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KINETICS OF THE REACTION IN Cu–Fe AND Cu–Cr MIXED OXIDES

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ABSTRACT

The kinetics of the copper ferrite and copper chromite spinel formation reactions were followed in the temperature range 500–800 °C. Kinetic analysis of fractional reaction-time data showed that the reactions are best described by the two-dimensional (D_2), Jander's (D_3) and Ginstling–Brounshtein (D_4) diffusion equations. The activation energies calculated according to these models were found to be model-independent and have the values 59.0 ± 1.5 and 97.6 ± 3.5 kJ mol^{-1} for the $CuFe_2O_4$ and $CuCr_2O_4$ formation reactions, respectively.

INTRODUCTION

Binary oxides are well known as catalysts in various industries. At high temperatures over long periods of time, they form spinel oxides. Spinels represent a large class of inorganic materials which possess many important properties not found in the more limited binary oxides. The study of the kinetics and mechanism of the reaction between MgO and Al_2O_3 to form $MgAl_2O_4$ (spinel) was reported by Carter [1] and Rossi and Fulrath [2]. Branson [3] studied the kinetics of the reaction between ZnO and Al_2O_3 using X-ray diffraction and found that the activation energy of $ZnAl_2O_4$ formation is 226.8 kJ mol^{-1} according to the diffusion-controlled reaction and 120.1 kJ mol^{-1} according to the phase boundary reaction. Diefallah et al. [4] studied the kinetics of the $MgFe_2O_4$ formation reaction in powdered mixtures of MgO and Fe_2O_3 with different mole ratios and the results were discussed in terms of Jander's diffusion equation.

In general, solid state reactions have shown a considerable diversity of mechanisms and there are a variety of factors which may control, determine, influence or modify the rate-limiting process [5]. Solid state reactions showing deceleratory fractional reaction (α)–time (t) curves have been classified according to [6–9] product growth controlled by diffusion through a continuous product layer, product growth controlled by phase boundary reac-

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tions, and the concept of an order of reaction. Sigmoid α–t curves have been discussed with respect to the Avrami–Erofeev equations for initial random nucleation followed by overlapping growth or from the point of view of the Prout–Tompkins equation for branching nuclei. A comparison of the α–t curves, measured for a particular reaction, with theoretical expressions derived for appropriate nucleation and growth models, has been used as evidence for the identification of the geometry of interface advance. This method has been widely used and has yielded important mechanistic information [8].

In the present study, the kinetics of the solid-state copper ferrite and copper chromite spinel formation reactions in powdered mixtures of CuO–Fe_2O_3 and CuO–Cr_2O_3, respectively, were followed in the temperature range 500–800 ° C, using a titrimetric technique. The results were discussed in view of the known mathematical expressions theoretically derived for various phenomenological models [6–9].

EXPERIMENTAL

Pure and mixed (1 : 1 mole ratio) hydrated oxides were obtained by precipitation and co-precipitation with ammonia from aqueous solutions of the AnalaR salt chlorides. The fine precipitates were filtered, washed with distilled water until free of chloride ion and dried at 110 ° C to a constant weight.

The spinel formation reactions were carried out in a muffle furnace in air under isothermal conditions in the temperature range 500–800 ° C. Samples were calcined for different durations of time at the desired temperature, then cooled to room temperature and chemically analysed. A titrimetric method which depends on dissolving the unreacted CuO in a solution of NH_4Cl, then titration with standard versene solution and using murexide indicator, was used to follow the rate of reaction. From the weight of the unreacted CuO in the sample, the weight fraction (α) of the reacted CuO was calculated. X-ray diffraction patterns of CuO–Fe_2O_3 and CuO–Cr_2O_3 reaction mixtures showed the progressive formation of $CuFe_2O_4$ and $CuCr_2O_4$ during the course of the reaction.

RESULTS AND DISCUSSION

The fractional reaction completed as a function of time has been analysed from the point of view of the solid state reaction models (listed in Table 1) based on product growth controlled by phase boundary reactions, product growth controlled by diffusion through a continuous product layer and nucleation-growth models [6–9]. Figures 1 and 2 show α–t curves obtained

TABLE 1

Kinetic equations examined in this work

Reaction model	$g(\alpha)$	Function symbol
One-dimensional diffusion	α^2	D_1
Two-dimensional diffusion	$\alpha + (1-\alpha)\ln(1-\alpha)$	D_2
Jander equation, three-dimensional diffusion	$[1-(1-\alpha)^{1/3}]^2$	D_3
Ginstling–Brounshtein equation, three-dimensional diffusion	$(1-\frac{2}{3}\alpha)-(1-\alpha)^{2/3}$	D_4
Two-dimensional phase boundary reaction	$[1-(1-\alpha)^{1/2}]$	R_2
Three-dimensional phase boundary reaction	$[1-(1-\alpha)^{1/3}]$	R_3
First-order kinetics	$[-\ln(1-\alpha)]$	F_1
Random nucleation: Avrami equation	$[-\ln(1-\alpha)]^{1/2}$	A_2
Random nucleation: Erofeev equation	$[-\ln(1-\alpha)]^{1/3}$	A_3

for the formation reactions of $CuFe_2O_4$ and $CuCr_2O_4$ spinels, respectively. It is evident that the spinel yields increase with temperature of calcination and that the curves do not have a sigmoid shape. Data obtained with α-values of less than 0.7 were analysed according to the functions listed in Table 1 and the results showed that the best fit of the data is obtained with the three-dimensional diffusion-controlled, Jander's equation (D_3 function) and with the two-dimensional diffusion (D_2 function) and, to a lesser extent,

