

SOLUBILITIES OF R_2O_3 OXIDES IN PERICLASE AND MONTICELLITE SYSTEMS

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Abstract. The solubility relationships of various R_2O_3 oxides in periclase in ternary systems at 1600–1700°C have been determined. Neither the X-ray powder method nor reflected light microscopy was found suitable for fixing the solubility boundaries. The presence of monticellite which is molten at experimental temperatures, however, produced so much grain growth that micrograph was used successfully to plot the projections of the solubility boundaries in MgO-monticellite- R_2O_3 systems.

INTRODUCTION

The use of higher temperature in the production of basic refractories has shown that considerably greater degree of solubility between phases exists at high temperature than had been realised earlier.

Systematic study of the reactions taking place in basic refractories is complicated by the fact that there are at least seven possible components: SiO_2 , Al_2O_3 , Cr_2O_3 , Fe_2O_3 , FeO, CaO and MgO. At first sight it appears impossible to relate chemical composition to mineralogical constitution but some 40 years ago an approximate solution was obtained by a process which involved writing down the possible combinations of compatible solid phases. Owing to the prevalence of solid solution, the relationships turned out to be simple and it was found possible to produce "phase assemblages", the constitutions of which are determined primarily by the CaO/ SiO_2 molar ratio. The four assemblages shown in Table 1 cover the constitutions of all basic refractories except dolomite.

The constitutions of all unused chrome-magnesite and magnesite-chrome bricks correspond to assemblage 1, but the absorption of lime during high-temperature services will progressively alter their constitutions to the right. Magnesite bricks are made corresponding to assemblages 1, 2 and 3, and their constitutions are also moved to the right during service.

The above assemblages describe the solid constitutions, i.e., in the absence of melt formation, and that solid solubility between phases is implied only in general terms. The term "magnesio-wustite" strictly applies to MgO-FeO solid solutions but these contain ferric iron, the content of which decreases as the temperature rises. Although it is now known that MgO at high temperatures will dissolve Al^{+++} and Cr^{+++} , as well as Fe^{++} and Fe^{+++} , the same magnesio-wustite term continues to be applied to the high temperature MgO constitution, which exists in all the phase assemblages.

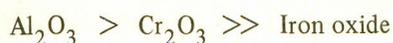
Al_2O_3 , Cr_2O_3 and iron oxide are partially soluble in MgO at high temperature. Alper et al. [1,2], Hayhurst [3]

Table 1. CaO/ SiO_2 Molar Ratio.

| 1 | 2 | 3 | 4 |
|------------------|------------------|--------------------|--------------------|
| 0 – 1.0 | 1.0 – 1.5 | 1.5 – 2.0 | 2.0 |
| Magnesio-wustite | Magnesio-wustite | Magnesio-wustite | Magnesio-wustite |
| Spinel | Spinel | Spinel | Spinel |
| Forsterite | Monticellite | Merwinite | Calcium aluminate: |
| | Merwinite | | Ferrites, |
| | | | Chromite |
| Monticellite | | Dicalcium silicate | Dicalcium silicate |

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and Woodhouse et al. [4] have shown that the solubilities of the three sesquioxides in solid MgO increase in the order.



EXPERIMENTAL

A small molybdenum-wound furnace [5] capable to fire up to 1750°C was used in this investigation. Starting materials like MgO were of Analar grade. It was ground in agate mortar to pass through 300 mesh. Chromic oxide was prepared by heating chromium trioxide in a platinum dish at 900°C for 2 hr. Ferric oxide was prepared from pure electrolytic iron, by first converting it to nitrate, and then firing at 1200°C for 1 hr to get ferric oxide. It was ground to pass through 300 mesh. Monticellite was prepared, by mixing equimolecular proportion of A.R. grade calcium carbonate, the high purity magnesia and high purity Belgian silica sand which was finely ground. The mixture was then ground in a mechanical agate to obtain intimate mixing, a small amount of a 5% aqueous starch solution was dispersed in it. The material was then made up in standard moulds and rammed. The resulting blocks were then fired in a gas furnace at 1400°C for 2 hr. The blocks were crushed and finely ground to pass through 300 mesh. Some of the powder was checked by observation through a microscope and by comparison of X-ray diffraction powder photographs to see if any excess MgO was present, but none was found.

