

# Study of Solid-State Reactions in the NiO/Fe<sub>2</sub>O<sub>3</sub> System

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*Received 4 June 1968, and in revised form 11 September*

Solid-state reactions in the NiO/Fe<sub>2</sub>O<sub>3</sub> system have been investigated in the temperature range 1100 to 1300° C. The optical microscope and the electron probe microanalyser were used. Kinetic parameters of the calcination process of this system: the reaction rate, time exponent and activation energy, have been determined by observing the changes in the reaction layer thickness with time and temperature. The analysis of the reaction layer composition was the basis for discussion concerning the possible mechanism of this reaction.

## 1. Introduction

The kinetics and mechanism of solid-state reactions in different systems have been for several decades the subject of investigation of numerous researches. The study of the rate and mechanism of the reaction is important both theoretically and practically, particularly in view of the increasing production and application of ferrites. Because of the complexity of reaction and the evergrowing production and application of ferrites, the study of solid-state reactions in these systems has become more and more important. Many authors have studied the reaction of Ni ferrite formation [1-5] and often obtained contradictory results. The purpose of this work was to contribute to a better understanding of the kinetics and mechanism of solid-state reactions in the NiO/Fe<sub>2</sub>O<sub>3</sub> system by studying the reaction using an electron probe microanalyser.

## 2. Experimental Procedure

### 2.1. Sample Preparation

The solid-state reaction between NiO and Fe<sub>2</sub>O<sub>3</sub> was investigated using specimens in which large grains of sintered NiO were surrounded by Fe<sub>2</sub>O<sub>3</sub> powder. The starting raw materials used for the preparation of these specimens were NiO-BDH and Fe<sub>2</sub>O<sub>3</sub>, Bayer type 1360 WF powders, whose characteristics are given in an earlier paper [6]. The NiO tablets obtained by pressing at 10<sup>3</sup> kg/cm<sup>2</sup> were sintered at 1200° C

for 2 h and then pulverised and passed through sieves to obtain a fraction with granules 200 to 300 μm in diameter. The NiO granules were then mixed with Fe<sub>2</sub>O<sub>3</sub> powder in a 20 : 80 weight ratio and the mixture homogenised. The mass was pressed using PVA as binder at 10<sup>3</sup> kg/cm<sup>2</sup> into tablets 8 mm in diameter and 10 mm thick. The tablets were air-dried and by heating at 300° C for 24 h the binder was removed from the specimens. Metallographic examination showed that the specimens were composed of large NiO grains, surrounded by Fe<sub>2</sub>O<sub>3</sub> powder. For the purpose of observing the calcination process the specimens thus prepared were fired in the temperature range 1000 to 1300° C for 1 to 7 h and then the thickness and composition of the Ni ferrite layer formed was investigated.

### 2.2. Study of the Kinetics of Formation of the Reaction Layer

The kinetics of reaction layer formation was studied by measuring the thickness of the Ni ferrite layer formed on the boundary surface of the NiO/Fe<sub>2</sub>O<sub>3</sub> phases. After keeping the specimens for a certain time at a certain temperature they were polished and the reaction layer thickness determined metallographically. The measurements were made by the method described earlier [7].

### 2.3. Study of the Change in the Chemical Composition

The reaction of nickel ferrite formation on the boundary surface of NiO and Fe<sub>2</sub>O<sub>3</sub> was investigated using an SEM-2 (AEI, Manchester UK) electron probe microanalyser. The specimens calcined from 1 to 7 h at temperatures from 1000 to 1300° C were examined on the electron probe microanalyser. To determine Fe and Ni the K<sub>α</sub> lines of these elements were used. The accelerating voltage of the electrons, which should be two to three times the excitation potential, was 20 kV, since the excitation potential of the K<sub>α</sub> line of Fe was 7.11 keV and of the K<sub>α</sub> line of Ni 8.33 keV [8]. All measurements were made with a LiF crystal and an X-ray proportional counter. X-ray photographs which show the distribution of Ni and Fe in the specimens were taken. The Ni and Fe distribution along the line intersecting the reaction layer formed on the surface of contact of NiO/Fe<sub>2</sub>O<sub>3</sub> was also photographed. The exact quantitative composition of the reaction layer was determined along this line at every 4 to 5 μm. In these measurements unreacted NiO and Fe<sub>2</sub>O<sub>3</sub> were used as the standards. The results obtained were corrected for absorption by the method of Colby [9, 10]. Evaluation of corrections for fluorescence and atomic number effect has shown that in this system they are negligible and need not be taken into account in determining the exact composition of the reaction layer.

