

## KINETICS OF THE FORMATION OF $\text{NiAl}_2\text{O}_4$ BY SOLID-STATE REACTION

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The rate of the solid-state reaction  $\text{NiO} + \text{Al}_2\text{O}_3 \rightarrow \text{NiAl}_2\text{O}_4$  taking place in a powder system over a temperature range of 1100–1300°C has been measured. The degree of conversion has been determined by means of X-ray diffraction using internal standard method. The kinetics has been for the given experimental arrangement most truthfully described by the Dunwald-Wagner equation. The activation energy of the reaction amounts to 126.0 kcal/mol for reaction mixtures containing aluminium oxide calcinated at 1300°C. Simultaneously, dependence of the reaction rate of  $\text{NiAl}_2\text{O}_4$  formation on temperature of the aluminium oxide calcination has been established.

The present state of knowledge on the formation of  $\text{NiAl}_2\text{O}_4$  by solid-state reaction is based on papers of a small group of authors<sup>1-5</sup>. The first quantitative study was made by Lindner and Akerström<sup>1</sup> who has used a platinum marker to distinguish the interface between aluminium oxide and nickel oxide tablets and who found that  $\text{NiAl}_2\text{O}_4$  is produced by diffusion of  $\text{Ni}^{2+}$  and  $\text{O}^{2-}$  ions through layer of the reaction product. Since the possibility of the oxygen transport through gaseous phase was not excluded in their experiments, Schmalzried<sup>2</sup> assumes their conclusions not to be quite unambiguous and supposes  $\text{NiAl}_2\text{O}_4$  to be produced by counter-current diffusion of cations through layer of the spinel produced.

Stone and Tilley<sup>3</sup> measured the rate of formation of a series of spinels in powder mixtures of various oxides. They used aluminium oxide made to ball shape by means of a modified Verneuil burner. They assumed that  $\text{NiAl}_2\text{O}_4$  is produced by counter-current diffusion of cations through the reaction product layer and came to a conclusion that the rate of  $\text{NiAl}_2\text{O}_4$  formation is within 1000–1320°C controlled by diffusion of  $\text{Ni}^{2+}$  ions.

Pettit and coworkers<sup>4</sup> examined formation of  $\text{NiAl}_2\text{O}_4$  in argon atmosphere and in the air. In order to mark the interface of aluminium oxide and nickel oxide tablets they used a platinum marker and the so-called "naturally marker". They came to the conclusion that the platinum marker is shifted during the experiments, which can lead to a wrong interpretation of the results obtained when using this experimental technique. They further found the rate of  $\text{NiAl}_2\text{O}_4$  formation in the argon atmosphere and in the air to be identical. Thus the assumption is confirmed that  $\text{NiAl}_2\text{O}_4$  is produced by counter-current diffusion of  $\text{Ni}^{2+}$  and  $\text{Al}^{3+}$ . The most significant conclusion of Pettit and coworkers<sup>4</sup> is the fact that the rate of  $\text{NiAl}_2\text{O}_4$  formation is controlled by the rate of diffusion of  $\text{Al}^{3+}$  ions over the temperature range up to 1400°C.

Experimental study of the formation of  $\text{NiAl}_2\text{O}_4$  was continued by Donnert<sup>5</sup> who used  $\eta$  and  $\gamma$  modification of  $\text{Al}_2\text{O}_3$  as the starting reaction component. He further studied reaction between nickel oxide and aluminium oxide whose crystal lattice contained  $\text{Ba}^{2+}$ ,  $\text{Ca}^{2+}$ , and  $\text{Sr}^{2+}$  ions and considered that total reaction rate of the  $\text{NiAl}_2\text{O}_4$  formation is controlled by rate

of diffusion of  $\text{Ni}^{2+}$  ions. His paper, however, brings no detailed characteristics of the aluminium oxide materials used so that it is not evident that in all the mixtures employed the initial magnitude of the reaction interface was the same. For that reason, no unambiguous conclusions can be made on the reaction mechanism of the  $\text{NiAl}_2\text{O}_4$  formation.