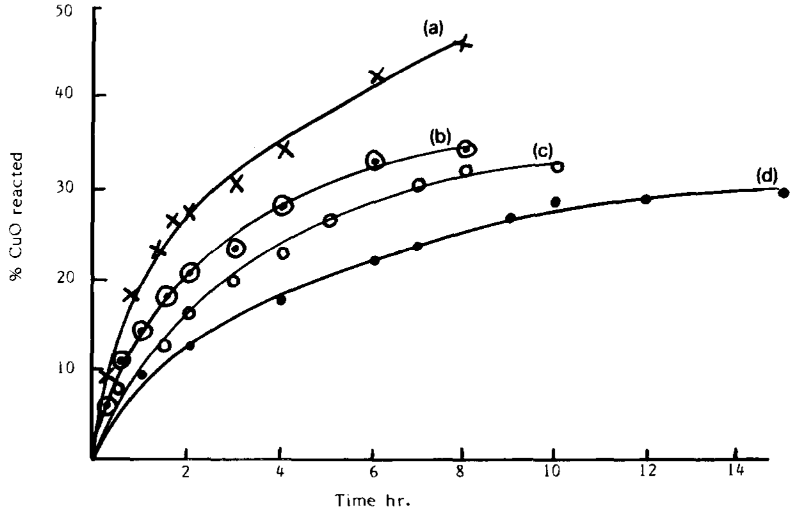

Fig. 1. Isothermal α-t curves for $CuFe_2O_4$ spinel formation: a, 810 °C; b, 750 °C; c, 710 °C; d, 610 °C.

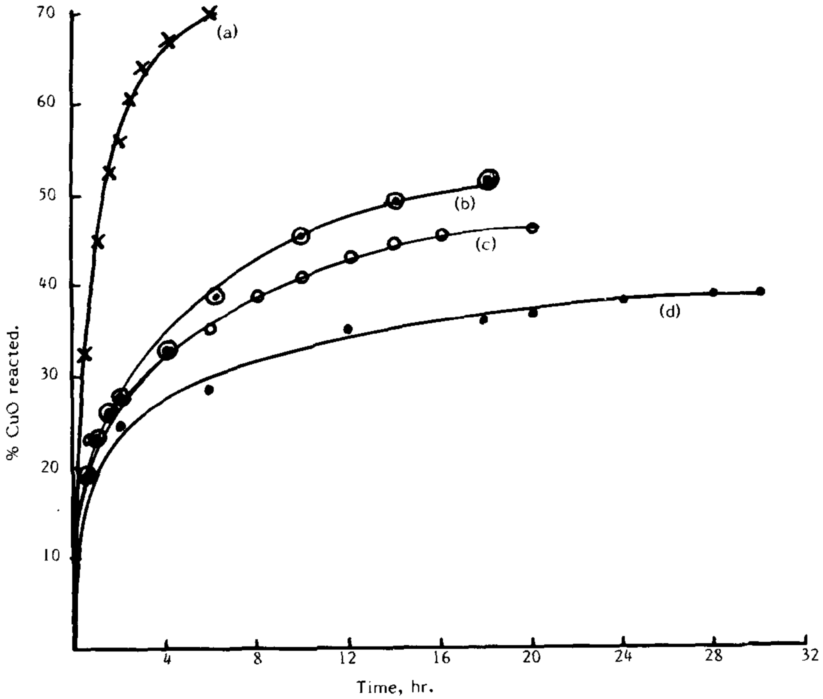

Fig. 2. Isothermal α-t curves for $CuCr_2O_4$ spinel formation: a, 800 °C; b, 640 °C c, 600 °C; d, 550 °C.

