

MATERIAL TRANSPORT IN SOLID-STATE REACTIONS

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INTRODUCTION

In this introductory lecture on material transport in solid-state reactions some of the well-known classical arguments and experimental techniques used in research on solid-state reactions will be reviewed in order to elucidate the predominant material transport mechanism governing a particular reaction.

The large number of possible solid-state reactions makes it at first sight desirable to present this review in a very general way.

Nevertheless I think that in such a broad field as the present one it will still pay to choose a particular solid-state reaction which we can use as a basis for discussing the general material transport phenomena that may occur in solid-state reactions.

In experimental research on solid-state reactions the formation of spinel is often chosen as a suitable model reaction because of its relative simplicity. The crystal lattices of the spinel and those of the reaction components are well-known and not very complicated and, moreover, the spinel reactions can be carried out in a model experiment with a restricted number of different ions.

The formation of spinel, and more specifically the ferrites, can be used as an ideal model for the purpose of this introductory lecture because, as will be shown, the material transport in this reaction has many general aspects.

It is hardly necessary to say that in practice, too, considerable interest is shown in the formation of spinel because of the successful application of ferrites as magnetic materials in modern electronic devices.

REACTION MECHANISMS

The possible mechanisms of solid-state reactions are usually discussed with the aid of a schematic diffusion-couple arrangement like that shown in *Figure 1* which demonstrates as an example the reaction $\text{MgO} + \text{Fe}_2\text{O}_3 \rightarrow \text{MgFe}_2\text{O}_4$.

In this situation the reaction proceeds by solid-state diffusion and the question is which of the different ions which are present are being transported and determine the course of the reaction.

When we consider the diffusion of the different ions across the reaction product the only restriction to be placed on these diffusion fluxes is that in

the steady state no space charges are created and thus no net flow of electrical charge is associated with the material flow.

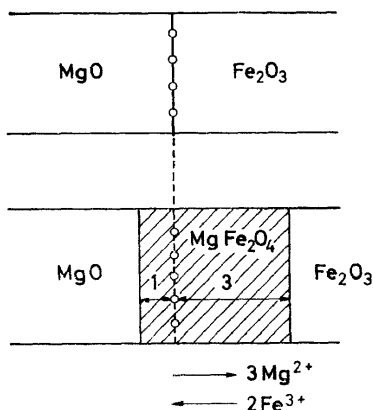


Figure 1. Case A: Counter diffusion of cations only (Wagner mechanism); no marker displacement

The possible mechanisms for the formation of MgFe_2O_4 may now be discussed with reference to a set of limiting cases.

Case A

As suggested by Wagner¹ the reaction might proceed by the diffusion of the cations only, *i.e.* in a counter-current through the reaction layer.

In the oxides concerned the O^{2-} anions are close-packed and the much smaller cations fill the octahedral and tetrahedral interstices.

The anions thus form the rigid matrix of the crystal lattice and it seems very plausible that in a reaction like the formation of MgFe_2O_4 only the Mg^{2+} and Fe^{3+} ions will diffuse through the octahedral and tetrahedral sites of the spinel lattice.

Thus if no oxygen diffusion takes place the cation fluxes will be as indicated in Figure 1. Upon diffusion of 3 gram-ion of Mg^{2+} to the right we get 3 mol of MgFe_2O_4 while the associated diffusion of 2 gram-ion of Fe^{3+} to the left will give 1 mol of MgFe_2O_4 .

An important consequence of this mechanism is that spinel phase growth takes place at *both* sides of the original $\text{MgO}/\text{Fe}_2\text{O}_3$ interface. If we mark the location of this interface we will observe that the reaction proceeds on the two sides with a volume ratio of 1:3.

In the case of metals a well-known phenomenon is that in a diffusion-couple of two metals the diffusion rates of the metals into each other may be unequal. This means that in such a case there is an excess flow of material from one side of the diffusion-couple to the other. This can be observed if the interface which joins the two metals is marked, for example, with thin wires of an inert material as shown in Figure 6a.

If for instance *B* diffuses faster into *A* than *A* into *B* then the distance between the wires will be diminished due to the excess flow of *A* across the

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planes marked by the wires. The displacements of the markers is known as the Kirkendall effect and, in the case of metals, is proof that the diffusion of the metals takes place by a point defect mechanism.