### 3. Results and Discussion

In following the course of the reaction with the electron probe microanalyser we took the X-ray photograph which shows the distribution of the investigated element in the specimen and the distribution of each element along the line intersecting the reaction layer. Fig. 1 shows, for the specimen calcined 1 h at 1300° C, the electron photograph and the distribution of Ni along the line which on the electron photograph intersects the NiO grain and the Ni ferrite layer formed around it. Fig. 2 shows the distribution of Ni in the specimen observed. Fig. 3 shows the distribution of Fe along the line indicated on the electron photograph, while fig. 4 shows the distribution of Fe in the specimen. Specimens calcined at other temperatures and times, have the same character of Fe and Ni distribution in the specimen and along the line intersecting the reaction layer, except that the reaction layer is thicker with higher temperatures and longer

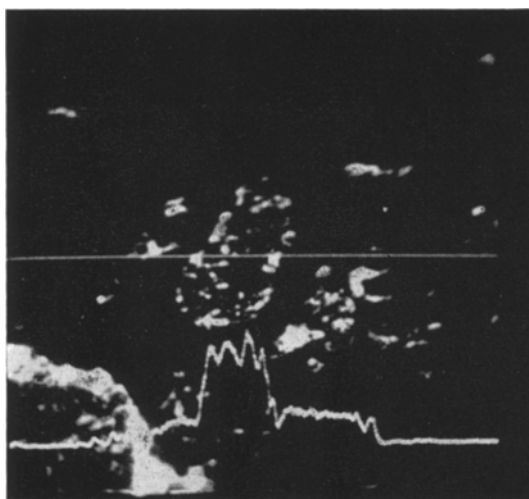


Figure 1 Electron picture and distribution of Ni along the line ( $\times 200$ ).

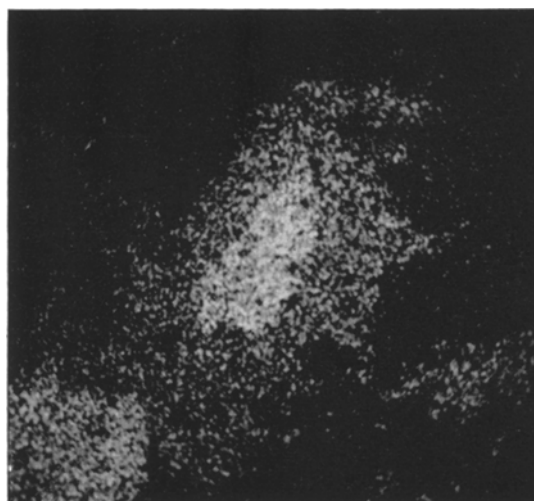


Figure 2 Distribution of Ni in the specimen.

times. All specimens show changes in composition along the reaction layer, as is apparent in figs. 1 and 3. In order to determine this change in Ni and Fe content along the reaction layer on all the specimens investigated we determined the concentration of Ni and Fe along the indicated lines at intervals of 4 to 5 μm. This measurement has shown that the reaction layer has fixed but different equilibrium concentrations at the NiO and Fe<sub>2</sub>O<sub>3</sub> interfaces respectively with a continuous change in concentration from one interface to the other. In the case of samples calcined

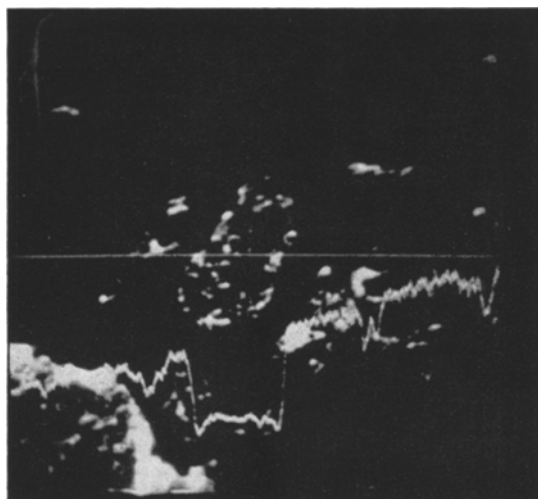


Figure 3 Electron picture and distribution of Fe along the line ( $\times 200$ ).

