SOLID-STATE REACTIONS IN THE SiO_2-Al_2O_3 BINARY SYSTEM

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Abstract

The solid-state reactions between SiO_2 and Al_2O_3 were studied at 1200°C up to 1550°C. Hot press technique was used to obtain very good contact between the reactants. The influence of pressure, time of reaction and the shape (powder or compact) and the form of solids (amorphus of crystalline) were studied and correlated. The reaction was either continued in the hot press conditions or annealed at different time. The thickness of the reaction product as well as its chemical composition was measured with scanning electron microprobe analyser. Surface area, pore size distribution and optical microscope were also used.

Introduction

The solid state reaction in the SiO_2-Al_2O_3 binary system was studied by Bowen and Greig(1). They observed the presence of mullite. Although numerous investigators have challenged this classical diagram, its validity has never been in doubt(2). Mullite is a solid solution between SiO_2 and Al_2O_3 which can be separated from the molten state. The marginal composition of mullite is 3 Al_2O_3. 2 SiO_2 (A_3S_2) with 72% by weight of Al_2O_3 while mullite 2 Al_2O_3. SiO_2 (A_2S) contains 78% Al_2O_3. Most of studies in this system were carried out by either static method of quenching or by differential thermal analysis and recently by splat-cooling and flame-spraying which led to obtain amorphous material(3), while the alkoxide method of r.f spattering was applied to obtain various amorphous products between SiO_2 and Al_2O_3 (4). Weisweiler and Serry(5) studied the reaction between SiO_2 crystal and Al_2O_3 powder by annealing the pre-hot pressed samples at 1000-1550°C for different times. They observed the presence of glass phases with mullite.

In the present investigation the kinetics and mechanisms of the solid-state reaction between SiO_2 and Al_2O_3 at 1200-1550°C are discussed. The reaction at the interface between the reactants was examined by light microscope while the analysis of the products was determined by scanning electron microprobe analyser (SEMPA).

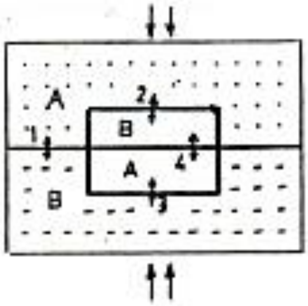

Fig.1 Reaction Diagram in the SiO_2- Al_2O_3 Binary System.

(1) Powder A- Powder B

(2) Powder A- Compact B

(3) Powder B- Compact A

(4) Comp. A- Comp. B

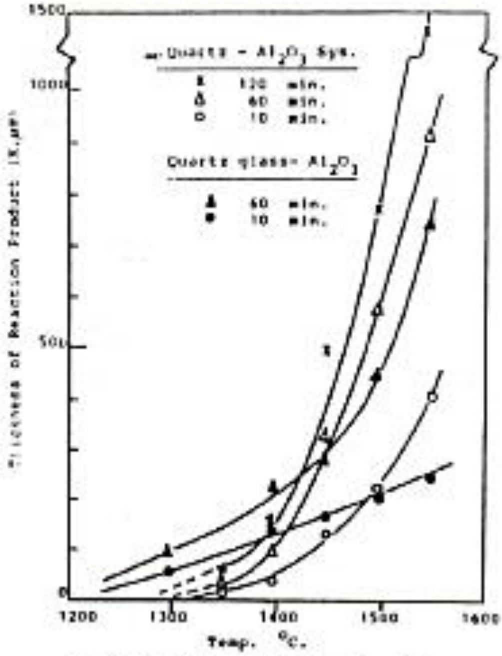

Fig 2. Thickness of Reaction Product as a function of Temperature in SiO_2-Al_2O_3 System under Pressure.

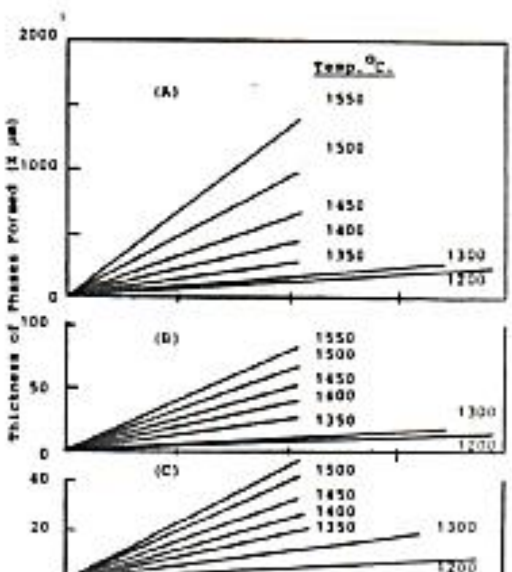

Fig. 3 Thickness of Phases formed as a function of Time.

(A) Mullite A_2S (B) Mullite A_3S_2

(C) Glass Phases.

