Pergamon

Cement and Concrete Research, Vol. 27, No. 7, pp. 979–982, 1997

0008-8846/97 $17.00 + .00

PII S0008-8846(97)00092-6

DIFFUSION STUDIES IN FORMATION AND SINTERING OF $CaAl_2O_4$ and $BaAl_2O_4$: A COMPARATIVE EVALUATION

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(Communicated by M. Daimon)
(Received January 31, 1997; in final form May 6, 1997)

ABSTRACT

Formation of $CaAl_2O_4$ in 1:1 molar mix of CaO and Al_2O_3 occurs at higher temperature through formation of mainly lime rich phases such as C_3A and $C_{12}A_7$. In BaO-Al_2O_3 mix, however stoitiometric formation of $BaAl_2O_4$ occurs at relatively higher temperature due to larger ionic size of Barium ions. The rate of $BaAl_2O_4$ formation is more as the interdiffusion coefficient values calculated for BaO-Al_2O_3 system were found much higher than in CaO-Al_2O_3. Sintering studies showed slower rate of densification in $BaAl_2O_4$ powder compacts and were due to higher molecular weight of $BaAl_2O_4$ though the values of apparent diffusion coefficients calculated were found to be comparable in both the systems. © *1997 Elsevier Science Ltd*

Introduction

The solid state reactions between constituent particles involve the nucleation of phase at separate points on the solid surface. These nuclei grow in size and form a continuous reaction interface. Further reactions occur by diffusion of reactants across the interface. Various factors such as particle, ionic size, mixing ratio, chemical potential gradient, retention time, sintering temperature and diffusion coefficients of the reacting species govern the product formation. In general reactions occur by diffusion of ions from lower oxygen affinity oxide to higher oxygen affinity oxide. Reaction leading to aluminate formation in CaO-Al_2O_3 and BaO-Al_2O_3 system have been reported to occur (1-3) by diffusion of Ca and Ba into Al_2O_3 through rigid oxygen lattice.

The sintering in $CaAl_2O_4$ and $BaAl_2O_4$ powder compacts at higher temperatures occur by bulk mass transport through volume diffusion. Studies reveal rapid sintering rate of $CaAl_2O_4$ compared to $BaAl_2O_4$ (4,5).

The present paper highlights the comparative evaluation of CaO-Al_2O_3 and BaO-Al_2O_3 systems.The thermodynamic functions and diffusion coefficients of the formation and sintering of aluminates have been presented.

1. Formation Reactions in CaO-Al_2O_3 and BaO-Al_2O_3 System. Studies carried out in 1:1 molar mixes of CaO-Al_2O_3 and BaO-Al_2O_3 reported formation of high lime intermediate phases such

TABLE 1

Thermodynamic Functions of Formation of $CaAl_2O_4$ and $BaAl_2O_4$

System	Temp (^oC)	Activation free energy (ΔG) (Kcal/mole)	Activation entropy (ΔS) (cal/mole/^oK)	Chemical potential gradient	Rate constant
	1200	113.67	-51370	12.0	4.16×10^{-4}
$CaAl_2O_4$	1250	116.08	-51270	13.2	6.94×10^{-4}
	1300	119.42	-51760	14.4	8.33×10^{-4}
	1380	122.79	-51290	15.0	2.00×10^{-3}
	1300	76.47	-4970	48.6	23.3×10^{-4}
$BaAl_2O_4$	1350	78.00	-5760	48.0	30.8×10^{-4}
	1380	78.87	-6180	47.7	36.6×10^{-4}

as C_3A,$C_{12}A_7$ in case of $CaO-Al_2O_3$. In $BaO-Al_2O_3$ system however there is a stoichiometric reaction leading to formation of $BaAl_2O_4$ under similar conditions of reaction. The formation of $BaAl_2O_4$ occur at relatively higher temperature. The rate constants and the activation thermodynamic functions determined for these oxides are given in Table 1.

The negative entropies in both cases imply a more ordered transition state than the reacting substances.

2. Interdiffusion Coefficients of Formation of $CaAl_2O_4$ and $BaAl_2O_4$. The interdiffusion coefficients calculated (1,6) at different temperatures for the formation of $CaAl_2O_4$ and $BaAl_2O_4$ are given in Table 2.

