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Note

SOLID STATE REACTION BETWEEN MAGNESIUM SULPHATE AND α-ALUMINA

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The widely accepted method of preparation of technologically important complex oxide materials is the reaction between solid reactants at elevated temperatures. Studies have been made on the kinetics and mechanisms of two solids interacting to give a third solid and gaseous products, with special emphasis on the sample mass, pelletization and the partial pressure of the evolved gases. Thus, the kinetics of the reaction between $MgSO_4$ and Cr_2O_3 to form $MgCr_2O_4$ have been correlated on the basis of a nuclei growth process [1]. The reaction between anhydrous magnesium sulphate and aluminium(III) oxide, α-alumina, has been undertaken to gain a better understanding of the solid state reaction in which the gaseous phase is one of the products. The studies have been followed by isothermal thermogravimetry with pelletized equimolar $MgSO_4$ and Al_2O_3 mixtures.

EXPERIMENTAL

Anhydrous magnesium sulphate was obtained by heating AnalaR $MgSO_4 \cdot 7\,H_2O$ at 400°C. α-Alumina was prepared by igniting the reagent grade $Al(NO_3)_3 \cdot 9\,H_2O$ at 700°C till the reaction was complete. Equimolar ratios of intimate mixtures of $MgSO_4$ and Al_2O_3 were prepared by repeated grinding and heating the required amount of the reactants in an agate mortar at 80°C for 1 h. The samples were pressed into pellets of various masses, 0.2–1 g, by applying pressures in the range 500–10000 kg cm^{-2}. A recording thermobalance was employed to note the change in weight at any time.

RESULTS AND DISCUSSION

The dehydration of magnesium sulphate heptahydrate has been studied by several workers [2–4] and it has been well established that complete dehydration occurs at 350°C. The continuous heating of the anhydrous magnesium sulphate reveals that it is stable up to 875° and loses SO_3 to give MgO in the

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temperature range 875–1080°C. An intimate equimolar mixture of $MgSO_4$ and Al_2O_3, however, decomposes in the temperature range 700–1030°C. The final product obtained is found to be a mixture of MgO, Al_2O_3 and $MgAl_2O_4$ on chemical and X-ray analyses, when the sample was taken in the powder form. But pure $MgAl_2O_4$ is obtained as the decomposition residue on heating the pelletized $MgSO_4$–Al_2O_3 mixture, a reaction similar to the $MgSO_4$–Cr_2O system [1]. The lowering of the decomposition temperature of $MgSO_4$ in the presence of α-Al_2O_3 is attributed to the catalytic influence of alumina and the chemical reaction taking place between the two solid reactants.

In order to determine the effect of processing pressure on the decomposition reaction, samples of 200 mg were heated at 955°C taken in the powder form and pellets prepared by applying a pressure of 500–10000 kg cm^{-2}. The powder form is found to react faster than the compact pellets prepared by applying pressures up to 1000 kg cm^{-2}. However, the reaction is found to be faster for the pellets obtained at 2000 kg cm^{-2} than for the powder sample and increases as the processing pressure increases up to 5000 kg cm^{-2}. Further increase in pressure, once again, retards the reaction rate. This complex behaviour of the reaction rate is explained as follows. In the powder sample, the number of interfacial contact points between the reactants are more and have a major effect on the rate of the reaction. An increase of processing pressure increases the number of interfacial points

