

T H E U N I V E R S I T Y O F M I C H I G A N
COLLEGE OF ENGINEERING
Department of Chemical and Metallurgical Engineering
Ann Arbor, Michigan

Technical Report

MgO-MgFe₂O₄ MICROSTRUCTURES

by

Howard McCollister and Lawrence H. Van Vlack

ORA Project 05612

under contract with:

OFFICE NAVAL RESEARCH
ONR Contract No: Nonr-1224(47)

administered through:

OFFICE OF RESEARCH ADMINISTRATION

November 1964

MgO-MgFe₂O₄ MICROSTRUCTURES

by

Howard McCollister and Lawrence H. Van Vlack

Periclase (MgO) dissolves iron oxide into its structure at elevated temperatures and produces a solid solution called magnesiowüstite. This solid solution is commonly encountered in MgO-containing basic refractories when those refractories are used in contact with iron or iron oxide. Because the solubility limit of Fe₂O₃ in periclase decreases from approximately 70 weight per cent at 1700°C to about 10 weight per cent at 1200°C⁽¹⁾, a two-phase microstructure develops during cooling.⁽²⁾ This microstructure contains an intimate mixture of magnesioferrite (MgFe₂O₄) in a matrix of periclase.

The distribution of magnesioferrite in the periclase varies considerably: (1) sometimes it exists as a grain boundary network; (2) elsewhere it has a Widmanstätten pattern within the grains, or (3) it may be present as spheroidized particles within the periclase grains. It has been assumed that these three basic microstructures are the result of thermal histories; however, this nature of their development has never been verified. This brief report relates these microstructures to variations in heat treatment and suggests their origins.

PROCEDURE

Fine powders of reagent grade MgO and Fe₂O₃ were mixed dry, then with alcohol before pressing into 1/4-inch cylindrical pellets. An 18-hour solution treatment at temperatures equal to or greater than 1400°C was used to give a uniform distribution of the two components in the magnesiowüstite solid solution.

Subsequent to solution treatment the samples were either water-quenched or slow-cooled. This was followed by annealings at sub-solvus temperatures for times ranging from 0.5 to 27 hours.

Standard grinding, mounting, and polishing procedures

were used in the preparation of samples for reflected light microanalysis. Lattice dimensions were determined by established diffraction procedures.

RESULTS AND DISCUSSION

The results are presented as photomicrographs of selected samples (Figs. 1-9).

Phase relationships are consistent with the MgO-Fe₂O₃ diagram (Fig. 10). For example, a 60-40 MgO-Fe₂O₃ composition does not dissolve all of the Fe₂O₃ but leaves excess magnesioferrite (Fig. 1). In contrast, this same composition shows only one phase when quenched from 1600°C. All compositions which show only one phase when quenched reveal precipitated magnesioferrite when reheated to sub-solvus temperatures (Fig. 2).

The size of the parent magnesio-wüstite grains varied with the solution-treating temperature as shown in Figs. 3 and 4. The original grains are faintly outlined with a precipitate of magnesioferrite. At 1600°C the "diameter" of the magnesio-wüstite grains was about five times greater than for similar treatments at 1400°C.

The nature of the magnesioferrite precipitate varies with the annealing temperature as shown in Figs. 2 and 5. Although otherwise similar, the lower annealing temperature (1100°C) shows a fine Widmanstätten pattern of magnesioferrite within the former magnesio-wüstite grains and has negligible grain boundary precipitation (Fig. 2). When the precipitation occurs while annealing at 1200°C (Fig. 5), intergranular magnesioferrite appears and the intragranular magnesioferrite spheroidizes.

