Phase Equilibria in the System Calcium Oxide-Manganese Zinc Ferrite

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determined by measuring the lattice constant of the ferrite. The ferrite has a spinel structure, and the lattice constant of the pure ferrite was determined to be 8.4812 Å with (731) and (553) lines using Fe-Kα_1, and Fe-Kα_2 radiations. The lattice constant of the series of spinel-the 3:1 compound, all equilibrated at 1277°C for 12 hr, was plotted against composition in Fig. 2. The horizontal line gives the maximum change in the lattice constant observed in a two-phase mixture, suggesting that solid solution of the 3:1 compound in spinel extends to approximately 12.2 mol% CaO at 1277°C.

The eutectic between the ferrite and the 3:1 compound was located at 1277°C with a composition containing 62.0 mol% CaO. This temperature was obtained by thermal analysis of samples containing 60.0, 62.0 and 64.0 mol% CaO. The photomicrograph for the composition containing 62.0 mol% CaO(Fig. 3) is essentially all eutectic and is the basis for positioning the eutectic at this composition. The liquidus line was determined by the quenching technique and thermal analysis below 1350°C as shown in Fig. 1. The solid solubility of the ferrite or CaO in the 3:1 compound was not observed both by x-ray diffraction and in microstructure.

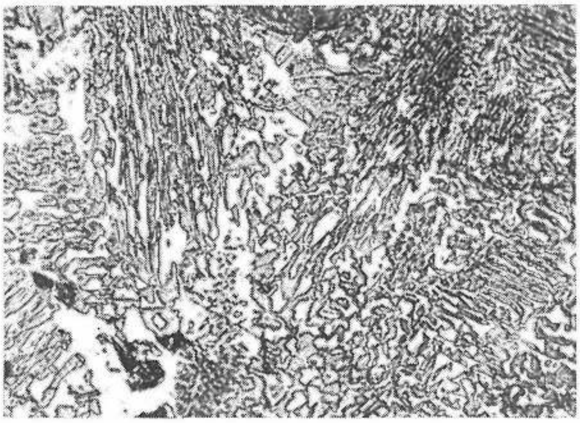

Fig. 3. Microstructure of sample of composition 62.0 mol% CaO (Etched ×400)

2. The 3:1 Compound

The 3:1 compound was determined to have the $2CaO\cdot Fe_2O_3$-type structure. The space group of $2CaO\cdot Fe_2O_3$ was classified as Pcmm (D_{2h}^{16}). Bertaut *et al*3) suggested that the iron ion should be found on two different sites in the crystal lattice of $2CaO\cdot Fe_2O_3$. One of the sites has a tetrahedron environment, the other an octahedron environment. The replacement of the iron ions on the two lattice sites by the manganese and zinc ions was analysed by x-ray diffraction and the Mössbauer technique. In $2CaO\cdot Fe_2O_3$ the replacement of the iron ions by the manganese ions caused a change in the lattice parameter. The formula for this system is $2CaO\cdot(Mn_2O_3)_x\cdot(Fe_2O_3)_{1-x}$. For $0<x<0.25$ homogeneous crystals could be obtained by calcination of mixture of $CaCO_3$, $MnCO_3$ and α-Fe_2O_3. The zinc ions could be observed not to replace the iron ions in $2CaO\cdot Fe_2O_3$ by x-ray diffraction examination; there existed three phases of CaO, ZnO and $2CaO\cdot Fe_2O_3$ in the composition of $2CaO\cdot xZnO\cdot(1-x/2)Fe_2O_3$ ($x=0.05\sim0.2$). However, the iron ions in $2CaO\cdot(Mn_2O_3)_{1/6}\cdot(Fe_2O_3)_{5/6}$ were replaced by the zinc ions when the zinc ions were less than the manganese ions.