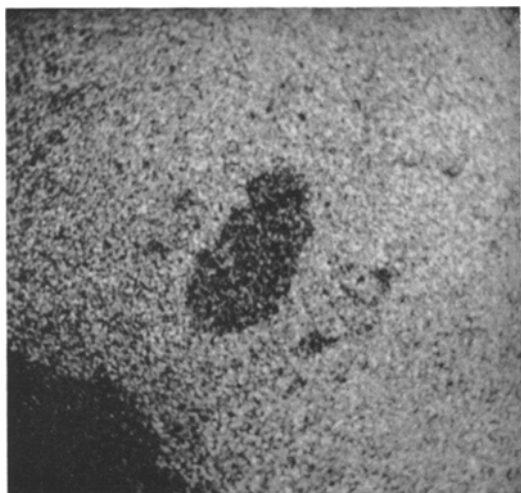


Figure 4 Distribution of Fe in specimen.

at the same temperature these concentrations did not change with time, which shows that at any temperature, an equilibrium composition of the layer is established in contact with the  $\text{Fe}_2\text{O}_3$  or NiO phase. The value of these equilibrium concentrations for various temperatures, expressed in molar percentages, are given in table I.

If we take these values to plot a curve for the composition of the interfaces versus temperature, we obtain a diagram as shown in fig. 5 which is, actually, part of the phase diagram of the system NiO/ $\text{Fe}_2\text{O}_3$  which corresponds to the

TABLE I Concentration of Fe in Ni ferrite on the boundaries of the reaction layer.

	1100° C	1150° C	1200° C	1300° C
Boundary NiFe <sub>2</sub> O <sub>4</sub> /NiO	53.0	53.1	52.9	54.0
Boundary NiFe <sub>2</sub> O <sub>4</sub> /Fe <sub>2</sub> O <sub>3</sub>	57.0	57.2	59.4	71.7

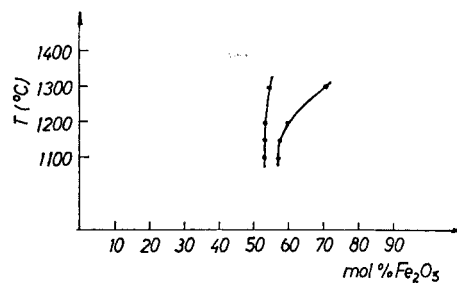


Figure 5 Boundary composition of Ni ferrite layer for various temperatures.

temperature range 1100 to 1300° C and the range of concentrations corresponding to the spinel structure. The diagram shows that the composition of Ni ferrite at the surface of contact with NiO is almost independent of temperature, while at the surface of contact with  $\text{Fe}_2\text{O}_3$  it considerably changes with temperature because of the increased dissolution of  $\text{Fe}_2\text{O}_3$  in the spinel with increasing temperature. The plot shown in fig. 5 is in good agreement with the phase diagram which Greifer [11] gave for this system.

In our experiments the kinetics of the reaction were followed by measuring the thickness of the reaction product as a function of time and temperature. Values of the thickness of the Ni ferrite layer formed by reaction of NiO and  $\text{Fe}_2\text{O}_3$  on the boundary surface of these phases are given in table II. A plot of the logarithm of the layer thickness versus calcination time at

TABLE II Thickness (in  $\mu\text{m}$ ) of reaction layers as a function of temperature and time.