Preparation of Pellets. The required percentage weights of the starting materials were intimately mixed for about 30 minutes in the mechanical "agate" mortar. To this mixed powder was then added aqueous starch solution as a binder; it was then pressed in a 6 mm diameter steel mould at a pressure of about 30 tons/in². The resulting pellets were ready for firing after drying in an oven.

Firing of Pellets. When X-ray examination of compositions containing MgO and the R_2O_3 oxides were required, considerable time was given to ensure complete reaction for forming single solid solutions. A given series of pellets was intimately fired to 1650°C in a gas furnace and allowed to cool slowly. They were then powdered and examined with a petrological microscope for homogeneity. If this had not been achieved, the powder was repressed into pellets and fired again. When homogeneous, individual pellets were finally fired in the molybdenum furnace at the selected temperature for 1 hr and then quenched in air.

Since reaction took place far more rapidly in mixtures containing monticellite, individual pellets were simply fired in the molybdenum furnace at the selected temperature for 3 hr and then quenched in air. Both the X-ray and polished section techniques [6] were used during these investigations. Since it was found difficult to establish the limits of the magnesio-wustite phase by X-rays owing to the diffuseness of the diffraction patterns, the method adopted was to add selected mixtures of the sesquioxides in progressively increasing amounts to selected mixtures of magnesia and monticellite, which at the firing temperatures used would consist of solid magnesia and a liquid phase. After firing, the samples were quenched, polished and examined under the microscope by reflected light to ascertain whether, at the firing temperature they had consisted of magnesio-wustite and a liquid phase or of magnesio-wustite plus spinel and a liquid phase.

Identification of Phases. The identification of the phases present in the polished section of a fired mixture is to some extent dependent on using the correct polishing technique to take advantage of the differing reflectivities of the compounds present. The compound which appeared as the least bright phase in the polished sections was monticellite, which formed a glassy structureless grey matrix between the solid grains. (The extent to which this glass, liquid at the firing temperature, penetrated between the solid grains was of course determined by the dihedral angle.) The next phase in order of brightness was periclase, the actual appearance of which varied considerably according to the amount and nature of the spinel crystallites precipitated out in the grain during the short period of cooling. It is perhaps unnecessary to point out that the presence of these crystallites within the MgO grains does not, in contrast with the X-ray method, invalidate the use of micrography to determine solubility limits, for it is obvious that the spinel precipitated must all have been in solution in the periclase at the working temperature. Such spinel has been derived entirely from the R_2O_3 addition and no correction to the solubility limit is therefore needed.

When the solubility limit was exceeded, larger bright crystals of spinel appeared outside the periclase grain boundaries and within the monticellite matrix. Plates 1, 2 and 3 illustrate the effect generally observed: no excess spinel is visible in plate 1, a few crystals are present in plate 2 and in plate 3, which shows a section of a fired mixture in which the solubility limit had been appreciably exceeded, the larger proportion of spinel can be detected. It will

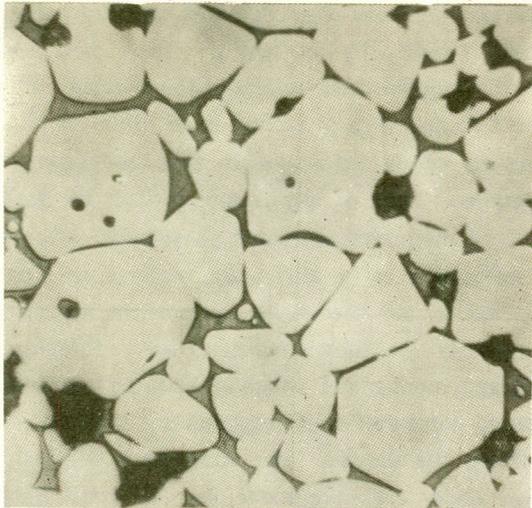


Plate 1. Micrograph ($\times 400$) showing no crystals of spinel.

