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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. 1.¹ 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. 2.² 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 Fe₂O₃; in presence of Fe₂O₃--7.9 w/o MgO, 16.2 w/o FeO, and 75.9 w/o Fe₂O₃. These compositions correspond to the following molar quantities: 0.994 MgO, 0.006 FeO, 1.000 Fe₂O₃ and 0.465 MgO, 0.535 FeO, 1.130 Fe₂O₃, 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 Fe₂O₃, however, has more than half of the Mg⁺² replaced by Fe⁺² and some Fe₂O₃ in solid solution. The calculated atomic fraction of Fe, from these values, in the ferrite in equilibrium with MgO is 0.287 and with Fe₂O₃, 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 Reijnen⁴ who showed a very small solubility of MgO in the spinel phase, but not by Paladino.⁵

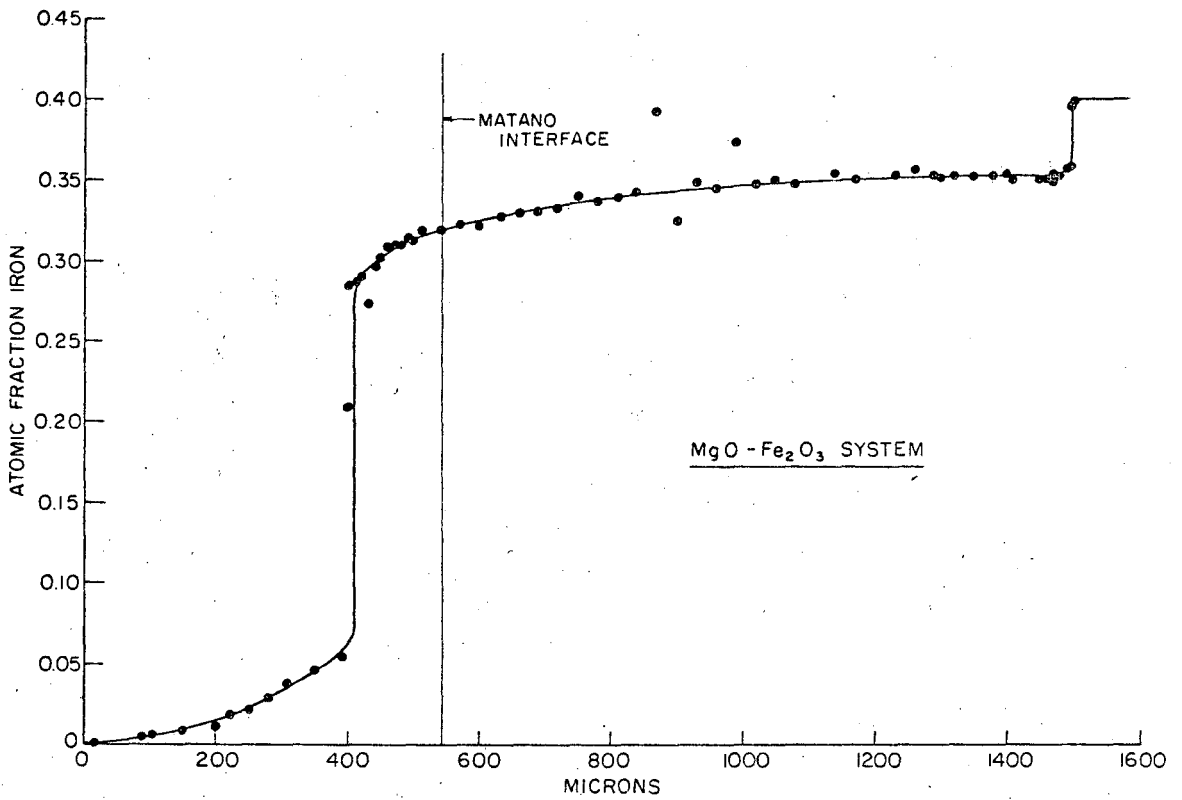
It then can be assumed that the 0.063 atomic fraction of Fe in the MgO at the ferrite interface, shown by the diffusion profile, is the equilibrium solubility limit at 1300°C. The solubility in MgO was not determined by Speidel, but Fig. 2 does indicate that approximately 0.2 w/o FeO would be present in the MgO under these conditions. Taking this value and calculating the balance of the total Fe as Fe₂O₃, 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 Fe₂O₃, or 93.0 mole % MgO, 0.14 FeO, and 6.86 Fe₂O₃. This agrees well with the value of 21.8 w/o Fe₂O₃

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.