Due to the increase in volume, in case of quartz crystal, under constant pressure resulted large number of cracks in which Al_2O_3 can easily diffuse and reacted with SiO_2 giving more reaction interfaces. Consequently the rate of reaction (dR/dt) increased than that in quartz glass compact. In both cases the reaction increased with time and temperature. The elemental analysis of the line scan obtained from the heat treated samples at 1200-1550°C, in the system quartz glass compact Al_2O_3 powder showed the presence of mullite A_3S_2 and A_2S and glass phase. Mullite A_2S is most probably formed inside SiO_2 compact by solid state diffusion of Al_2O_3 in SiO_2 as was indicated by SEMPA. The formation of A_3S_2 and glass was attributed to the solid state diffusion of SiO_2 in Al_2O_3. The thickness of these phases was plotted against the reaction time (t) at various temperatures as shown in Fig. 3. The straight lines obtained follow the relationship;

$$X = C\,t^{1/2}$$

where

(X) is the thickness of reaction zone and (C) is constant. The ratio between A_2S: A_3S_2: glass is 100: 6: 4 below 1450°C while above it the ratio is 10: 1: 1. This shows clearly the influence of temperature on the rate of formation of different phases. Fig. 4 shows the photomicrograph of the reacted sample at 1400°C for 2 hours. It shows clearly the reaction zone between SiO_2 compact and Al_2O_3 powder. The relationship between the reaction rate constant, K, and the reciprocal of absolute temperature, 1/T, is given in Fig. 5. The computed values of activation energy obtained, from Arrhenius plots, were 415, 340 and 210 KJ/mole for A_2S, A_3S_2 and glass. These reflects the easier formation of glass than mullite. This glass phase is not stable, depending on the rate of cooling of the reacted samples. This may be decomposed to mullite as an intermediate phase(5).

Reaction Between α-Al_2O_3 Compact and SiO_2 Powder

Compact of α-Al_2O_3 (corundum or pressed α-Al_2O_3) was embeded in SiO_2 powder, then hot presed under 275 bar at 1200-1550°C for 10-360 minutes. The samples were examined at the reaction interface with SEMPA and light microscope. The measured thickness of the reaction product at different temperatures was plotted against the corresponding time of reaciton as shown in Fig. 6. In this reaction system, the rate of reaction is very low compared to the reaction in quartz compact-Al_2O_3 powder system. On the other hand, the annealing of pre-hot pressed samples showed that below 1400°C no reaction between α-Al_2O_3 compact and SiO_2 powder was detected even for long time of reaction (168 hrs.). At 1400°C, at the reaction interface only, one phase is present which is composed of 85% SiO_2 and 15% Al_2O_3 or AS_{10}. This phase may be formed by the solid state diffusion of Al_2O_3 in SiO_2 as was indicated from the lines of scan. The thickness of this phase is plotted against corresponding time of reaction at 1400-1550°C as shown in Fig. 7. The value of apparant activation energy obtained from Arrhenius plots Fig. 8, is 540 KJ/mole. This indicates that the formation of this phase is not as simple as the other glass obtained in the SiO_2 compact-

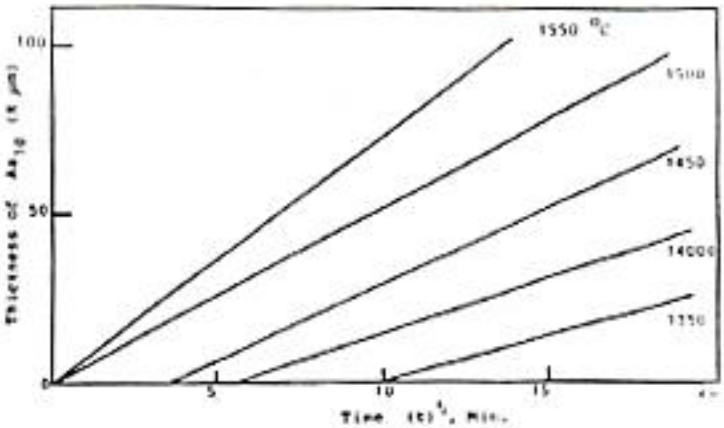

Fig.6 Thickness of Phase AS_{10} as a function of Time.

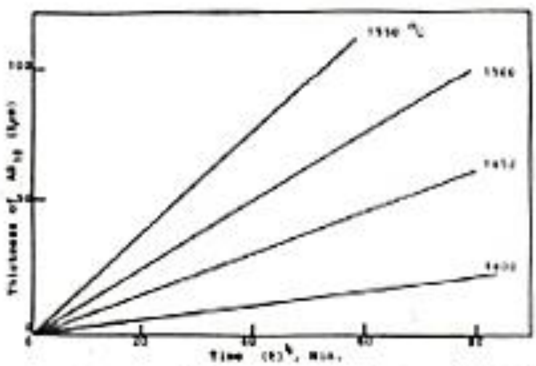

Fig. 7 Thickness of AS_{10} as a function of Time at 1400-1550°C.