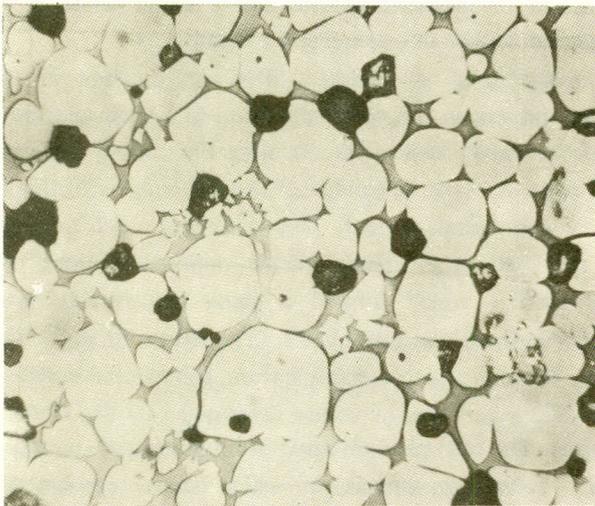


Plate 2. Micrograph ($\times 400$) showing a few crystals of spinel.



Plate 3. Micrograph ($\times 400$) showing excess spinel. Spinel (angular bright crystals), periclase (big rounded grains), monticellite (light grey) and black spots are pores.

be observed that their angularity is as prominent a feature as their brightness.

As Al_2O_3 was progressively replaced by Cr_2O_3 and the latter progressively by Fe_2O_3 the size and reflectivity of these spinel crystals increased; these changes were not, however, accompanied by an increase in the case with which the solubility limit in a particular mixture could be fixed. In fact, considerable difficulty was encountered in deciding when excess spinel made its appearance in the mixtures containing Mg_2O_3 and Fe_2O_3 . This was due to the fact that when magnesio-wüstites (MgO high in iron oxide) were quenched the precipitated spinel concentrated in the MgO grain boundary, instead of being scattered throughout the grain.

By repeating this procedure at different MgO/CMS ratios with the same sesquioxide mixture, the boundary curve between these two-phase and three-phase fields at this particular sesquioxide composition could be drawn and when extrapolated to zero CMS content would give the limit of the magnesio-wustite phase at this sesquioxide composition with, it was hoped, reasonable accuracy.

RESULTS AND DISCUSSION

In the absence of melt the size of periclase and spinel grains in the synthetic mixtures was so very small that reflected light examination of polished sections of such mixtures provided no real solution to the determination of solubility limits. Even with the greatest magnification available, it was not possible to be sure whether excess spinel was present or not. This situation was, however, transformed when as little as 5% of melt was present, since considerable grain growth occurred and it became easy in most cases to detect the presence of excess spinel.

An extrapolation technique for determining the solubility of spinel in periclase alone was, however, necessary and it became obvious that the solubility boundary must be explored by firing and examining mixtures containing progressively increasing amounts of monticellite. At each monticellite content the R_2O_3 content (of given binary composition) was varied until the solubility limit could be "bracketed" between two mixtures of R_2O_3 contents separated by as little as 1-2% by weight. Fig.1 shows the scheme adopted thus to fix the boundary between the phase fields containing periclase + monticellite and periclase + monticellite + spinel. This figure shows the compositions of all the experimental mixtures; the subsequent figures of this type show only the two determina-

tive mixtures. In the course of the work over 210 solubility limits were fixed by microscope examination of about 1000 fired and quenched mixtures. Like Fig. 1 various figures were drawn after examining over 1000 specimen. The firing was done at 1600 and 1700°C. It will be observed that in all cases the mixtures have been made up in terms of the percentage weights of the three components — MgO, monticellite and R_2O_3 . This procedure was found to be the simplest from the experimental point of view, for it was a simple matter to calculate the respective weights of, for instance, MgO, CMS, Al_2O_3 and Cr_2O_3 , to give a ternary mixture with a monticellite content of (say) 20% and an R_2O_3 content of (say) 10%, when the Al_2O_3/Cr_2O_3 weight ratio had been decided.