The magnesioferrite precipitate agglomerates with extended annealings. Figure 6 may be compared with Fig. 5 for a 1200°C anneal, and Fig. 7 may be compared with Fig. 2 for a 1100°C anneal. As expected, the agglomeration proceeded more rapidly at the higher temperature (Contrast Fig. 6 with Fig. 7). Magnesioferrite precipitates rapidly from the magnesio-wüstite solid solution. This is illustrated by different areas of the same 1/4-inch quench sample. The microstructure

in Fig. 1 was near the surface, and that in Fig. 8 was near the center. Incipient precipitation from the solid solution occurred in a matter of seconds. This rapid precipitation from solid solution is closely related to the crystal structures of the two phases. Each has the same fcc pattern of oxygen ions; as a result, the precipitation occurs simply by movement of smaller cations.

With slower cooling (33 minutes from 1400°C to 1100°C) a different microstructure is developed as shown in Fig. 9. Both the grain boundary and the Widmanstätten precipitate are coarser and better defined. Furthermore, there is a magnesioferrite-free zone around each of the former magnesiowüstite grains. This microstructure is best analyzed by concluding that the grain boundary precipitate was the first to form after the temperature was lowered below the solubility limit. The excess Fe_2O_3 from the adjacent grain diffused toward the boundary as cooling continued, thus depleting the rim of the grain of extra iron oxide. The center of the grain remained supersaturated with Fe_2O_3 , however, until a Widmanstätten precipitate was finally initiated. Of course this Widmanstätten structure could not grow into the outer zone of the grain which had lost Fe_2O_3 to the boundary. This slow-cooled sample had fewer but coarser Widmanstätten plates than a comparable quenched and annealed sample (Fig. 2), indicating that most of the precipitation occurred before 1100°C was reached.

The above microstructure (Fig. 9) shows that the Widmanstätten pattern was initiated within the grain rather than at the boundaries. A Widmanstätten structure implies a crystallographic correlation between the two phases. In these microstructures the maximum number of plate orientations ever observed with any single periclase grain was three. This is significant since the maximum number of plate orientations corresponds with the number of distinctly oriented planes within the form $\{hkl\}$. Since all cubic forms other than $\{100\}$ have more than three distinctly oriented planes, this strongly suggests that the magnesioferrite (MgFe_2O_4) precipitates along the $\{100\}$ planes of the periclase (MgO). If so, it is probably safe to conclude that the matching plane in the magnesioferrite spinel is also of the $\{100\}$ form since each phase has

the same fcc pattern of oxygen ions, differing only in the interstitial locations of part of the cations.

CONCLUSIONS

Magnesioferrite-periclase microstructures can be correlated to their thermal history. Grain boundary precipitation occurs at higher temperatures, whereas a Widmanstätten precipitation is favored at lower temperatures. Magnesioferrite which is cooled slowly through the solubility limit will first produce magnesioferrite at the grain boundary, followed by a Widmanstätten precipitate of magnesioferrite within the grains. Prolonged heat treatments at any temperature favor the spheroidization of the magnesioferrite within the periclase matrix.

ACKNOWLEDGEMENTS

This work was performed under a grant from the Office of Naval Research. Its support is gratefully acknowledged.

REFERENCES

1. Phillips, B., Somiya, S. and Muan, A., "Melting Relations of Magnesium Oxide - Iron Oxide Mixtures in Air," J. Amer. Ceram. Soc., Vol. 44, [4], pp. 167-169, (1961).
- 2a. Wells, R. G. and Van Vlack, L. H., "Mineral and Chemical Changes in Periclase Brick Under Conditions of Steel Plant Furnaces," J. Amer. Ceram. Soc., Vo. 34, [2], pp. 64-70, (1951).
- 2b. Trojer, F. and Konopicky, K., "Die Kristallisationsformen von Magnesiumferrit bei Ausscheidung aus dem festem Zustand," Radex Rundschau, [7/8], pp. 149-153, (1948).
- 2c. Homer, P. N. and Richardson, H. M., "The Reaction of Some Synthetic Spinel with Magnesia at High Temperatures," Trans. Brit. Ceram. Soc., Vol. 63, [8], pp. 389-415, (1964).

