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A Study of the Formation of $CuAl_2O_4$ from CuO and Al_2O_3 by Solid State Reaction at 1000°C and 950°C

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With 3 Figures

Abstract. The formation of the spinel $CuAl_2O_4$ from the oxides CuO and Al_2O_3 has been studied at 1000 and 950°C in air by measuring the fraction reaction completed as a function of time. In the experiments the molar oxide ratios were $CuO/Al_2O_3 = 0.5, 1.0$ and 2.0 and the grain size for CuO was 1–3 μ throughout while for Al_2O_3 fractions of 40–60 μ, 71–100 μ and 100–125 μ, were used. The rate of reaction could be explained quite well assuming a three-dimensional diffusion mechanism.

Über die Bildung von $CuAl_2O_4$ aus CuO und Al_2O_3 durch Reaktion im festen Zustand bei 1000 und 950°C

Inhaltsübersicht. Die Bildung des Spinells $CuAl_2O_4$ aus den Oxiden CuO und Al_2O_3 ist bei 1000 und 950°C in der Luft untersucht worden. Die Umsetzung der Oxide in Spinell wurde als Funktion der Zeit gemessen. Während der Experimente waren die Molbrüche $CuO/Al_2O_3 = 0{,}5$, 1,0 und 2,0. Die Korngröße des CuO war durchgehend 1–3 μ, dagegen wurden für Al_2O_3 folgende Fraktionen verwendet: 40–60 μ, 71–100 μ und 100–125 μ. Die Reaktionsgeschwindigkeit konnte unter der Annahme eines Diffusionsmechanismus erklärt werden.

Introduction

Pure Al_2O_3 in sintered form is very often used in high temperature studies as a resistent material, e. g. in tubes, crucibles and vessels. Despite its frequent use in high temperature work, from a thermodynamic point of view Al_2O_3 is in fact not stable in contact with many metal oxides. In other circumstances a rapid reaction is desired between Al_2O_3 and the metal oxide, e. g. in forming various spinels. Whatever the case, it is desirable to know more about the factors which influence the speed of reaction between Al_2O_3 and metal oxides.

Because of our interest in various Cu-systems ¹)²) it was natural to choose CuO as the metal oxide component in this connection. At temperatures

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¹) G. Eriksson and E. Rosén, Acta polytechn. scand., Chem. includ. Metallurgy Ser. 99, 3 (1971).

²) G. Eriksson and E. Rosén, Scand. J. Met. 2, 95 (1973).

below 1026 °C and in air the product formed is the spinel $CuAl_2O_4$[3]. In the present investigation of the formation of $CuAl_2O_4$ from the oxide components Al_2O_3 and CuO, the influence of temperature, particle size and ratio of initial oxides was studied and the rate controlling reaction mechanism was established.

A limited study of this reaction was earlier performed by STONE and TILLEY[4] at 900 and 960 °C.

Experimental

Method. To determine the fraction of conversion of the oxide components CuO and Al_2O_3 to $CuAl_2O_4$, the "single-pellet technique" was used. The samples were prepared by carefully mixing the oxides and pressing to form pellets. The pellets were placed in alumina crucibles and put into a furnace kept at 1000 or 950 °C. After various reaction times a pellet was removed and quenched, finely ground and, finally, the amount of unreacted CuO was determined by electrolytic Cu-determination in the solution obtained by dissolving the residual CuO in dilute acid.

Chemicals. The starting materials, CuO (Merck, p. a.) and Al_2O_3 (Fischer, p. a.) were heated 24 hours at 1000 °C and 120 hours at 1200 °C respectively. To establish the cell parameters, powder photographs were taken with $CuK_{\alpha 1}$-radiation in a GUINIER-HÄGG type camera ($\lambda = 1.54051$ Å) with $Pb(NO_3)_2$ (a = 7.8575 Å) as internal standard. The cell parameter values obtained at 25 °C are: for CuO (with monoclinic symmetry) a = 4.6886(3) Å, b = 3.4231(2) Å, c = 5.1037(4) Å, $\beta = 99.574(6)°$ and for Al_2O_3 (with hexagonal symmetry) a = 4.7606(4), c = 12.9970(16). These parameter values are in good agreement with corresponding values given in the literature[5][6].

To check which phases are formed in the reaction, pure $CuAl_2O_4$ was also prepared and investigated by powder X-ray. The spinel $CuAl_2O_4$ was synthesized by the intimate mixing of CuO and Al_2O_3 in the required proportions and heating the pellets at 1000 °C for about 100 hours with several intermediate grindings. A slight excess of CuO was used and then removed by dissolution in dilute nitric acid. The observed values of $\sin^2 \Theta$ and of relative intensities, I, are given in Table 1.