It was however necessary also to fix the position of the CMS-spinel joints on each figure and, although this was straightforward when the spinel was formed by union of MgO with one of the three sesquioxides, it was more complex for R_2O_3 mixtures and a standard formula had to be evolved for the purpose.

At both experimental temperatures the results have been arranged in the same order of changing R_2O_3 composition. The first diagram in each series is for Al_2O_3 , which is then progressively replaced (at 20% by weight intervals) by Cr_2O_3 ; the latter is in turn replaced progressively by Fe_2O_3 which is in turn replaced by Al_2O_3 up to the composition containing 80% Al_2O_3 : 20% Fe_2O_3 , i.e., the diagram containing Al_2O_3 alone is not repeated.

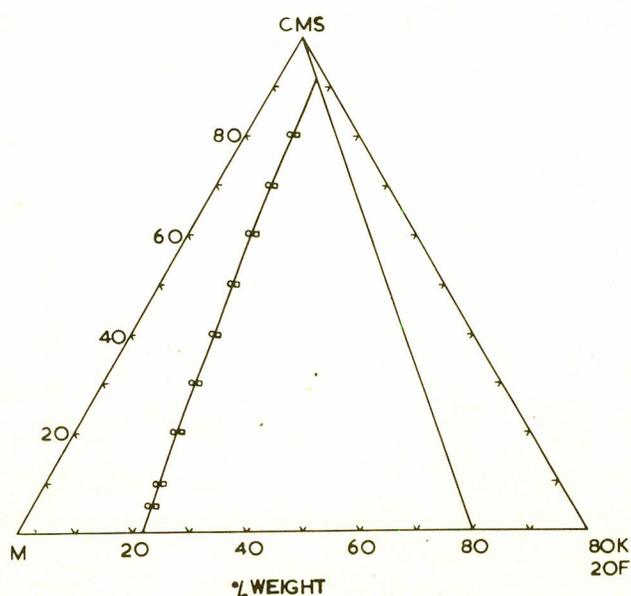


Fig. 1. Solubility limits in a periclase-80 wt. Cr_2O_3 and 20 wt. Fe_2O_3 -monticellite system at 1700°C.

Since the solubilities in periclase and in monticellite were to be obtained by extrapolation, considerable pains were taken to establish the correct forms of the boundaries between the periclase + monticellite and periclase + monticellite + spinel fields. A survey of the 30 diagrams shows that complete success in this respect was not achieved but in many cases, particularly with the Cr_2O_3/Fe_2O_3 containing mixtures, straight lines seemed to represent the form of the boundaries most satisfactorily. The greatest difficulty in deciding the form of the boundaries lay with the Al_2O_3/Cr_2O_3 containing mixtures. This may have been due to the fact that the solubilities of the two oxides in periclase and in monticellite bear an inverse relationship to each other; the boundary between the two phase fields must therefore pivot as its two ends move in opposite directions.

From the practical point of view, the solubilities of the three R_2O_3 oxides and their mixtures in the MgO grain and in the liquid silicate are of direct importance. In Figs. 2 and 3 the extrapolated values for these solubilities are shown for 1600°C and 1700°C, respectively. The top diagrams in these figures emphasize the inverse nature of the relationships for Al_2O_3/Cr_2O_3 containing mixtures and show that the differences between the solubilities in