The aim of our study was to determine the kinetic dependence of the reaction of  $\text{NiAl}_2\text{O}_4$  formation taking place in the solid phase in the powder mixture of starting reaction components as well as to determine dependence of the reaction rate on the calcination temperature of aluminium oxide. We were interested in these problems in connection with the production of thermally stable carrier of nickel catalysts designed for oxidation of hydrocarbons.

## EXPERIMENTAL

Aluminium oxide was prepared by precipitation of 5.6% aluminium nitrate solution R. G. with 10% ammonium hydroxide at 20°C. The precipitation was finished at pH 8. The gel thus produced was washed by decantation with about 300 l of distilled water to a reaction negative for nitrate ions. After filtration, the precipitate was dried first for 48 hours at a temperature of 20°C and afterwards for further 48 hours at 130°C. The ninety-hours calcination within 1100°–1500°C always led to  $\alpha$ -modification of aluminium oxide. For the reaction itself, a fraction of 63–90  $\mu\text{m}$  was separated.

Nickel oxide was prepared by thermal decomposition of nickel nitrate R. G. at 600°C. The product of decomposition was additionally stabilized by calcination at 1100°C for a period of 2 hours. The grain size of the powder thus obtained, of the bunsenite structure, did not exceed 1  $\mu\text{m}$ .

The equimolecular powder mixture of aluminium oxide and nickel oxide was agitated in alcohol for a period of two hours. Alcohol was after this procedure evaporated so that the segregation of components should not occur. The powder mixture was dried and pressed to tablets, of weight 1.3 g, diameter 15 mm, and approx. height 3 mm, using a pressure of 800  $\text{kp}/\text{cm}^2$ .

The reaction to produce  $\text{NiAl}_2\text{O}_4$  proceeded on putting the tablet into isothermal zone of tubular resistance furnace. The height of the isothermal zone was 35 mm and temperature variation within  $\pm 3^\circ\text{C}$ .

The degree of conversion was determined by X-ray diffraction using the internal standard method<sup>6</sup>. The standard deviation varied from  $\pm 1$  to  $\pm 2\%$  for the region of the conversion degree from 10–80% and for the experimental arrangement used.

## RESULTS AND DISCUSSION

For the solid-state reactions whose total rate is characterized by the rate of diffusion of ions through the reaction product layer, kinetic equations describing course of these reactions were derived on the basis of theoretical considerations which are summarized and discussed by Jander<sup>7</sup>, Schmalzried<sup>8</sup>, and Hulbert<sup>9</sup>. In order to determine which is the best of the kinetic equations, achieved theoretically, that describes the kinetics of  $\text{NiAl}_2\text{O}_4$  formation for the given experimental arrangement, values  $k\tau$  calculated by Giess<sup>10</sup> were employed, where  $k$  is the rate constant and  $\tau$  the

reaction time. Analysis of the relation  $k\tau - \tau$  obtained for individual kinetic models has shown that kinetic equation of Dunwald-Wagner

$$\alpha = 1 - 6/\pi^2 \sum_{n=1}^{\infty} (n^{-2}) \exp(-k_{\text{DW}}\tau)$$

is the most suitable one to characterize kinetics of the formation of  $\text{NiAl}_2\text{O}_4$ .  $\alpha$  is the degree of conversion and  $k_{\text{DW}}$  the rate constant of the Dunwald-Wagner equation.

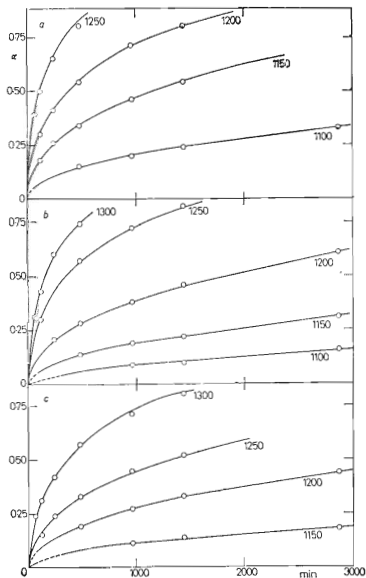


FIG. 1

Time Dependence of Conversion Degree of the Reaction Leading to  $\text{NiAl}_2\text{O}_4$  for the Reaction Mixture Containing Aluminium Oxide

Calcinated at A 1100, B 1300, C 1500°C; the reaction temperature is for the curves given in °C.