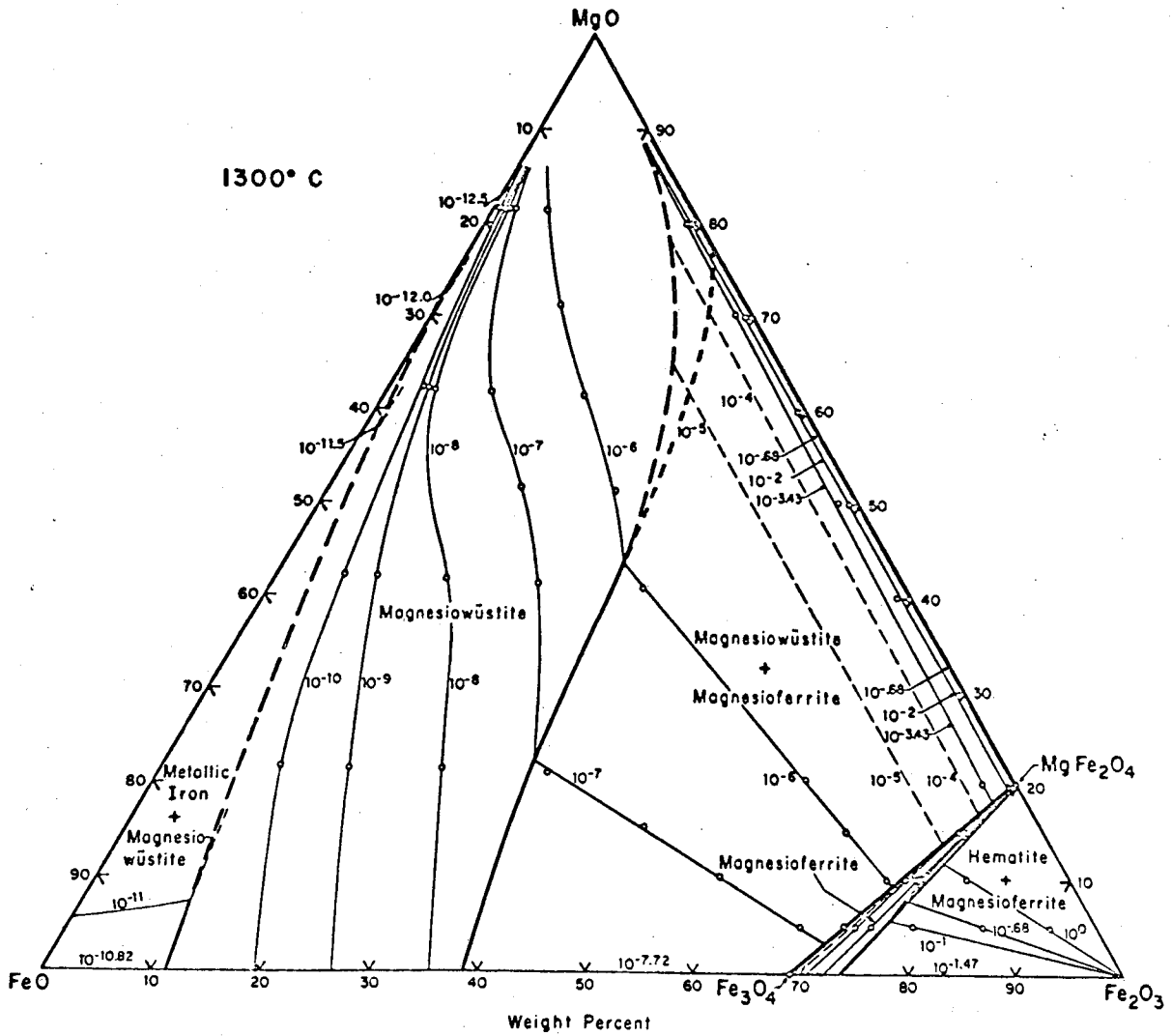
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XBL 685-753

Fig. 1 Diffusion profile in the Fe₂O₃ system in air at 1300°C for 43 hours



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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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