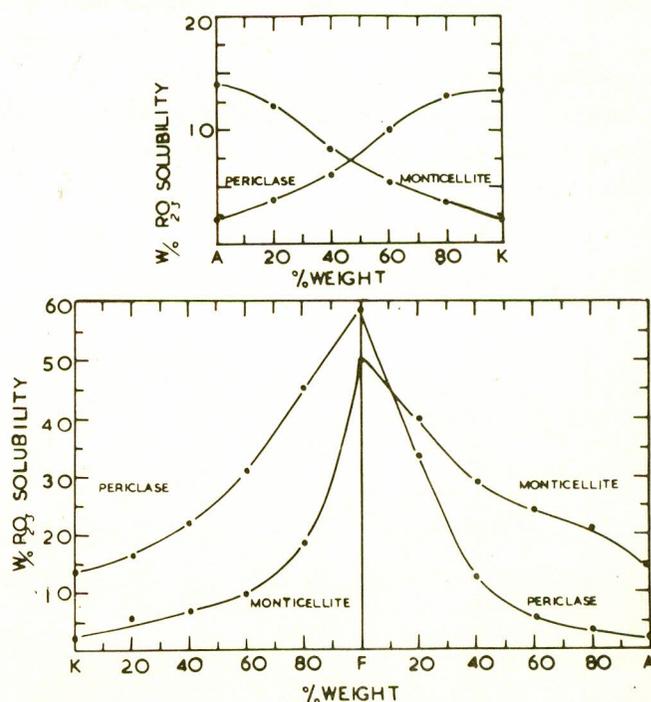


Fig. 2. Showing % wt. solubilities of R_2O_3 oxide mixtures in periclase and monticellite at 1600°C

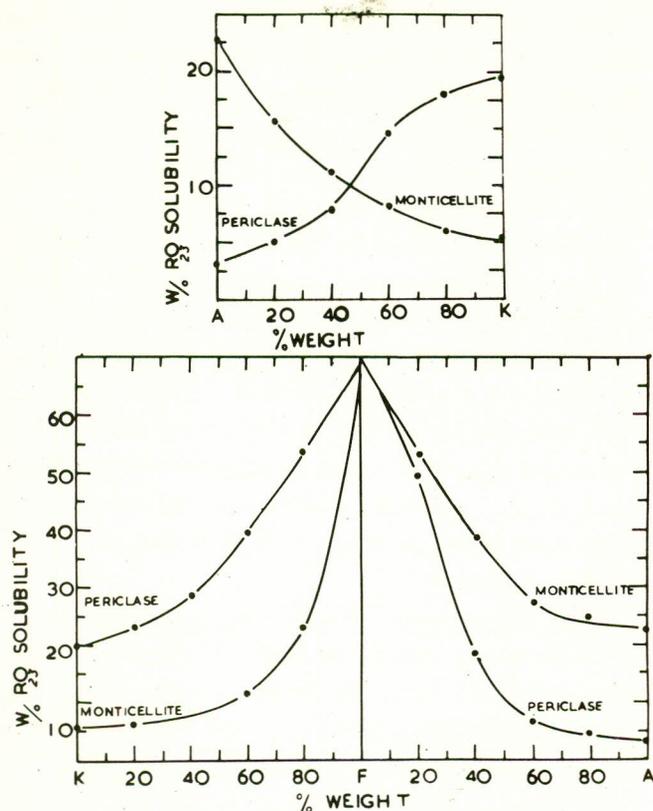


Fig. 3. Showing % wt. solubilities of R_2O_3 oxide mixtures in periclase and monticellite at 1700°C .

periclase and in monticellite are increased by the increase in the experimental temperature. It will be seen that, in confirmation with other results [7], Al_2O_3 is more soluble in periclase than in the liquid silicate, and that a mixture consisting of 52.5% Al_2O_3 : 47.5% Cr_2O_3 by weight has equal solubilities in both phases at both temperatures.

As Cr_2O_3 is progressively replaced by Fe_2O_3 the solubility in both periclase and monticellite rise appreciably to very high values and then fall again as Fe_2O_3 is replaced by Al_2O_3 . At the lower experimental temperature of 1600°C the solubility relationships for the Fe_2O_3/Al_2O_3 containing mixtures cross, but, that at 1700°C the solubilities in both periclase and silicate of Fe_2O_3 are identical so that no crossing of the solubility curves is possible. It will also be noted that, due to the difficulties in determining excess spinel, certain irregularities of the curves are noticeable for the mixtures containing Al_2O_3 and Fe_2O_3 .

Finally, within the limits of the experimental accuracy, the solubilities of the three R_2O_3 oxides in periclase at both temperatures agreed closely with the results of Alper et al. [2].

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