In the case of the interdiffusion of oxides the displacement of markers will indicate whether oxygen has been transported from one side of the marked interface to the other because oxygen ions in the lattice of the oxide determine the macroscopic size of the crystals.

If the MgFe_2O_4 formation proceeds by the diffusion of the cations only, then there will be no diffusion of oxygen anions and hence no displacement of the markers which will become embedded in the spinel phase.

Case B

However, another possibility is that one of the cations is immobile and the diffusion of the other cation is associated with the equivalent diffusion of oxygen ions. Then in this limiting case reaction takes place by the diffusion of one reactant only.

If for instance in the formation of MgFe_2O_4 again only the Fe^{3+} ions and O^{2-} anions migrated then as a consequence the spinel reaction layer would extend on one side of the markers only. In this case spinel would be formed at the MgO side only. It will be evident that the markers of the original $\text{MgO}/\text{Fe}_2\text{O}_3$ interface will remain on the $\text{MgFe}_2\text{O}_4/\text{Fe}_2\text{O}_3$ interface and will thus be displaced (*Figure 2*).

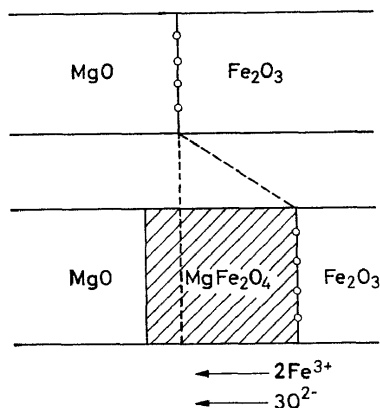


Figure 2. Case B: Diffusion of only one cation with associated diffusion of O^{2-} anions; markers are displaced and remain on the $\text{MgFe}_2\text{O}_4/\text{Fe}_2\text{O}_3$ phase boundary

Case C

In the preceding models it has been tacitly assumed that the ions retain their initial valency upon diffusion through the reaction product. This need not be the case and in fact the change of valency of the ions upon crossing the reaction layer is another important feature of solid state reactions which has to be taken into account^{2a}.

In the formation of MgFe_2O_4 , for example, we may suppose that only cation diffusion takes place in a Wagner-type reaction, but that the Fe ions

cross the reaction layer in the 2-valent state instead of the 3-valent one as assumed in case A.

The condition of no net electrical flow then requires that the diffusion of 1 gram-ion of Mg^{2+} is now compensated by 1 gram-ion of Fe^{2+} .

In this case too the spinel phase will grow on both sides of the original $\text{MgO}/\text{Fe}_2\text{O}_3$ interface but the volume ratio of the spinel will now be 1:2 as shown in Figure 3.

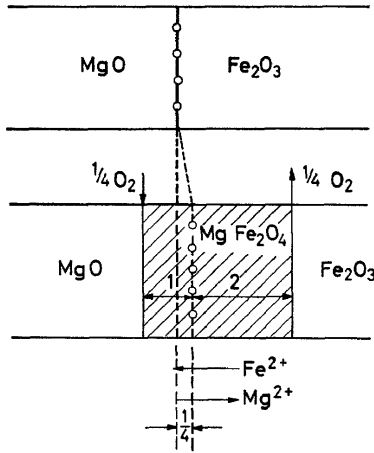


Figure 3. Case C: Counter-diffusion of Mg^{2+} and Fe^{2+} ions; no diffusion of O^{2-} anions through the MgFe_2O_4 lattice but reduction and oxidation of Fe ions, at the respective phase boundaries, which is equivalent to an oxygen transport through the gas phase; marker displacement will occur owing to this transport

Whether or not the cations of the reaction component will change their valency when they dissolve in the reaction product will depend on the ability of oxidation-reduction conditions in the particular phase system.

These three postulated mechanisms as illustrated for the formation of MgFe_2O_4 contain the principal elements of transport phenomena which can be observed in solid-state reactions of this type.

A common approach is to follow the kinetics of the conversion of the solid-state reaction in powders with a view to determining the activation energy. If the activation energies of the self-diffusion of the ions taking part in the solid-state reaction are known (which is not usually the case) these may be compared with the activation energy determined experimentally for the overall solid-state reaction rate. From this, conclusions are drawn about the rate-determining ion and hence about the reaction mechanism.