The intensities were visually estimated following the 6-fold scale: ss = very strong, s = strong, m = medium, w = weak, vw = very weak, vvw = extremely weak. In Table 1 are also given the calculated quantities d_{calc} and $\Delta = (\sin^2 \Theta_{obs} - \sin^2 \Theta_{calc})$. The cell parameter value obtained was a = 8.0788(2) Å, in excellent agreement with the value a = 8.078 ± 0.001 Å recently given by COOLEY and REED[7].

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[3] A. M. M. GADALLA and J. WHITE, Trans. Brit. ceram. Soc. **63**, 39 (1964).

[4] F. S. STONE and R. J. D. TILLEY, Reactivity of Solids, G.-M. SCHWAB (ed.), 5th Intern. Symposium, Munich 1964.

[5] S. ÅSBRINK and L.-J. NORRBY, Acta crystallogr. [Copenhagen] **B 26**, 8 (1971).

[6] J. P. JAN, S. STEINEMANN and P. DINICHERT, Physics and Chemistry of Solids **12**, 349 (1960).

[7] R. F. COOLEY and J. S. REED, J. Amer. ceram. Soc. **55**, 395 (1972).

Table 1 X-ray powder diffraction data for $CuAl_2O_4$ at 25 °C taken with $CuK_{\alpha 1}$-radiation ($\lambda = 1.54051$ Å) and using $Pb(NO_3)_2$ ($a = 7.8575$ Å) as internal standard

h k l	I_{obs}	$\sin^2 \Theta_{obs}$	$\Delta \cdot 10^5$	d_{calc}, Å
1 1 1	vvw	0.02740	13	4.6643
2 2 0	s	0.07278	6	2.8563
3 1 1	ss	0.10001	1	2.4358
4 0 0	m	0.14547	2	2.0197
3 3 1	vw	0.17269	−3	1.8534
4 2 2	m	0.21813	−3	1.6491
5 1 1	s	0.24546	2	1.5548
4 4 0	ss	0.29094	5	1.4281
6 2 0	m	0.36356	−5	1.2774
5 3 3	m	0.39081	−8	1.2320
6 2 2	vw	0.39997	−0	1.2179
4 4 4	w	0.43647	13	1.1661
7 1 1	vvw	0.46355	−6	1.1313

Preparation of samples. The pre-heated CuO was wet-ground in a mill to a grain size of 1—3 μ (μ = 10^{-6} m). The calcined Al_2O_3 was passed through sieves into several fractions and those representing the sieve openings (d) 40—63 μ, 71—100 μ and 100—125 μ were used in the experiments. Optical observations indicated that the Al_2O_3-grains were fairly spherical in form. After drying and weighing, pellets were pressed from the oxide mixture with a specified CuO/Al_2O_3 composition ratio. The pellets were fabricated with a pressure of about 200 kp/cm², had a diameter of 13 mm and were 2—3 mm thick.

Analysis showed that the initial oxide composition ratio remained constant throughout the various operations.

Heating procedure. The sampels were heated in a ceramic furnace of conventional form, equipped with a temperature regulator. To obtain a more uniform and stable temperature around the samples, an inner compartment was built with ceramic bricks (c. f. Fig. 1). With this arrangement the reaction temperature could be kept within ±2 °C. The pellets were placed in individual boats of recrystallized Al_2O_3. These boats with their samples were removed from the furnace at various times and quenched in air.

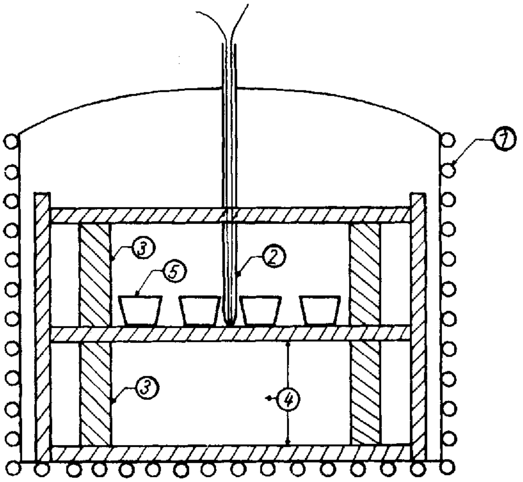

Fig. 1. Sketch of the reactor. 1 Heating windings; 2 Pt—Pt (10% Rh) thermocouple; 3 Ceramic stones; 4 Square plates of sillimanite; 5 Alumina crucibles for samples

The temperature was measured with a Pt—Pt (10% Rh) thermocouple and the emf obtained was measured with a precision potentiometer (Leeds and Northrup, K 3 Universal Potentiometer).