It is apparent from the table that the values of interdiffusion coefficients of formation of $BaAl_2O_4$ are more compared to $CaAl_2O_4$ indicating that the reaction leading to formation of

TABLE 2

Interdiffusion Coefficients of Formation of $CaAl_2O_4$ and $BaAl_2O_4$

System	tempeature (^oC)	Interdiffusion coefficient (cm^2/sec)
	1200	13.03×10^{-9}
$CaAl_2O_4$	1250	21.31×10^{-9}
	1300	29.14×10^{-9}
	1380	41.85×10^{-9}
	1300	7.18×10^{-4}
$BaAl_2O_4$	1350	9.62×10^{-4}
	1380	11.52×10^{-4}

$BaAl_2O_4$ is faster than that of the formation of $CaAl_2O_4$. This is also evident from the higher values of rate constants for $BaAl_2O_4$ formation as given in Table 1. Since the ionic radius of Ba^{+2} ion is 1.43 A° and higher than that of Ca^{+2} ions 1.06 A° (7), the formation reaction of $BaAl_2O_4$ involves rapid growth of product layer at the interface.The requirement of higher temperature of reaction is due to higher size of Ba ions for transport compared to that of Ca ion. The temperature dependences of the interdiffusion coefficients for $CaAl_2O_4$ and $BaAl_2O_4$ formation are given as

$$D = 4.165 \times 10^{-4}(-\frac{36,600}{RT})cm^{2}\ sec^{-1} \qquad ..... \text{for } CaAl_2O_4$$

and

$$D = 9.596 \times 10^{-4}(-\frac{24,800}{RT})cm^{2}\ sec^{-1} \qquad ..... \text{for } BaAl_2O_4$$

<u>3. Sintering of $CaAl_2O_4$ and $BaAl_2O_4$ and Diffusion Parameters</u>. The sintering studies of $CaAl_2O_4$ and $BaAl_2O_4$ powder compacts reported (4,5) showed rapid rate of sintering of $CaAl_2O_4$ compared to $BaAl_2O_4$ under similar temperature conditions. Diffusion is apparently the mechanism of mass transport in sintering of solids. In volume diffusion, the atoms move through the lattices to the neck region and the particles come closer causing shrinkage of compact. Based on the values of linear shrinkage, the sintering kinetics of $BaAl_2O_4$ and $CaAl_2O_4$ have been given and the values of apparent diffusion coefficients calculated (4,5) are given in Table 3.

TABLE 3

Apparent Diffusion Coefficients in the Sintering of $CaA_{12}O_4$ and $BaAl_2O_4$

System	Temperature (°C)	Apparent diffusion coefficient (cm^2/sec)
$CaAl_2O_4$	1350	9.59×10^{-11}
	1400	19.82×10^{-10}
	1420	48.25×10^{-10}
	1440	71.46×10^{-10}
	1460	14.10×10^{-09}
$BaAl_2O_4$	1300	3.38×10^{-09}
	1350	5.16×10^{-09}
	1400	8.91×10^{-09}
	1450	11.20×10^{-09}

From the Table 3, it is clear that the values of apparent diffusion coefficients of the $CaAl_2O_4$ and $BaAl_2O_4$ are comparable. The activation energy requirement for sintering of $BaAl_2O_4$ is 188 Kcal/mole and is slightly higher than that for $CaAl_2O_4$ which is 167 Kcal/mole. The relatively higher energy requirement for the densification of $BaAl_2O_4$ is due to the higher molecular weight of $BaAl_2O_4$. The higher molecular weight of $BaAl_2O_4$ affects the rate of mass transport adversely. The temperature dependence of self diffusion of the $CaAl_2O_4$ and $BaAl_2O_4$ are also shown in equations

$$D = 6.28 \times 10^{-9}(-\frac{167,000}{RT})cm^2 \ sec^{-1} \qquad \ldots\ldots \text{for } CaAl_2O_4$$

and

$$D = 8.04 \times 10^{-9}(-\frac{188,000}{RT})cm^2 \ sec^{-1} \qquad \ldots\ldots \text{for } BaAl_2O_4$$

Conclusions

1. The interdiffusion coefficients of $BaAl_2O_4$ formation is higher as compared to $CaAl_2O_4$ which indicates relatively rapid formation of $BaAl_2O_4$. This is also evident from the lower value of activation energy for interdiffusion of BaO into Al_2O_3 as compared to $CaO\text{-}Al_2O_3$.
2. The apparent diffusion coefficients leading to sintering of $CaAl_2O_4$ and $BaAl_2O_4$ are much lower than the formation in $CaO\text{-}Al_2O_3$ and $BaO\text{-}Al_2O_3$ mixes. Thus the formation reactions are faster than the sintering processes.
3. The apparent diffusion coefficients of sintering of $BaAl_2O_4$ arecomparable to that of $CaAl_2O_4$.

Acknowledgement

The authors have freely drawn the information/data from published literature of the NCB. This paper is being published with the permission of the Director General, National Council for Cement and Building Materials, New Delhi.

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