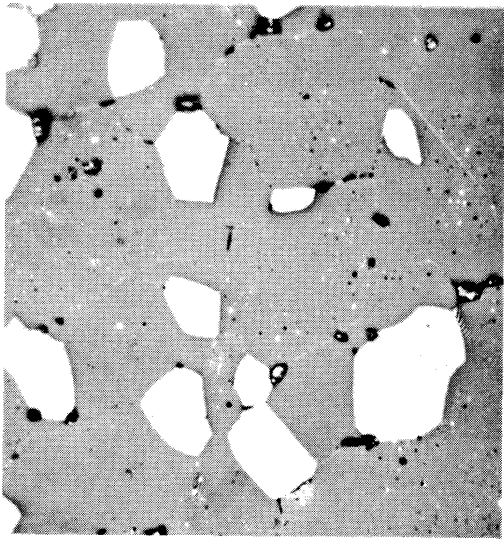


Fig. 1. MgO-Fe₂O₃ microstructure. Example: 60 MgO-40 Fe₂O₃ heated for 18 hours at 1400°C and quenched. The two-phase microstructure was retained. In all microstructures the bright phase is magnesioferrite (MgFe₂O₄), and the dark phase is an FeO-containing periclase. X 1000.

Fig. 2. MgO-Fe₂O₃ microstructure. Example: 70 MgO-30 Fe₂O₃ heated for 18 hours at 1600°C, quenched in water, reheated to 1100°C one hour. A Widmanstätten precipitate of magnesioferrite (bright) formed within the original single-phase magnesiowüstite. X 1000.

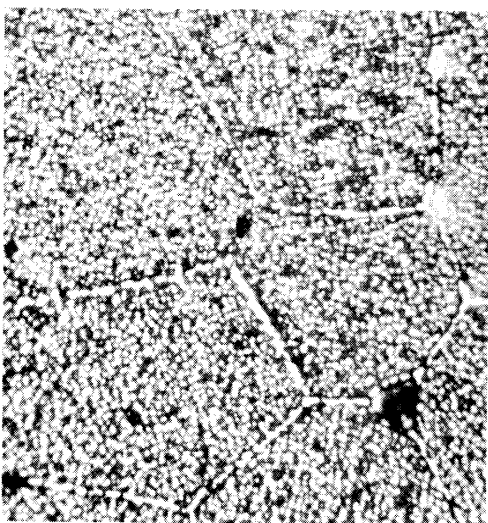


Fig. 3. MgO-Fe₂O₃ microstructure. Example: 80 MgO-20 Fe₂O₃ heated 18 hours at 1600°C, quenched in water, reheated to 1200°C one hour. Compare the initial magnesiowüstite grain size with Fig. 4. X 1000.

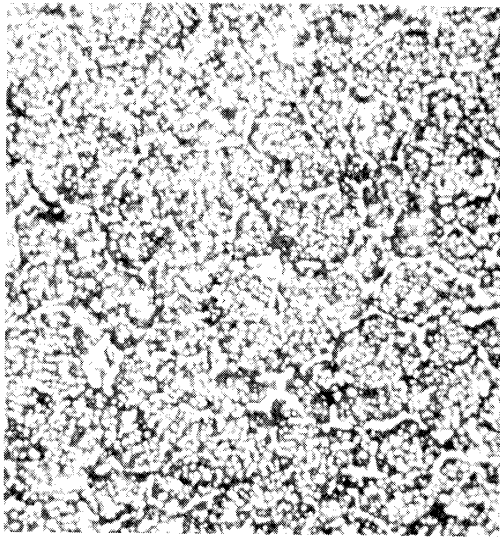


Fig. 4. MgO-Fe₂O₃ microstructure.
Example: 80 MgO-20 Fe₂O₃ heated for 18 hours at 1400°C, quenched in water, reheated to 1200°C for one hour. There was less growth of the initial magnesio-wüstite grains than in a 1600°C anneal (Fig. 3). X 1000.

Fig. 5. MgO-Fe₂O₃ microstructure.
Example: 70 MgO-30 Fe₂O₃ heated for 18 hours at 1600°C, quenched in water, reheated to 1200°C for one hour. There is more grain boundary precipitate and more spheroidization of the intra-granular precipitate than in the comparable microstructure treated at 1100°C (Fig. 2). X 1000.