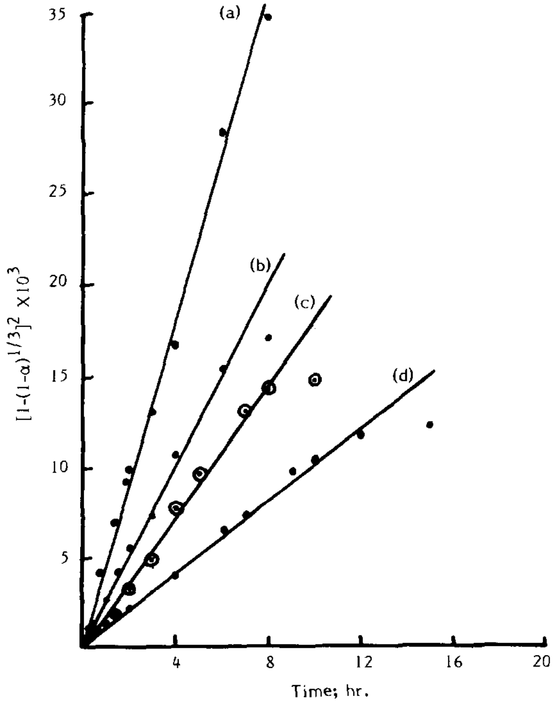

Fig. 3. Formation of $CuFe_2O_4$ according to Jander's diffusion model: a, 810 °C; b, 750 °C; c, 710 °C; d, 610 °C.

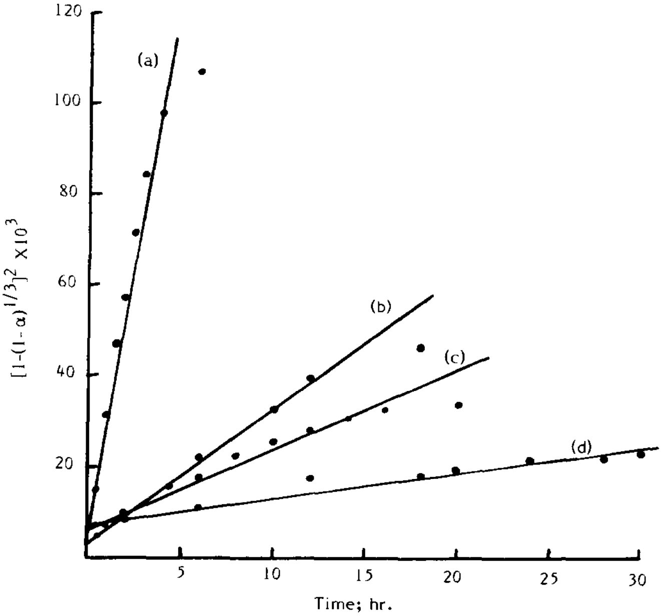

Fig. 4. Formation of $CuCr_2O_4$ according to Jander's diffusion model: a, 800 °C; b, 640 °C; c, 600 °C; d, 550 °C.

with the Ginstling–Brounshtein three-dimensional diffusion-controlled equation (D_4 function). The phase boundary and growth models gave a less satisfactory fit. Figures 3 and 4 show the fit of data according to Jander's diffusion equation.

Activation energies were calculated from the temperature dependence of the rate constants on the basis of diffusion-controlled reactions and the results are shown in Table 2. The average activation energy for the $CuFe_2O_4$ formation reaction is 0.62 ± 0.02 eV, whereas for $CuCr_2O_4$ spinel formation, it is 1.01 ± 0.04 eV. The Pauling empirical ionic radii are 0.69 and 0.64 Å for Cr^{III} and Fe^{III} ions, respectively. Carter [1] showed that in the reaction between Fe_2O_3 and MgO, $MgFe_2O_4$ is formed by counter-diffusion of Mg^{2+}

TABLE 2

Activation energies of $CuFe_2O_4$ and $CuCr_2O_4$ spinel formation reaction, calculated on the basis of diffusion models

Kinetic model	$CuFe_2O_4$		$CuCr_2O_4$	
	E_a (kJ mol^{-1})	r	E_a (kJ mol^{-1})	r
D_2	58.0	0.983	94.1	0.998
D_3	60.9	0.979	101.1	0.999
D_4	59.4	0.983	96.5	0.999

and Fe^{3+} through a relatively rigid oxygen lattice. It was found that the ratio of ferrite formed on the MgO side of the initial interface to that on the Fe_2O_3 side was 1 : 2.7, which was considered consistent with the diffusion of Fe^{3+}. The smaller Fe^{III} ions relative to Cr^{III} ions results in a lower energy of activation for diffusion of Fe^{III} in the $CuO-Fe_2O_3$ system than that of Cr^{III} in the $CuO-Cr_2O_3$ system.

The activation energies of solid-state reactions could vary between relatively large limits depending on the nature and the method of preparing the starting materials. For the ferrite formation reaction in the Fe_2O_3-MgO system, the activation energy decreases from 1.24 to 0.56 eV when the percentage of Fe_2O_3 in the sample increases from 20 to 80 wt.% [4]. Wuensh and Vasilos [10] reported a value of 1.8 eV as an activation energy for iron diffusion, while Shelly et al. [11] reported 2.06 eV and Chen and Peterson [12] reported 1.26 eV. In the present study, heating the mixed hydroxides produces numerous vacancies and cavities which in turn facilitate the diffusion process and lowers the activation energy of the reactions.

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