This line of attack must however be considered with a great deal of reserve because the activation energy of the overall reaction may be more complex than that determined from investigations of the self-diffusion of the ions with radioactive tracers.

Even though by way of comparison of activation energies a particular ion may be identified as the rate-determining one, in the solid-state reaction one does not get any information about the other ions which may diffuse. Conversion rates have been determined in this way, for example, for different

ferrites in powder reactions². This line of research is characterized by the fact that only the *total amount* of spinel formed is determined.

As will be clear from the discussion above of the three possible reaction mechanisms there is a wealth of information which can be obtained by the observation of the spinel *volume ratios* and marker displacements which is ignored in the conversion rate studies.

Observation of these ratios and the marker displacements mostly by metallographic or other techniques gives a direct and simple insight into the predominant material transport mechanism of the solid state reaction.

It is my opinion that these techniques should be improved and used far more widely in solid-state reaction research.

As a matter of interest, which of the mechanisms we have discussed is mainly operative for the formation of MgFe_2O_4 and analogous ferrites?

Carter³ has shown by elegant marker-type experiments in which he used pores as inert markers that, in the formation of the similar spinel MgAl_2O_4 from MgO and Al_2O_3 , no Kirkendall effect could be observed. This means that MgAl_2O_4 is formed by the counter-diffusion of Mg^{2+} and Al^{3+} ions only in complete agreement with the Wagner model. In the case of MgFe_2O_4 he determined the volume ratio of spinel formed on both sides of the marked interface to be 1:2.7.

In view of the experimental inaccuracies and the great similarity to the reaction of MgAl_2O_4 , Carter concluded that this is in good agreement with the 1:3 ratio which must be expected for the Wagner reaction model in this case.

The more-or-less generally accepted model for the formation of the ferrites is that no oxygen diffusion takes place and the reaction proceeds as discussed in mechanism *A*. The formation of the ferrites is however just a little more complex than the formation of MgAl_2O_4 .

PHASE EQUILIBRIA

An astonishing thing in solid-state reaction research is that so little attention is given to the *phase equilibria* which may occur at the different interfaces present in the intermediate stage of the solid-state reaction.

Most attention seems to be focused on the activation energy. However, as is well-known the fluxes of the diffusing ions are determined not only by the ionic mobilities but also by the driving chemical gradients across the reaction layer. The reacting components are separated from each other by the reaction product and there are thus two different phase boundaries where locally the phases which are in contact will try to maintain equilibrium. The equilibrium concentrations at these phase boundaries will therefore have a large influence on the driving concentration gradients across the reaction layer.

Phase equilibria considerations are essential because they may give not only an insight into the magnitude of the concentration gradients across the reaction layer but also additional information about the probable mechanism. In this respect the formation of the ferrites as discussed in the paper by Reynen⁴ is an instructive illustration of how knowledge of the phase equilibria can lead to a better understanding of the reaction mechanism and reactivity.

The generally accepted model in which MgFe_2O_4 , for example, is being formed by the counter-diffusion of Mg^{2+} and Fe^{3+} ions, tacitly assumes that Fe_2O_3 at the $\text{MgFe}_2\text{O}_4/\text{Fe}_2\text{O}_3$ phase boundary dissolves in the spinel without the loss of any oxygen and that all the Fe ions remain in the 3-valent state. However, from the published data⁵ on the phase diagrams of the system $\text{MgO-FeO-Fe}_2\text{O}_3$ we know that this is not the case: the solution of Fe_2O_3 in spinel is accompanied by a loss of oxygen. In *Figure 4* the phase diagram, at constant oxygen pressure, is shown with a number of isotherms.