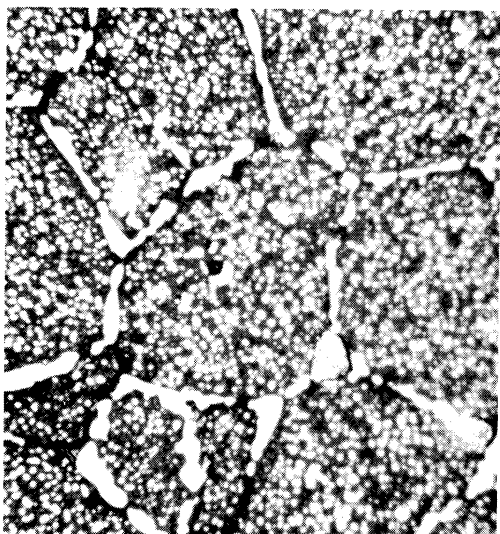
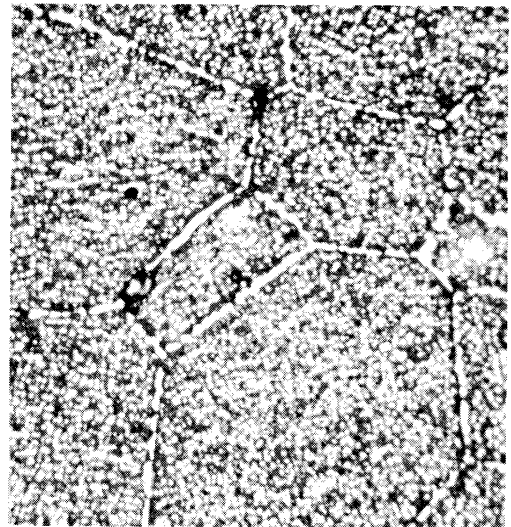


Fig. 6. MgO-Fe₂O₃ microstructure.
Example: 70 MgO-30 Fe₂O₃ heated for 18 hours at 1600°C, quenched in water, reheated to 1200°C for 27 hours. As contrasted to the one-hour treatment (Fig. 5), there has been a major relocation of the magnesioferrite to the grain boundaries. X 1000.

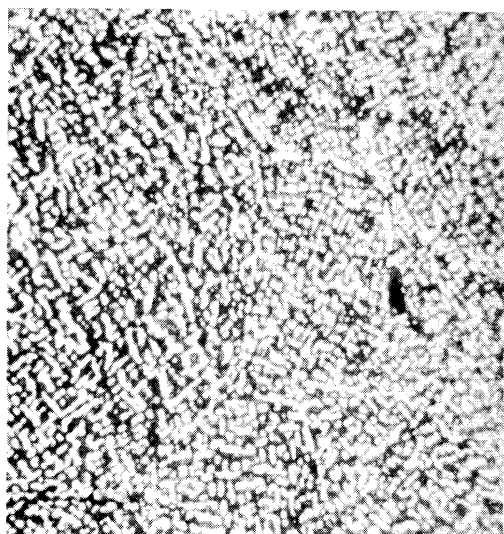


Fig. 7. MgO-Fe₂O₃ microstructure. Example: 70 MgO-30 Fe₂O₃ heated for 18 hours at 1600°C, quenched in water, reheated to 1100°C for 27 hours. Extended times at this temperature permitted spheroidization of the magnesioferrite (cf. Fig. 2) but did not produce a relocation of the magnesioferrite to the boundaries (cf. Fig. 6). X 1000.

Fig. 8. MgO-Fe₂O₃ microstructure. Example: 60 MgO-40 Fe₂O₃ heated for 18 hours at 1400°C and quenched. Unlike Fig. 1 from the same 1/4 in. sample, this microstructure occurred at the center where the quenching rate was slower. Therefore the magnesiowüstite developed some magnesioferrite precipitate without a heat treatment. X 1000.