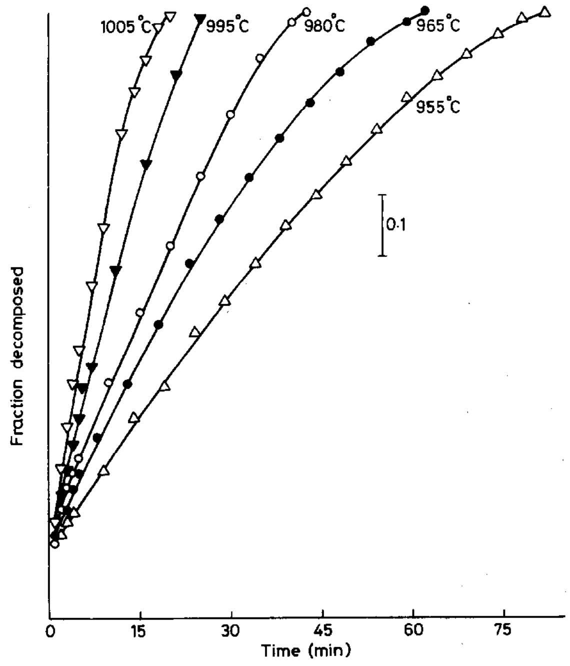

Fig. 1. Isothermal reaction rate curves of equimolar ratios of $MgSO_4$ and Al_2O_3 mixtures.

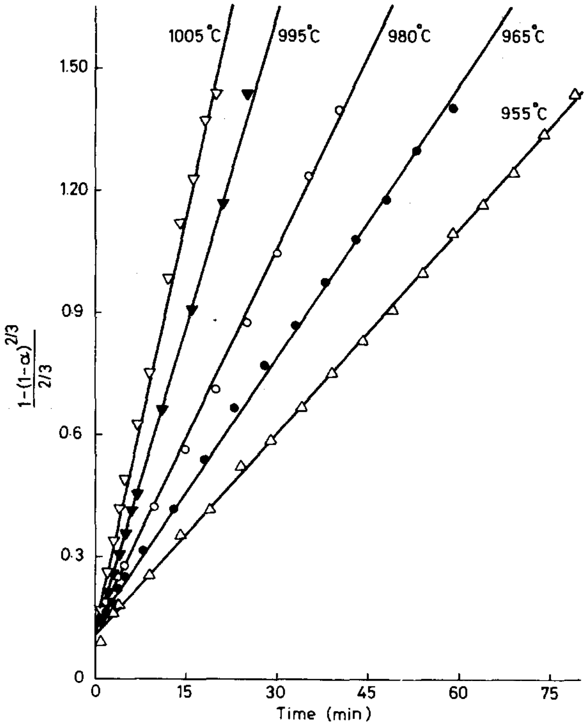

Fig. 2. Reaction rate constant curves of $MgSO_4$ and Al_2O_3 at different temperatures.

which in turn increases the rate of the reaction. However the gaseous product, SO_3, created during the reaction finds it difficult to escape due to the increase of processing pressure, and hence the reaction rate decreases.

The decomposition reaction was carried out at different temperatures for samples of 0.2 mg prepared at 1000 kg cm^{-2}. The plot of weight fraction of the material against time for various temperatures are given in Fig. 1. The curves suggest that as the temperature increases the reaction rate increases. The reaction was also followed by heating at 955°C pellet samples of mass 0.2, 0.4, 0.6, 0.8 and 1.0 g prepared by the application of 1000 kg cm^{-2} pressure. The shapes of the curves are similar to those obtained at different temperatures and the reaction is found to be slower as the sample mass increases. The decrease in temperature and increase in mass make it more difficult for the SO_3 formed during the reaction to be evolved from the reactant mixture, thus decreasing the reaction rate.

The kinetics of the solid state decomposition of the reaction are described by the rate constant, k, and the order of the reaction, n. The plot of fraction decomposed vs. time (Fig. 1) indicates that the reaction proceeds by contraction of the reaction interface. The mathematical equation [5,6] employed for such processes is

$$(1-\alpha)=[1-kt(1-n)]^{1/(1-n)}$$

where $n < 1$. Analysis of the data was carried out using the above equation and it was found that with $n = 1/3$, the plot of $[1-(1-\alpha)^{2/3}]/(2/3)$ vs. time gave satisfactory straight lines for different temperatures (Fig. 2). Making use of this relation, the rate constants were calculated for different temperatures and an Arrhenius plot was constructed. The activation energy thus calculated for the reaction

$$MgSO_4 + Al_2O_3 \rightarrow MgAl_2O_4 + SO_3$$

is found to be 87 kcal mole^{-1}.

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