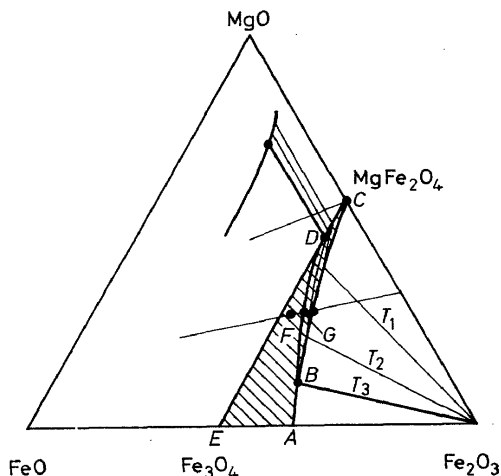


Figure 4. Phase diagram $\text{FeO-MgO-Fe}_2\text{O}_3$ after Reynen⁴; at constant oxygen pressure with isotherms $T_1 < T_2 < T_3$

The compositions of the spinel phase in equilibrium with Fe_2O_3 at different temperatures is represented by the line AC and will, at a given temperature T_3 , be given by point B . The isotherm of T_3 indicates that the composition of the spinel phase in equilibrium with MgO will be given by point D on the line CE . In a reacting diffusion-couple, $\text{MgO/spinel/Fe}_2\text{O}_3$, the compositions of the spinel phase at the phase boundaries will thus be given by these points B and D . We may see from the phase diagram that approximately 1 out of 3 Fe^{3+} ions entering the spinel phase from the Fe_2O_3 is reduced to Fe^{2+} . Thus Fe_2O_3 dissolves in spinel with a $\text{Fe}^{3+}/\text{Fe}^{2+}$ ratio corresponding roughly to that in Fe_3O_4 . Only a small fraction of the Fe_2O_3 dissolves with all the Fe^{3+} in the 3-valent state and produces cation vacancies such as occur in $\gamma\text{-Fe}_2\text{O}_3$, which has a spinel structure, and may be written as



In view of the composition at the phase boundaries one arrives at the conclusion that MgFe_2O_4 is formed by the counter-diffusion of Mg^{2+} and Fe^{2+} ions instead of Fe^{3+} ions.

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This is immediately apparent if we approximate the composition at the phase boundaries by MgFe_2O_4 and $\text{Fe}^{2+}\text{Fe}_2\text{O}_4$. In that case there are concentration gradients for Mg^{2+} and Fe^{2+} only. Although there will of course be only one effective diffusion coefficient for the Fe-ions on account of the easy electron transfer between Fe^{2+} and Fe^{3+} ions in the spinel layer, the charge transfer associated with the total diffusion of Fe across the reaction layer will be as if only Fe^{2+} ions were migrating.

The formation of MgFe_2O_4 takes place predominantly by the exchange of Mg^{2+} and Fe^{2+} ions and only for a small part by the exchange of Mg^{2+} and Fe^{3+} ions.

At the spinel/ Fe_2O_3 phase boundary oxygen will be given off due to the reduction of Fe^{3+} to Fe^{2+} during the solution of Fe_2O_3 in the spinel phase. At the MgO /spinel side however oxygen will be taken up for the conversion of the Fe^{2+} to Fe^{3+} .

An important consequence of the fact that the transport of Fe across the reaction layer takes place mainly by Fe^{2+} -ions is that the ferrite reactions become dependent on the oxygen partial pressure of the atmosphere and that oxygen transport takes place in the surrounding gas atmosphere. For this we may consider the MgO - FeO - Fe_2O_3 phase diagram at constant temperature but with different oxygen pressures as shown in *Figure 5*.

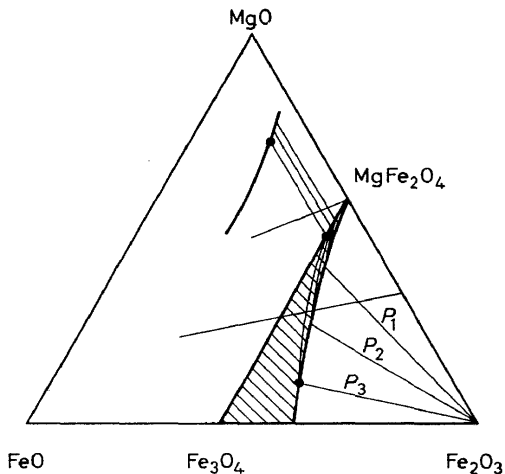


Figure 5. Phase diagram of MgO - FeO - Fe_2O_3 at constant temperature with isobars $P_1 > P_2 > P_3$

We notice from the isobars in this diagram that the spinel/ Fe_2O_3 phase equilibrium is much more sensitive to the oxygen partial pressure of the atmosphere than the $\text{MgO}/\text{Fe}_2\text{O}_3$ equilibrium. This causes the rate of formation of the ferrite to be dependent on the gas phase. High oxygen partial pressures will retard the formation of MgFe_2O_4 because less Fe_2O_3 can be dissolved into the spinel phase resulting in a decrease of the concentration gradients.