Temperature (° C)	Time (h)				
	1	2	3	5	7
1100	12	17	21	29	32
1150	22	34	38	52	65
1200	37	50	65	80	100
1300	85	103	110	118	—

various temperatures gives a straight line (fig. 6). From this plot it may be concluded that the

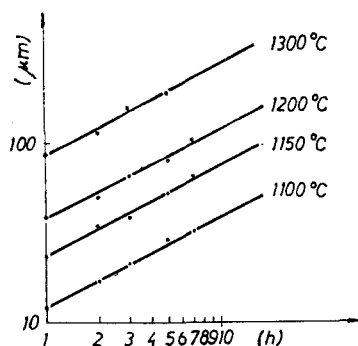


Figure 6 Layer thickness of Ni ferrite versus time for various temperatures.

thickness of the reaction layer in Ni ferrite formation increases according to the equation

$$x = (kt)^n \quad (1)$$

where:  $x$  = reaction layer thickness in  $\mu\text{m}$ ;  $k$  = rate constant of layer thickness for a given temperature;  $t$  = calcination time in hours;  $n$  = time exponent.

In our experiments, the time exponent obtained from the slope of the curves in fig. 6 is constant, i.e. 0.5. The rate constants of layer thickness obtained from the intercept on the ordinate for  $t = 1$  are plotted versus the reciprocal of temperature in fig. 7. This shows that  $\log k$  is rectilinear versus  $1/T$ , i.e. the temperature-dependence of the rate constant for the calcination process follows the Arrhenius equation:

$$k = k_0 e^{-Q/RT} \quad (2)$$

A value of 80 kcal/mol was obtained for the energy of activation and  $1.47 \times 10^4 \text{ cm}^2/\text{sec}$  for the pre-exponential factor so that the law of Ni ferrite reaction layer growth may be expressed by the equation.

$$x^2 = 1.47 \times 10^4 e^{-\frac{80000}{RT}} t \quad (3)$$

This equation is in accordance with that obtained by Economos and Clevenger in their studies of the rate of increase of the reaction layer in the NiO/Fe<sub>2</sub>O<sub>3</sub> system [1]. It should be emphasised that the obtained activation energy can be only considered as the experimental value. Comparison of the obtained activation energy with the values given for the diffusion of Fe<sup>3+</sup> or Ni<sup>2+</sup> in the spinel phase [12, 13] can hardly show whether the control process is Fe<sup>3+</sup> or Ni<sup>2+</sup> diffusion. The conditions of diffusion in

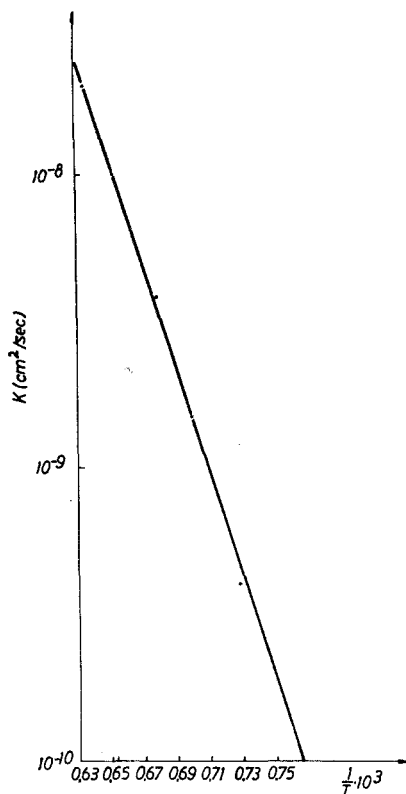


Figure 7 Rate constant of Ni ferrite formation versus temperature.

the reaction layer differ considerably from those in the investigation of self-diffusion of Fe<sup>3+</sup> or Ni<sup>2+</sup> in NiFe<sub>2</sub>O<sub>4</sub>.

From these results it may be concluded that initially at phase contact between NiO and Fe<sub>2</sub>O<sub>3</sub>, Ni-ferrite is formed whose composition corresponds to that of the layer on the boundary towards NiO. In our experiments (1100 to 1300°C) this value is 53 to 54 mol % Fe<sub>2</sub>O<sub>3</sub>, which at low temperatures probably approaches the composition with 50 mol % Fe<sub>2</sub>O<sub>3</sub>. The layer thus formed has two interfaces on which chemical reaction takes place. On the side towards NiO, a layer whose composition corresponds to the left side of the diagram in fig. 5 is formed, while on the side towards Fe<sub>2</sub>O<sub>3</sub>, a layer forms whose composition corresponds to the right side of the diagram in fig. 5, i.e. a ferrite richer in Fe<sub>2</sub>O<sub>3</sub>. With increase in the thickness a layer is formed whose composition is not constant but it is a continual transition of the composition from one interphase boundary to the other. Therefore, diffusion of Ni and Fe through the reaction layer proceeds under the condition of a concentration

gradient which will influence the speeds of these elementary processes and, therefore, the rate of the reaction of Ni-ferrite formation.

