EXPERIMENTAL STUDIES ON THE PELLET-PELLET SYSTEM CuO-Fe$_2$O$_3$

4.1 INTRODUCTION

In this Chapter the experimental results obtained on the system CuO-Fe$_2$O$_3$ are reported. To start with, a few experiments were carried out with different systems to examine the feasibility of using these systems for verification of the model developed in Chapters 2 and 3. The systems studied were: succinic anhydride-m-nitroaniline, succinic anhydride-urea, Cu(I)thiocyanate-thiourea, CuO-Cr$_2$O$_3$, Bi$_2$O$_3$-MoO$_3$, BaSO$_4$-ZnS, CuO-Ni$_2$O$_3$ and CuO-Fe$_2$O$_3$.

Basically the system should be free of complications like presence of gaseous product, change in weight during reaction, structural changes, appearance of amorphous phases, etc. These factors were examined using differential thermal analysis (DTA), thermogravimetric analysis (TGA), X-ray diffraction, microscopy and electron probe microanalysis (EPMA).

Another important criterion used in the choice of a system was that it should satisfy the assumptions made in the theoretical development. The major assumption is that of one-way diffusion.
Based on the above tests and the information available in the literature, the system CuO–Fe₂O₃ was chosen for further analysis. Concentration profiles for the system were obtained by EPMA, and the model developed earlier was tested with these data.

4.2 EXPERIMENTAL

4.2.1 Materials and their properties

(a) Copper oxide

Analytical grade cupric oxide (CuO) powder was obtained from REACHIM (USSR) with maximum impurity percentage of 0.445. The DTA of this powder showed a small exothermic peak at around 400°C; it also showed a slight increase in weight at 600°C. The increase in weight was probably because of the presence of trace quantities of cuprous oxide. The powder was, therefore, calcined at 800°C in atmospheric air for 24 hours. This was then cooled and ball milled for three days using porcelain balls to obtain a very fine powder. The DTA of this powder showed a constant weight up to about 1020°C. The X-ray pattern of the powder showed sharp diffraction lines indicating a purely crystalline material. Absence of cuprous oxide was also confirmed by chemical analysis.
(b) Iron oxide

Ferric oxide (α-Fe₂O₃) powder was obtained from Robert Johnson. The powder was calcined at 1000°C for 24 hours in air, cooled, and ball milled for three days using porcelain balls. The stability and crystallinity of this powder was confirmed by DTA/TGA and X-ray diffraction studies. Absence of ferrous ions in the sample was confirmed by chemical analysis.

4.2.2 The system CuO-Fe₂O₃

The phase diagram of the system CuO-Fe₂O₃ has been presented by Yamaguchi (1966). The diagram shows that up to 1000°C, only the spinel CuFe₂O₄ is formed throughout the range of compositions. Above 1015°C, CuO reacts with the spinel to give CuFeO₂. Also, at about 1026°C, CuO starts decomposing, giving cuprous oxide Cu₂O. Thus, the reaction between CuO and Fe₂O₃ to give CuFe₂O₄ can be safely carried out below 1000°C.

Kinetic studies on the formation of copper ferrite from the reactants in mixed powder form have been reported by Saull et al (1970). In these studies, Saull et al found that a significant difference exists between calcined and uncalcined ferric oxide. However, pellet-pellet studies on
Navrotsky and Kleppa (1968), in their studies on the thermodynamics of formation of simple spinels, have reported data on the system CuO-Fe₂O₃. The spinel CuFe₂O₄ was prepared by ceramic technique. The recommended conditions are: temperature 900°C and time 90 hours. They obtained the heat of formation of CuFe₂O₄ at 970°C as

\[ \Delta H_{970} = +5.05 \pm 0.20 \text{ kcal/mole.} \]

This shows that the reaction is slightly endothermic. In fact, from the whole range of spinels investigated, copper spinels in general were found to have typically positive enthalpies of formation. This has been explained on certain structural grounds - copper ferrite has an inverse spinel structure.

In view of the above discussion, actual experiments were carried out at 950°C (isothermal) in air.