Reducing conditions will however increase the reaction rate. This has

been found experimentally for example by Okamura^{2f} for NiFe_2O_4 and by Jáky *et al.*⁶ for the similar case of formation of CdFe_2O_4 .

The considerations on the phase equilibria as given above thus present a satisfactory explanation of their experimental results.

In these considerations we have tacitly assumed that equilibrium will be maintained at the different phase boundaries during the reaction. This may be correct if we assume that the ferrite reaction is controlled by diffusion across the reaction layer and not by the phase boundary reactions. However, even if equilibrium is not maintained, the results will be affected only quantitatively but not qualitatively.

The Kirkendall effect

Owing to the oxygen transport through the gas phase during the formation of MgFe_2O_4 a Kirkendall effect must be present. However, experimental confirmation of the existence of the Kirkendall effect in these types of solid-state reaction seems to be difficult.

Various authors observed that Pt and Ir marker wires seemed to dissolve in the spinel³. In addition to the problem of finding really inert markers it is difficult to make a diffusion-couple with good interfacial contacts.

Our metallurgical colleagues have here the advantage that a good contact area can be ensured because of the plasticity of their materials.

A different technique may however be used to render the Kirkendall effect visible while avoiding these difficulties, *i.e.* the technique of *diffusion through a restricted contact area*.

In a normal diffusion set-up the diffusion area is large as shown in *Figure 6*. If the diffusion rates of the metals *A* and *B* are unequal then there will be a displacement of the markers. There will however be *no* displacement of block *A* with respect to block *B*.

If we choose reference points in the lattices of *A* and *B* which are still outside the penetration regions of the diffusion then it will be evident that the distance between these points will be unaffected by the diffusion (apart from secondary effects like changes of lattice constants in the regions penetrated).

However if the diffusion area is restricted then displacement of *A* with respect to *B* will occur, owing to the geometry of the diffusion set-up.

In the case of MgFe_2O_4 formation we may explain this in the following way.

Diffusion through the small contact area will result in approximately hemispherical regions of spinel in the MgO and Fe_2O_3 block. If the reaction proceeds with the mechanism as discussed in *C* then the volume ratio of these hemispherical regions will be 1:2 as indicated in *Figure 6b*.

Further reaction takes place on solution of Fe_2O_3 in the spinel and the accompanying reduction will give an evolution of oxygen at the hemispherical spinel/ Fe_2O_3 phase boundary. If there is a sufficient diffusion of oxygen laterally along the phase boundary then the loss of oxygen at this boundary can be accommodated by a homogeneous shrinkage and no pores will be created.

After the diffusion of the Fe^{2+} ions through the restricted contact area an equivalent amount of oxygen will be taken up again at the MgO /spinel phase boundary.

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Because the radii of the hemispherical spinel regions are different, the displacements of the MgO and Fe₂O₃ blocks involved in the loss and uptake of the same amount of oxygen at the two boundaries is different, resulting in a net displacement of the MgO and Fe₂O₃ blocks relative to each other; hence the gap width between the blocks will increase as shown in *Figure 6b*.

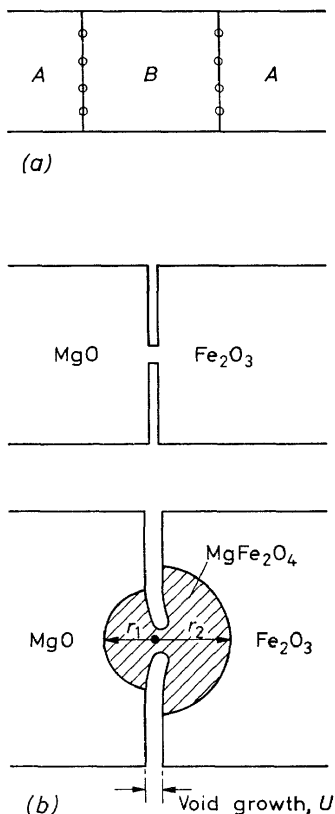


Figure 6(a). Diffusion-couple with large contact area. Measurement of the distance between two marker planes establishes the magnitude and direction of the marker displacements due to unequal diffusion rates; no displacement of block *B* with respect to block *A*
(b) Restricted diffusion area: void growth due to the transport of oxygen by reduction at spinel/Fe₂O₃ interface and oxidation at MgO/spinel phase boundary

Oxygen is transported through the gas phase from a shell with a *large* radius to a shell with a *smaller* radius.