Analysis. It was found that CuO rapidly and totally dissolves in a dilute nitric acid solution, while Al_2O_3 and $CuAl_2O_4$ are insoluble. A quenched pellet was ground, a sample of about 500 mg was put in a beaker containing 25 ml dilute HNO_3 (0.9 M) and H_2SO_4 (0.75 M) and boiled for about 90 minutes. After cooling and sedimentation for about 60 minutes an electrolytic determination of copper was performed. In control experiments starting with pure $CuAl_2O_4$ no copper could be detected.

From stoichiometric considerations it can be shown that the quantity α (the relative molar amount of $CuAl_2O_4$ formed) can be calculated according to the relation

$$\alpha = \frac{n_{CuAl_2O_4}}{n^{max}_{CuAl_2O_4}} = \frac{n^*_{CuO} - n_{CuO}}{n^{max}_{CuAl_2O_4}} \qquad (1)$$

Here n stands for the number of moles at an arbitrary time t and the superscript * indicates the condition in the initial mixture (t = 0). The quantity $n^{max}_{CuAl_2O_4}$ is the maximum amount of the spinel $CuAl_2O_4$ which can possibly be formed. Thus, in cases $n^*_{CuO} \leq n^*_{Al_2O_3}$, $n^{max}_{CuAl_2O_4} = n^*_{CuO}$ and in cases $n^*_{CuO} \geq n^*_{Al_2O_3}$, $n^{max}_{CuAl_2O_4} = n^*_{Al_2O_3}$.

In the electrolytic determination the amount of copper deposited (W_{Cu}) and n_{CuO} is calculated according to the relation

$$n_{CuO} = n_{Cu} = \frac{W_{Cu}}{M_r(Cu)} \qquad (2)$$

where $M_r(Cu)$ is the relative molecular mass of copper.

Results and Discussion

The results obtained for α at various reaction times with different values for the parameters considered, i. e. temperature, particle size and the oxide ratio $n^*_{CuO}/n^*_{Al_2O_3}$, are given in Table 2 and plotted in Figs. 2 and 3. At 1000 °C an effort was made to choose reaction times in such a way that the resultant α-values were rather evenly distributed from 0 to 100% while at 950 °C only α-values less than 30% were obtained.

In order to determine the rate controlling reaction mechanism, the α-values obtained at 1000 °C were plotted against $t/t_{0.5}$ (c. f. Fig. 3), where $t_{0.5}$ indicates the time for 50% reaction. The feature of this curve can indicate the type of reaction mechanism by comparison with the calculated curves representing different types of idealized reaction mechanisms[8]). As seen from Fig. 3 the experimental data agree quite well with the curve valid for a three-dimensional diffusion mechanism and significantly deviate from curves representing other types of rate controlling reaction mechanisms, e. g. a phase-boundary mechanism.

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[8]) J. H. Sharp, G. W. Brindley and B. N. Narahari Achar, J. Amer. ceram. Soc. **49**, 379 (1966).

Table 2 Amount of $CuAl_2O_4$ formed (in mole percentage) at various reaction times for different values on the oxide ratio CuO/Al_2O_3 and for different particle sizes

mole ratio	$d_{Al_2O_3}$, μ	reaction time, h	α · 100
a) Measurements at 1000°C			
1.0022	40–63	0.50	4.30 ± 0.18
		1.00	5.78 ± 0.34
		2.00	9.69 ± 0.07
		4.00	17.99 ± 0.14
		10.00	34.85 ± 0.23
		21.17	51.02 ± 0.04
		67.25	74.41 ± 0.37
0.9979	71–100	0.50	3.37 ± 0.05
		1.00	4.77 ± 0.19
		2.00	9.19 ± 0.19
		4.00	18.71 ± 0.18
		10.00	31.74 ± 0.11
		21.17	44.70 ± 0.10
		67.25	64.68 ± 0.07
0.9979	100–125	0.50	1.34 ± 0.23
		1.00	2.74 ± 0.10
		2.00	6.20 ± 0.01
		4.00	11.91 ± 0.22
		10.00	22.28 ± 0.33
		21.17	32.72 ± 0.08
		67.25	52.65 ± 0.07
0.5008	71–100	0.50	4.20 ± 0.11
		1.00	7.43 ± 0.02
		2.00	16.03 ± 0.10
		4.00	29.63 ± 0.02
		10.00	51.60 ± 0.06
		21.17	71.41 ± 0.07
		67.25	86.24 ± 0.02
2.0053	71–100	0.50	3.07 ± 0.01
		1.00	5.23 ± 0.40
		2.00	9.81 ± 0.65
		4.00	18.31 ± 0.06
		10.00	33.37 ± 0.01
		21.17	48.77 ± 0.19
		67.25	72.50 ± 0.08
b) Measurements at 950°C			
0.9979	71–100	2.00	1.43 ± 0.11
		4.00	3.33 ± 0.31
		8.00	5.34 ± 0.15
		16.00	9.57 ± 0.26
		32.00	19.40 ± 0.05
		64.00	27.21 ± 0.25