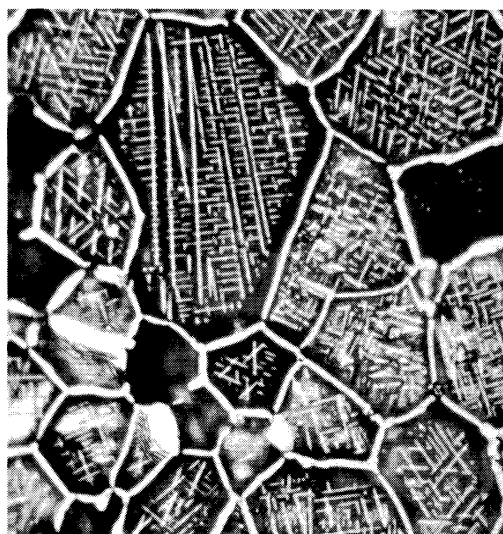
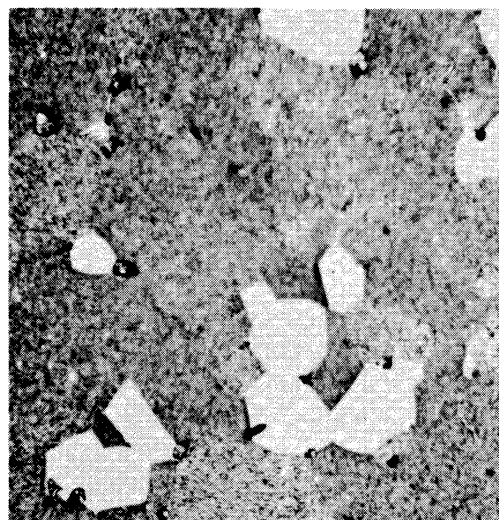


Fig. 9. MgO-Fe₂O₃ microstructure. Example: 70 MgO-30 Fe₂O₃ heated for 18 hours at 1400°C, cooled slowly (33 minutes) from 1400°C to 1100°C, held one hour at 1100°C. A coarse boundary precipitate of magnesioferrite formed by depleting Fe₂O₃ from the adjacent part of the magnesiowüstite grains. A Widmanstätten precipitate formed in the supersaturated interior of the grains. This latter precipitate could not grow into the depleted zone along the boundary. The transparency of the matrix phase indicates that very little iron oxide remains in the pericase. X 1000.

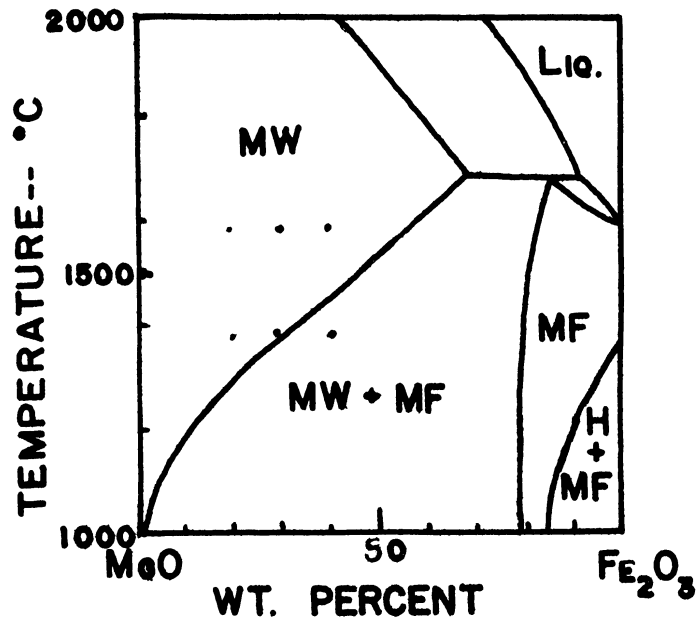


Fig. 10. MgO-Fe₂O₃ phase diagram (in air). After Phillips, et al, Reference 1. MW = magnesiowustite, MF = magnesioferrite, H = hematite.