For an estimation of this void growth we approximate the spinel regions by hemispheres. The volumes of these hemispheres according to the reaction mechanism, as discussed in case *C*, will be related by

$$2r_1^3 = r_2^3 \quad (1)$$

At the Fe₂O₃ side there will be a displacement du_2 towards the MgO block associated with the increase of the spinel radius by dr_2 owing to the loss of oxygen on solution of Fe₂O₃ in the spinel. The Fe₂O₃ dissolves mainly with

a composition of Fe_3O_4 . From the reduction equation $3\text{Fe}_2\text{O}_3 \rightarrow 2\text{Fe}_3\text{O}_4 + \frac{1}{2}\text{O}_2$ we note that 1/9 of the oxygen of the original Fe_2O_3 is transferred to the atmosphere while 8/9 remains as oxygen ions in the spinel lattice. Hence we have

$$du_2 = \frac{1}{8} dr_2 \quad (2)$$

The oxidation of the spinel hemisphere at the MgO side gives a displacement du_1 of the MgO block away from the Fe_2O_3 block.

du_1 and du_2 are related by

$$r_1^2 du_1 = r_2^2 du_2 \quad (3)$$

For the total displacement dU we get

$$dU = du_1 - du_2 \quad (4)$$

which upon substitution and integration results in

$$U = \frac{1}{8} \left[\left(\frac{r_2}{r_1} \right)^{2/3} - 1 \right] r_2 \quad (5)$$

From this it follows that the gap width between the MgO and Fe_2O_3 as a function of the reaction will be

$$U = 0.04(r_1 + r_2) \quad (6)$$

The linear expansion due to the change in lattice constants in the formation of MgFe_2O_4 from MgO and Fe_2O_3 is 2.25 per cent so that for the total increase in gap width we should find

$$\frac{U}{r_1 + r_2} \approx 6.25 \text{ per cent}$$

A restricted diffusion area can easily be obtained experimentally, *e.g.*, by taking a sphere in contact with a plate. The result of such a diffusion arrangement is shown in *Figure 7*.

The interdiffusion of the MgO and Fe_2O_3 components has resulted in the growth of a spinel phase extending in nearly hemispherical regions around the originally small contact area. From the geometry of the set-up it can be seen that the MgO sphere has been displaced away from the Fe_2O_3 . The displacement seems to be in rough agreement with what we should expect but with longer diffusion times, however, different phenomena may be observed.

In the discussion of the mechanism of the formation of MgFe_2O_4 , the oxidation and reduction during the reaction was considered to take place at the spinel phase boundaries of spinel with MgO and Fe_2O_3 . It must be expected however that when the intermediate compositions which occur in the spinel reaction layer are exposed to the atmosphere oxidation may also occur at these spinel/gas phase boundaries.

For instance, a spinel in the reaction layer of composition given by point *F* in the $\text{FeO-MgO-Fe}_2\text{O}_3$ phase diagram (*Figure 4*) may oxidize upon