The same conclusion may be drawn also when comparing experimentally found values of the conversion degree and course of the achieved isothermal curves illustrating kinetics of the  $\text{NiAl}_2\text{O}_4$  formation (Fig. 1), which were calculated with use of the Dunwald-Wagner equation.

Activation energy of the reaction under study was established from the Arrhenius equation using the least squares method. The activation energy amounted to 114.4 kcal/mol for the reaction mixture containing aluminium oxide calcinated at 1100°C. When using aluminium oxides calcinated at 1300°C or 1500°C, the activation energies were 126.0 or 128.0 kcal/mol, respectively.

Most of the kinetic equations derived for the solid-state reactions which are controlled by the rate of diffusion through a layer of the product, and hence also the Dunwald-Wagner equation, start from the assumption that a continuous layer of the reaction product is produced on particles which are covered. This continuous layer of the reaction product can be produced either due to the fact that in the reaction mixture the covering reaction component continually surrounds the second reaction component, or if it holds that the rate of surface diffusion is by order of magnitude greater than that of the volume diffusion.

In the experiments made, always the samples of  $\alpha$ -aluminium oxide were used, of the same history and very similar granulometric composition. Neither the different

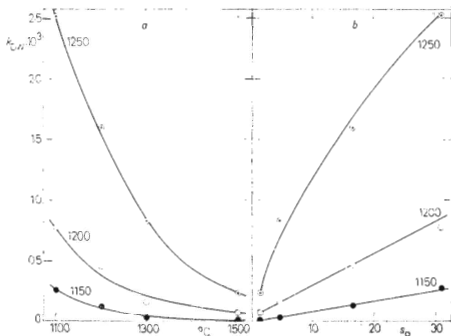


FIG. 2

Dependence of Rate Constant  $k_{DW}$  ( $\text{min}^{-1}$ ) on Temperature of Aluminium Oxide Calcination (a) and on Specific Surface Area,  $S_p$  ( $\text{m}^2/\text{g}$ ) of Aluminium Oxide Samples (b); The reaction temperature is for the curves given in °C.

reactivity of various crystallographic modifications nor the differences in the size of external geometric surface could be therefore applied in the formation of  $\text{NiAl}_2\text{O}_4$ . The differences in the reactivity, which were found with individual reaction mixtures containing aluminium oxide samples calcinated at various temperatures (Fig. 2a), are a function of the aluminium oxide internal surface area (Fig. 2b). It follows from what has been here presented as well as from the fact that the rate of  $\text{NiAl}_2\text{O}_4$  formation is controlled by the rate of diffusion, that rate of the surface diffusion of the covering component is by order of magnitude greater than the rate of the volume diffusion through layer of the nickel spinel produced.

The dependence of rate constant  $k_{\text{DW}}$  on specific surface area ( $S_p$ ) of aluminium oxide was at lower reaction temperatures  $1150^\circ\text{C}$  and  $1200^\circ\text{C}$  linear, but at the reaction temperature  $1250^\circ\text{C}$  the effect of secondary sintering of aluminium oxide during the reaction on the course of the  $k_{\text{DW}} - S_p$  dependence might be applied, which probably led to the diminishing of the reaction interface and thus of the rate of reaction (Fig. 2a). This secondary sintering becomes markedly evident if difference between the temperature of the reaction of  $\text{NiAl}_2\text{O}_4$  and that of the aluminium oxide calcination is greater than or equal to  $150^\circ\text{C}$ . In the experiment, secondary sintering resulted in a lower value of the activation energy, if aluminium oxide calcinated at  $1100^\circ$  was employed.

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