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KINETICS AND DIFFUSION STUDIES IN $BaAl_2O_4$ FORMATION

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ABSTRACT

The paper presents formation kinetics of monobarium aluminate, $BaO.Al_2O_3$,(BA) in the temperature range of 1100-1380°C. Activation energy of its formation from barium and aluminium oxide is calculated to be 68.6 Kcal/mole. In the presence of MgO, its formation is accelerated and the activation energy of reaction is found to be 47.3 Kcal/mole. The activation free energies of the reaction were found to increase in the presence of MgO (1.5% by weight). Diffusion coefficients (D) of reactions have also been calculated and the temperature dependence obeys the relationship,

$$D = 9.596 \times 10^{-4} \left(- \frac{24,800}{R\ T} \right) \ cm^2\ sec^{-1}$$

and

$$D = 9.552 \times 10^{-4} \left(- \frac{20,900}{R\ T} \right) \ cm^2\ sec^{-1}$$

without and with MgO respectively.

Introduction

The solid state reaction between barium carbonate and aluminium oxide has been studied to understand the kinetics of BA formation. In the presence of a small amount of MgO, its formation is substantially accelerated (1) even at a lower temperature of reaction. High temperature reaction kinetics of formation of

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A = Al_2O_3 B = BaO C = CaO

calcium and magnesium aluminates have been reported to occur by counter diffusions of positively charged ions through a relatively rigid oxygen lattice of spinel (2-5). In the formation of tricalcium aluminate from calcium oxide and aluminium oxide, Mackenzie and Banerjee (6) have reported that during the reaction the diffusing species of Ca^{2+} ions move through an interface layer, the composition of which varies with distance from pure oxide.

In a solid state reaction between particles, the formation of product layer at the interface will depend on temperature and time of reaction. Assuming a unidirectional process, the rate of growth of product layer thickness (y) is inversely proportional to time t (7,8). Hence dy/dt = Dk/yt, where D is diffusion coefficient and k is a constant. On integration under boundry condition y=0 at t=0, $y^2=2kDt$. If V denotes the volume of material still unreacted at time t, then $V= 4/3\pi(r_o-y)^3$ where r_o is the initial radius of the reacting particles. If x is the fraction reacted at time t, the volume of the material unreacted is also given by $4/3\pi r_o^3(1-x)$. Hence the Jander's equation can be given as

$$[1-(1-x)^{1/3}]^2 = \frac{2kD}{r_o^2}\, t = K\, t$$

The plot of $[1-(1-x)^{1/3}]^2$ vs time (t) is a straight line relationship, the slope of which gives the value of rate constant K.

In the present paper, the values of rate constant and activation energy of the reactions given in table 1,have been used to calculate activation thermodynamic functions and the interdiffusion coefficients of the formation of BA at different temperatures. The activation thermodynamic functions such as the free energy of reaction (ΔG) and the activation entropy (ΔS) for formation of BA have been calculated at different temperatures by using the equations given below (6)

$$\Delta G = R\,T\,\left(\ln \frac{R\,T}{N\,h} - \ln K\right)$$

and

$$\Delta S = \frac{(Q - \Delta G)}{T}$$

where, R-gas constant, h-Planck's constant, N-Avogadro number, T-temperature (^{o}K), K-rate constant and Q-activation energy of reaction. Activation free energy of reaction (ΔG) calculated was used to calculate chemical potential gradient (k) for BA formation at different temperatures using the equation as given below (10)

$$k = \frac{\Delta G}{T(^{o}K)}$$

Diffusion coefficient D was calculated by equating the slope of the plot of $[1-(1-x)^{1/3}]^2$ against t to kD/r_o^2. The average radius of reacting particles (r_o) taken as 15 microns. Plots of log D vs 1/T are again straight line relationships,the slope of which was used to calculate the activation energy of diffusion in BA formation.

Results and Discussions

The values of rate constants, activation energies of reaction and thermodynamic functions are given in table 1. The formation of the BA is increased in the presence of MgO as evident from the low values of activation energy (1).