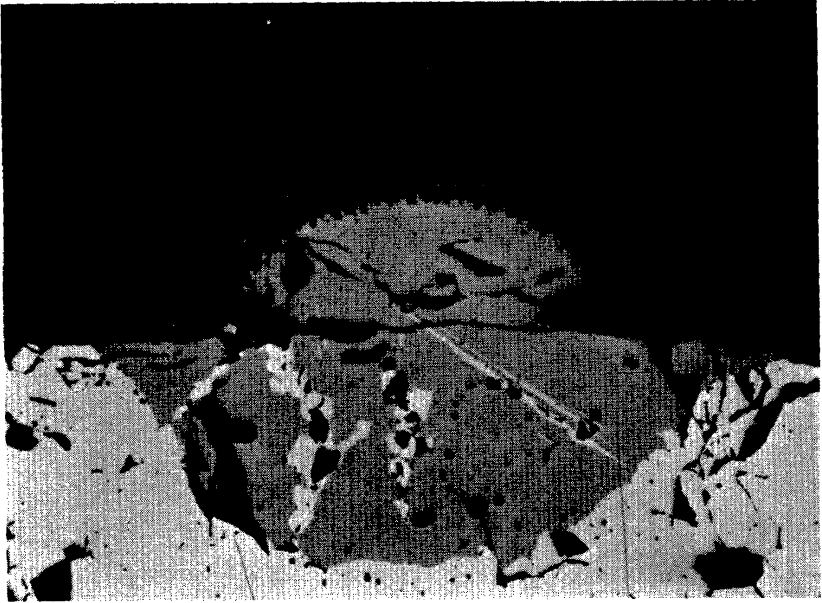


Figure 7. Micrograph of cross-section of polycrystalline sphere of MgO on polycrystalline plate of Fe_2O_3 : hemispherical regions of spinel around initial point of contact of MgO and Fe_2O_3

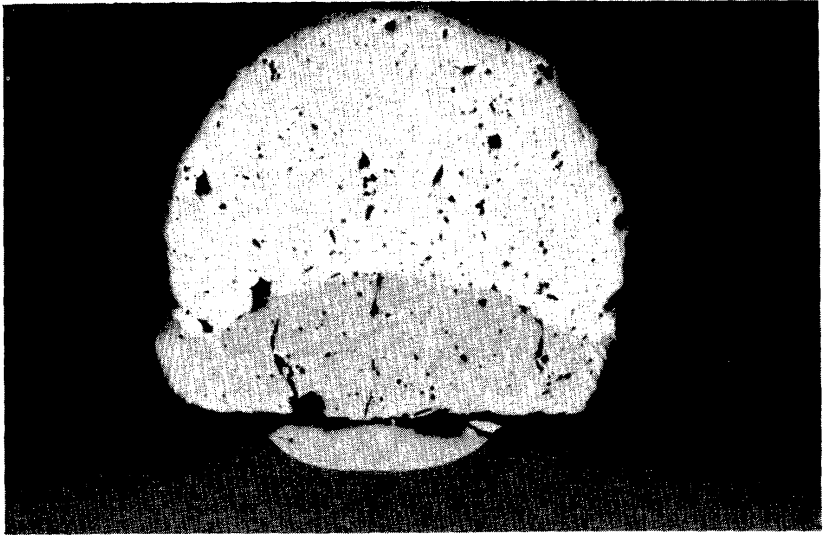
Diffusion: 48 h at 1300° in oxygen

Magnification: $150\times$

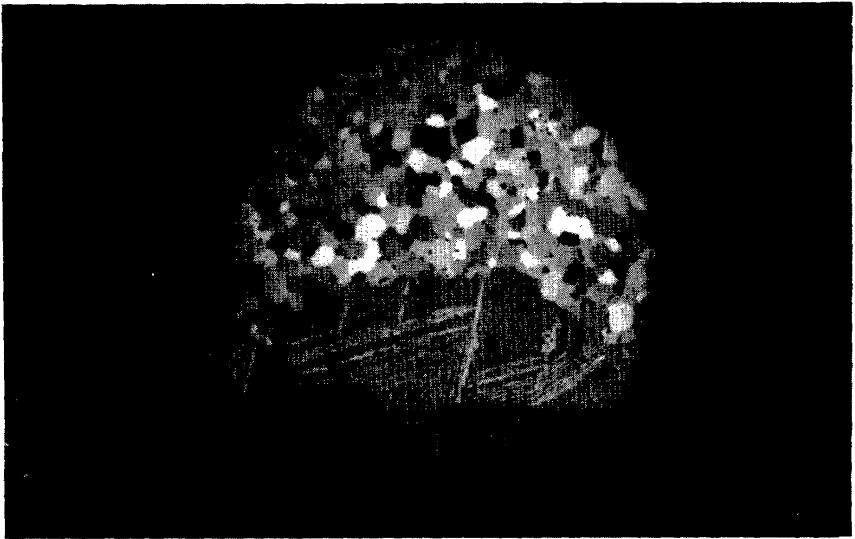
MgO-sphere has been displaced away from the Fe_2O_3 plate