The formation of a solid solution of  $\text{Fe}_2\text{O}_3$  in the spinel phase causes the formation of cation vacancies in both octahedral and tetrahedral positions of the spinel lattice. This considerable increase in the number of vacancies also accelerates the diffusion by the vacancy mechanism because the probability of exchange of cations with vacancies increases. We must point out that for the purpose of maintaining electroneutrality in the case of immobile anionic lattice, the migration of 3  $\text{Ni}^{2+}$  in one direction causes diffusion of 2  $\text{Fe}^{3+}$  in the other. Based on this fact Wagner [14] developed his well-known hypothesis on the mechanism of ferrite formation which necessitates a three times faster increase in the reaction layer thickness on the side of  $\text{Fe}_2\text{O}_3$  than on the side of NiO in relation to the given original interface. However, we consider that because of the formation of solid solutions this ratio does not hold for the course of the reaction because the  $\text{NiFe}_2\text{O}_4$  formed on the side of  $\text{Fe}_2\text{O}_3$  dissolves a considerable amount of  $\text{Fe}_2\text{O}_3$  which causes further increase in the reaction layer thickness. Hence, it may be concluded that in the case of equivalent amounts of  $\text{Fe}_2\text{O}_3$  and NiO,  $\text{Fe}_2\text{O}_3$  will disappear much earlier than NiO which also points to the problems which arise in the investigation of the kinetics of the reaction rate. This is that different kinetic characteristics of reaction are obtained, if the reaction is followed through the disappearance of  $\text{Fe}_2\text{O}_3$  or NiO, or through the formation of the reaction product. This particularly holds in those cases in which the reaction is observed at high temperatures through the change of the magnetic characteristics in which case the formation of pure  $\text{NiFe}_2\text{O}_4$  is usually assumed. However, it is certain that in the case of the formation of a series of solid solutions the magnetic properties of the reaction product change in comparison with pure  $\text{NiFe}_2\text{O}_4$ , so that the results obtained cannot give the right picture regarding the rate of reaction.

In accordance with the preceding discussion, equation 3, which gives the dependence of the reaction layer growth on temperature and time, may actually be considered as experimental. Simultaneous development of the reaction and dissolution of  $\text{Fe}_2\text{O}_3$  involve difficulties in the theoretical interpretation of the equation  $y = (kt)^n$ . The experimentally obtained value for the exponent  $n$  ( $n = 2$ ) may lead to the con-

clusion that diffusion is the control process, which is quite acceptable, since the dissolution of  $\text{Fe}_2\text{O}_3$  is also a diffusional process. However, as already mentioned, no definite theoretical explanation for the activation energy can be presently given because of the nonhomogeneity of the reaction product.

#### 4. Conclusion

The study of the kinetics of Ni ferrite formation has shown that the layer thickness of the ferrite formed can be expressed by the equation

$$x^2 = kt$$

where  $k = 1.47 \times 10^4 e^{-\frac{80000}{RT}}$ .

Analysis of the composition of the reaction layer with an electron probe microanalyser has shown that Ni ferrite of a fixed composition is first formed on the initial boundary surface of the NiO and  $\text{Fe}_2\text{O}_3$  phases. The further increase in the thickness of this layer proceeds by chemical reactions on both sides of this layer, in which case Ni ferrite of the initial composition is formed on the side towards NiO, while on the side towards  $\text{Fe}_2\text{O}_3$  a ferrite richer in  $\text{Fe}_2\text{O}_3$  is formed. Diffusion of Ni and Fe through the reaction layer continually proceeds under conditions of the concentration gradient.

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