4.2.3 EPMA studies

Sample preparation

The fine cupric oxide powder obtained by the procedure described above was pressed in the form of pellets using a hand-operated hydraulic press at a pressure of about 4 tons. The pellets thus obtained were sufficiently hard. They were 11 mm in diameter and 5 mm in height.
Following a similar procedure ferric oxide pellets of the same dimensions were prepared.

The pellets were then sintered at a specified temperature to eliminate the porosity. Thus, the cupric oxide pellets were sintered at just below 1000°C for 3 days in an electric furnace. The ferric oxide pellets were similarly sintered at 1100°C.

The flat faces of the sintered pellets were then polished. The following procedure was adopted for polishing:

(i) Initially, grinding was done on silicon carbide papers, first with 400 and then with 600 paper (the number indicates the mesh size of the coated SiC powder) using a foamless detergent solution as vehicle.

(ii) The grinding was followed by polishing on a polishing machine with a chamois leather base and successively using 600, 900 and 1800 mesh silicon carbide powder. Ethyl alcohol was used as vehicle.

(iii) Further polishing was done using a slurry of alumina powder of 1 micron particle size in water.

(iv) Final polishing was achieved with diamond paste of 0.5 micron size using again ethyl alcohol as vehicle. During the polishing operation, to facilitate a firm grip
on the pellets, they were encapsulated in wax.

The polished faces were observed under a microscope. They had a roughness of less than 1 micron. The pellets were then cleaned in an ultrasonic cleaner using various solvents.

The cleaned pellets were annealed in a tube furnace at 950°C for 12 hours to eliminate any defects introduced due to cold work during polishing. Pairs were prepared for carrying out reaction by placing the polished faces of CuO and Fe₂O₃ pellets in contact in each case. Each pair was held in perfect contact by wedging it tightly into a stainless steel holder, shown in Figure 4.1(a). Pieces of platinum foil were placed on the top and the bottom of the pair to avoid direct contact with the holder.

The holders containing the reactant pairs were then kept one by one in a tube furnace preheated to 950°C. The temperature was monitored by a chromel-alumel thermocouple connected to a calibrated potentiometer through a cold junction. The furnace was maintained at a constant temperature of 950±5°C with the help of a Sunvic Platinum resistance temperature controller and a voltage stabiliser. The platinum sensing element of the controller was inserted in the furnace along with the thermocouple, so that the
(a) STAINLESS STEEL PELLET HOLDER ASSEMBLY

(b) SCHEMATIC DIAGRAM SHOWING THE EXPERIMENTAL SET-UP

(c) SKETCH OF A SAMPLE ENCAPSULATED IN ARALDITE FOR EPMA ANALYSIS

FIGURE 4.1
temperature at the same position could be sensed by both of them. A constant temperature zone of about 6 inches within the furnace was obtained; hence along the holder length no temperature gradient was present. The complete set-up is shown schematically in Figure 4.1(b).

At the end of the specified time interval the holder was pulled out of the furnace by means of a wire tied to it and was quenched in air.

On cooling, the CuO and Fe₂O₃ pellets easily separated in each case. Product formation could be visually observed on the reacted faces of Fe₂O₃ pellets, but this was not observed in the case of CuO pellets.

The pellets were cut along the axis on a diamond wheel. The cut pieces were then encapsulated in an Araldite mould, with the cut faces exposed on one side of the mould. The moulds were 1 inch in diameter and 5 mm thick; this size was chosen on the basis of the holder size in the EPMA instrument to be used. The exposed faces along with the mould were polished following the procedure described earlier in this section. The sample thus prepared is illustrated in Figure 4.1(c).
Scanning with EPMA

The polished samples were coated with a thin layer of silver paint to get a conducting contact. A CAMECA Electron Probe Micro Analyser, Model MS 46 (at the Defence Metallurgical Research Laboratory, Hyderabad) was used for the analysis. On the silver coated surface a narrow electron beam was scanned perpendicularly to the reaction interface. For both Cu and Fe, Kα intensities were used. The accelerating voltage was 25 KV, the take off angle 18°, and the sample current 50 nA. With a counter and a recorder connected to the analyser, concentration profiles along the width of the sample were obtained.