TABLE 1

Thermodynamic functions for the formation of $BaAl_2O_4$

System	Temp (°C)	Rate constant (K)*	Activation energy (Q) Kcal/mole*	Activation free energy (ΔG) Kcal/mole	Activation entropy (ΔS) Kcal/mole/°K
$BaCo_3$	1300	23.3×10^{-4}	68.64	76.47	-49.7×10^{-4}
+	1350	30.8×10^{-4}		78.00	-57.6×10^{-4}
Al_2O_3	1380	36.6×10^{-4}		78.87	-61.8×10^{-4}
$BaCO_3$ +	1150	35.8×10^{-5}	47.31	105.98	-41.2×10^{-3}
Al_2O_3 +	1200	46.0×10^{-5}		109.07	-41.9×10^{-3}
MgO	1250	57.7×10^{-5}		112.19	-42.6×10^{-3}

* Reference 1

The activation free energies of BA formation (table 1) are found to increase in the presence of MgO as mineralizer. The negative sign of the entropies implies that the transition state in the overall reaction is more ordered than the reacting substances. The presnce of MgO has not shown any change in the crystalline phase composition of monobarium aluminate as given in earlier studies (1). The values of diffusion coefficients calculated and chemical potential gradients are given in table 2. It is clear that the diffusion coefficient of BA formation increases with the temperature of the reaction. The temperature dependence of the diffusion coefficient is shown in fig's 1(a) and 1(b).

TABLE 2

Interdiffusion coefficients in the formation of $BaAl_2O_4$

System	Temp (°C)	Chemical potential gradient (k) Cal/degree	Diffusion coefficient (D) cm^2/sec	Activation energy of diffusion Kcal/mole
$BaCO_3$	1300	48.61	7.18×10^{-4}	
+	1350	48.05	9.62×10^{-4}	24.8
Al_2O_3	1380	47.71	11.52×10^{-4}	
$BaCO_3$ +	1150	74.47	7.21×10^{-5}	
Al_2O_3 +	1200	74.04	9.31×10^{-5}	20.9
MgO	1250	73.66	11.76×10^{-5}	

The temperature dependence of the diffusion coefficient can be expressed in the form of equations

$$D = 9.596 \times 10^{-4} \left(- \frac{24{,}800}{R\,T} \right) cm^2\ sec^{-1}$$

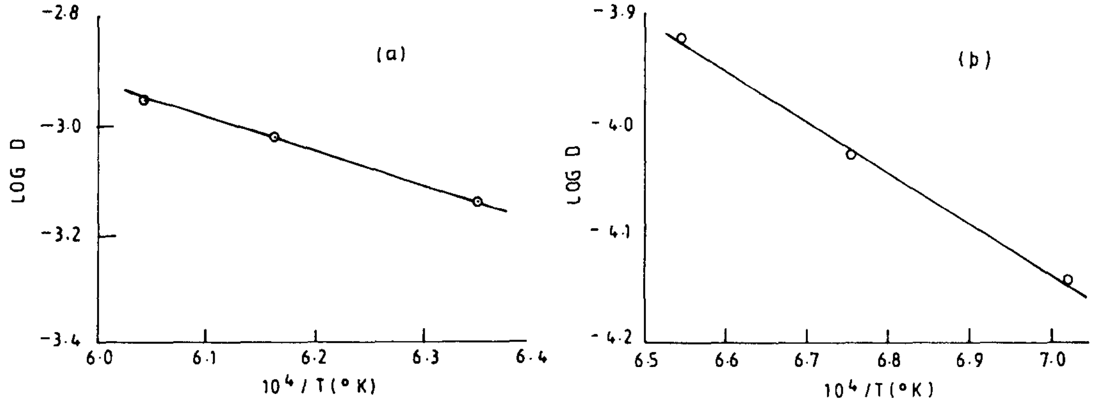

Fig 1. Temperature dependence of diffusion coefficient (a) without MgO and (b) with MgO

and

$$D = 9.552x10^{-4} \left(- \frac{20,900}{R\ T} \right) \quad cm^2\ sec^{-1}$$

without and with MgO as mineralizer.

Conclusions

1. The value of the activation energy of formation of BA is decreased in the presence of a mineralizer.
2. The diffusion coefficient of the BA formation increases with temperature in both cases (without and with MgO) without affecting the crystalline phases in XRD.
3. The activation energies of diffusion were found to be 24.8 and 20.9 Kcal/mole without and with the addition of MgO as mineralizer.

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