Figure 8. Micrograph of polycrystalline MgO sphere on top of polycrystalline Fe_2O_3 plate: humps in the spinel region at the Fe_2O_3 side are due to oxidation of spinel of intermediate composition the reaction layer; pores are created by the loss of oxygen at the spinel/ Fe_2O_3 .
in Magnification $48.5\times$ (reduced by a factor of 0.6 in reproduction)



(a)



(b)

Figure 9(a) and (b). Micrograph of cross section of poly crystalline sphere of Fe_2O_3 on top of a single-crystal plate of MgO

(a) bright field illumination

(b) taken with polarized light and nearly crossed nicols: humps on the Fe_2O_3 sphere are due to oxidation of spinel of intermediate composition in the reaction layer. The sphere has been displaced *towards* the plate because most of the oxidation of the Fe^{2+} ions produced on solution of Fe_2O_3 in the spinel phase took place at the spinel surface and not at the MgO /spinel phase boundary

Diffusion: 220 h at 1250° in oxygen
Magnification: $48.5\times$

exposure to oxygen yielding a composition represented by point *G*. In an experiment with restricted contact area large parts of the spinel layer are readily accessible to the atmosphere. Owing to the continuous oxidation the spinel phase will swell up at these outer surfaces.

These outer regions of the spinel phase which are kept in a more oxidized state than the interior bulk spinel will as a consequence contain more cation vacancies. This may further enhance diffusion in the surface regions and attract Mg^{2+} and Fe^{2+} ions.

This gives a considerable change in geometry as may be seen in *Figures 8* and *9*. In *Figure 8* one can observe that after prolonged diffusion times extensive neck growth and swelling of the Fe_2O_3 plate has taken place.

Apparently the oxidation of the spinel phase takes place predominantly at the spinel surface instead of at the MgO /spinel phase boundary. In *Figure 9* which shows a polycrystalline sphere of Fe_2O_3 on top of a single crystal plate of MgO , the situation is also reversed, after a prolonged diffusion time. In this case it is the Fe_2O_3 in the sphere which has been converted to the spinel phase and which has taken up the oxygen from the atmosphere.

This agrees with the case shown in *Figure 8*; in both cases the spinel at the Fe_2O_3 side taking up most of the oxygen. This is of course quite understandable because the original Fe_2O_3 outer surface after the conversion to the spinel phase will be nearer to the spinel/ Fe_2O_3 phase boundary and thus form the most effective drain for the Fe^{2+} ions.

We notice also that the displacement of the sphere to the plate is different for both cases.

In *Figure 9* the Fe_2O_3 sphere has moved *towards* the MgO plate. It will be evident from the geometry of the diffusion paths, which can easily be deduced, that such a displacement must occur.

There is a loss of oxygen at the spinel/ Fe_2O_3 phase boundary while most of it is taken up again at the spinel surface near the neck. Only a small fraction of the oxygen will be taken up at the MgO side of the spinel. The displacement will thus be approximately equal to $U = 0.125r_2$ (equation 2). From *Figure 9* we estimate $U \approx 0.18r_2$ which is thus in reasonable agreement with what we should expect in view of the inaccuracies. In *Figure 8* many voids and pores may be seen in the spinel phase converted from the Fe_2O_3 plate. Apparently at this conversion the loss of oxygen and thus of material could not be accommodated homogeneously along the spinel/ Fe_2O_3 phase boundary and has resulted in the creation of these pores. This contributes to the displacement of the MgO sphere *away* from the plate. In this case no quantitative estimation can be made of what the total displacement should be. Similar experiments have been done by Kuczynsky⁷ who interpreted the swelling of the Fe_2O_3 plate as being due to an excess diffusion of MgO into the Fe_2O_3 .

In view of the phase equilibria and the discussion given above however we believe his explanation to be erroneous.

CONCLUSION

The simple application of the knowledge of phase equilibria to the intermediate stages of the formation of MgFe_2O_4 as an example of a solid-state reaction has led to an understanding of this ferrite reaction which has not

been achieved by the numerous studies which result only in evaluation of an activation energy for the overall reaction.

In the investigations of solid-state reaction mechanisms the metallographic techniques are of great value and should be used more often, because, as has been shown, the observation of marker displacements and the volume ratios of the reaction product on both sides of the markers will give valuable information on the reaction mechanism.

This information is lost in all those experiments in which only the total volume of the reaction product is being determined in order to obtain an activation energy.

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