The concentration profiles of Cu within the Fe₂O₃ pellet after 24 and 48 hours of reaction at 950°C are shown in Figure 4.2. A number of trial experiments had to be conducted (to eliminate practical difficulties) before getting the final results. Because of this and particularly due to the nonavailability of the instrument, more results could not be obtained. The model was therefore tested with the data for 24 and 48 hours only.

4.3 RESULTS AND DISCUSSION

In the CuO samples examined no Fe profile could be
EXPERIMENTAL CONCENTRATION PROFILES OF Cu IN Fe₂O₃ AT 950°C AS OBTAINED FROM EPMA STUDIES

FIGURE 4.2
detected, whereas in the Fe$_2$O$_3$ samples Cu profiles were obtained. Within the product layer, no concentration gradient was observed. Thus, the system fulfills the two basic assumptions of the model, viz. (i) absence of diffusional resistance in the product layer, and (ii) one-way diffusion.

4.3.1 Steady state model

The procedure for predicting the concentration profile of the steady state model has already been described in Section 2.3. Now, the apparent reaction zone thickness value corresponding to the concentration profile for 24 hours is $\Delta z = 0.3$. Using Equation 2.17 the value of $\varphi_r$ for $\Delta z = 0.3$ is found: $\varphi_r = 10$. Hence, from Equation 2.14, taking $\omega_p = 1$, values of $\omega$ for different values of $z$ are computed and plotted in Figure 4.3. The experimental profile is also shown in the figure for comparison. The profiles show a reasonably good match. This is also true for the case of 48 hours (figure not shown).

It may be noted that the agreement between the experimental and predicted profiles is not as good in this case as for some of the reported systems used for testing the model in Chapter 2. This may be because steady state was already established in those cases; here it is obviously not so.
COMPARISON OF THE THEORETICAL PROFILE CALCULATED FROM THE STEADY STATE MODEL WITH THE EXPERIMENTAL PROFILE OBTAINED FROM EPMA STUDIES (FOR THE SAMPLE OF 24 HOURS)

FIGURE 4.3
4.3.2 Unsteady state model

A method has been described in Section 3.3 for obtaining the diffusivity \((D)\) and rate constant \((k)\) values from the concentration profiles obtained by EPMA. The \(D\) and \(k\) values thus obtained can be used to predict concentration profiles.

Since the limit of detectability in the present case could not be determined precisely, the alternative method suggested in Section 3.3 was used here. Accordingly the plot for \(\omega_m = 0.5\) shown in Figure 3.4 was used. The method can be summarised as follows:

(1) A rate constant value was assumed. Hence for the two times, \(m_3\) values were computed, since \(m_3 = \sqrt{kt}\).

(2) From the plot in Figure 3.4, the corresponding values of \(m_2\) were obtained.

(3) From the \(m_2\) values thus obtained, \(D\) values in the two cases were computed using the relation

\[
D = \frac{x_{0.5}}{m_2 \sqrt{t}}
\]

where \(x_{0.5}\) is the distance at which \(\omega_m = 0.5\).
The difference between the $D$ values thus obtained for two times was minimised by trials at several values of $k$. The procedure was programmed on a MOSCAL 1080 PS programmable calculator. The best values of $k$ and $D$ thus obtained are: $k = 1 \times 10^{-7} \text{ sec}^{-1}$ and $D = 1.0689 \times 10^{-9} \text{ cm}^2 \text{ sec}^{-1}$.

Using these values of $k$ and $D$, concentration profiles were predicted. These are shown in Figure 4.4 along with the experimental profiles. The plots show remarkably good match. The deviation towards the end is likely to be due to the limit of detectability of the instrument for the system studied. In fact, from the theoretical plot, the limit of detectability value can be determined.
COMPARISON OF THE THEORETICAL PROFILES COMPUTED FROM THE UNSTEADY STATE MODEL WITH THE EXPERIMENTAL PROFILES OBTAINED FROM EPMA STUDIES

FIGURE 4.4