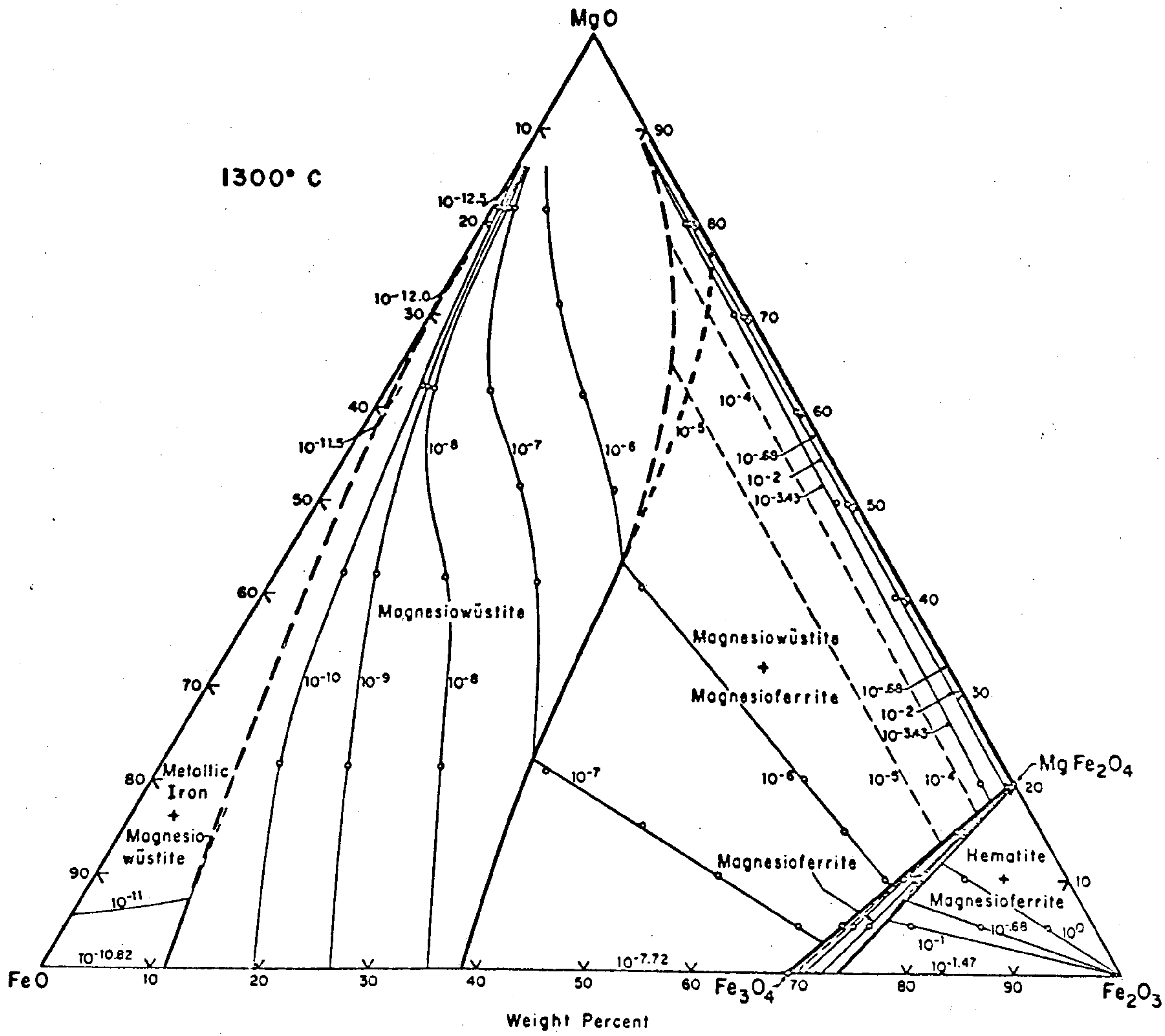

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Fig. 2 The 1300°C isothermal section for the MgO-FeO-Fe_2O_3 system, from Speidel,[2] with addition of lower short-dash line as discussed in text.

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