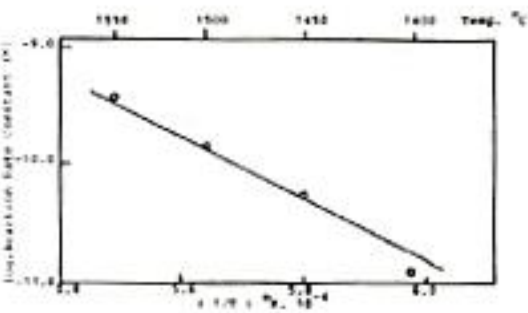

Fig. 8. Arrhenius Plots for the Reaction α-Al_2O_3 Compact-SiO_2 Powder.

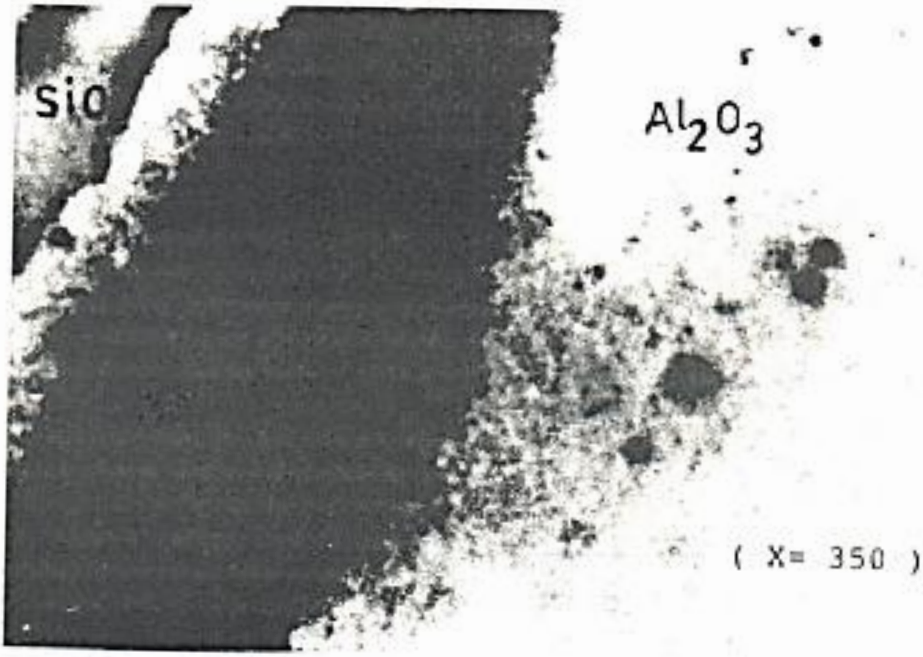

Fig. 9 Photomicrograph showing two Zones of Reaction between SiO_2 Powder and Al_2O_3 Powder.

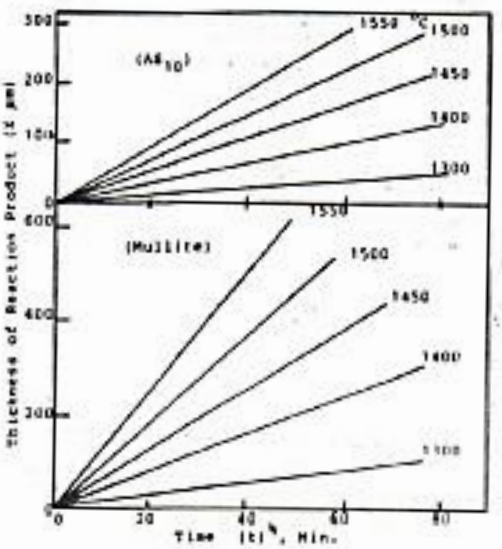

Fig.10 Thickness of Phases formed as a function of Time.

Table 3. Phases formed between SiO_2 and Al_2O_3

Reaction system	Reaction products	ΔE KJ/mole	Diffusion state
Compact SiO_2- powder Al_2O_3	mullite A_2S	415	Al_2O_3 in SiO_2
	mullite A_3S_2	340	SiO_2 in Al_2O_3
	glasses	210	SiO_2 in Al_2O_3
Compact Al_2O_3- powder SiO_2	glass AS_{10}	540	Al_2O_3 in SiO_2
Powder SiO_2- Powder Al_2O_3	mullite A_2S		Al_2O_3 in SiO_2
	mullite A_3S_2	185	SiO_2 in Al_2O_3
	glasses		SiO_2 in Al_2O_3
	glass AS_{10}	350	Al_2O_3 in SiO_2
Compact SiO_2- Compact Al_2O_3	glass AS_{10}	570	Al_2O_3 in SiO_2

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