In order to more carefully analyse the diffusion-controlled reaction, the VALENSI-CARTER[9]) model was considered

$$\frac{Z}{Z-1} - (1-\alpha)^{2/3} - \frac{1}{Z-1}[1+(Z-1)\alpha]^{2/3} = \frac{2k \cdot t}{r_0^2} \qquad (3)$$

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[9]) R. E. CARTER, J. physic. Chem. **34**, 2010 (1961).

where k is the rate constant, r_0 the mean particle size and Z is a term accounting for the relative change in molar volume, V in $cm^3\,mole^{-1}$ (the V-values used were taken from the literature)

$$Z = V_{CuAl_2O_4}/V_{Al_2O_3} = 1.15$$

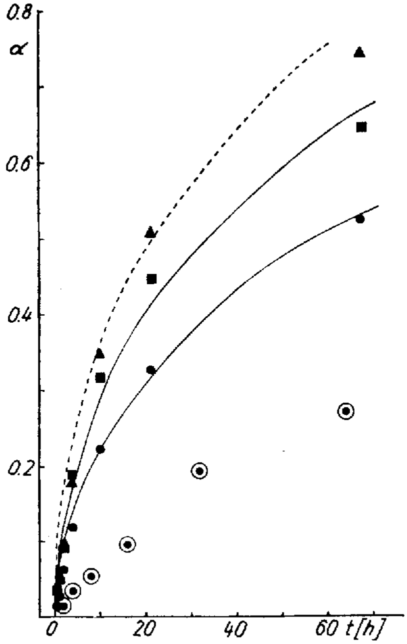

Fig. 2. Amount of $CuAl_2O_4$ formed (α) as a function of reaction time for the oxide ratio $CuO/Al_2O_3 = 1.0$
▲ d = 40—63 μ, T = 1000°C; ■ d = 71—100 μ, T = 1000°C; ●, d = 100—125 μ, T = 1000°C; ⊙ d = 71—100 μ, T = 950°C
The curves at 1000°C are calculated using eq. (3) and with the rate constant value k = $1.1 \cdot 10^{-8}$ $cm^2\,h^{-1}$ (full-drawn curves) and k = $0.6 \cdot 10^{-8}\,cm^2\,h^{-1}$ (broken curve)

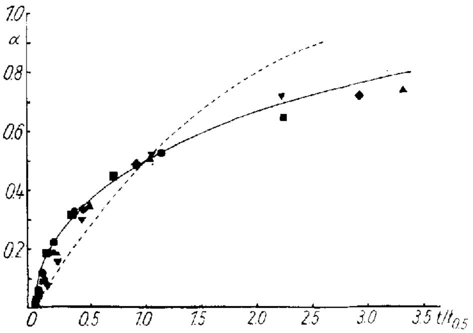

Fig. 3. Amount of $CuAl_2O_4$ formed (α) as a function of reduced reaction time, $t/t_{0.5}$, at T = 1000°C.
▲ d = 40 — 63 μ, $CuO/Al_2O_3 = 1.00$;
■ d = 71 — 100 μ $CuO/Al_2O_3 = 1.00$;
● d = 100—125 μ $CuO/Al_2O_3 = 1.00$;
▼ d = 71—100 μ, $CuO/Al_2O_3 = 0.50$;
◆ d = 71—100, d $CuO/Al_2O_3 = 2.00$.
The broken curve is valid for a phase-boundary reaction mechanism while the full-drawn curve for a diffusion-controlled reaction mechanism.

From the CARTER plot (or equally well from numerical calculations) a value on the ratio $2\,k/r_0^2$ can be obtained. Assuming the particles have a rectangular distribution, for the ratio $n^*_{CuO}/n^*_{Al_2O_3} = 1.0$ values on the rate constant were calculated for each fraction. For the fractions 71—100 μ and 100—125 μ the experimental data could be explained quite well with a rate constant value $k = 1.1 \cdot 10^{-8}$ cm^2 h^{-1} (see Fig. 2), while for the fraction 40—60 μ a somewhat lower value, $k = 0.6 \cdot 10^{-8}$ cm^2 h^{-1}, was obtained. The spread in the k-values may be due mainly to irregularities in the shapes and sizes of the particles from one fraction to the other. The corresponding rate values obtained for the fraction 71—100 μ and $n^*_{CuO}/n^*_{Al_2O_3} =$ 0.5 and 2.0, were $k = 1.7 \cdot 10^{-8}$ cm^2 h^{-1} and $k = 4.4 \cdot 10^{-8}$ cm^2 h^{-1} respectively, indicating that for equal molar ratios of the two oxides, the reaction rate is minimal and increases when an excess of either oxide is present.

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