Growth Rate of Reaction Layer between SiO$_2$ and Molten Al above 1473 K

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Growth rate of reaction layer between molten Al and SiO$_2$ was measured in a temperature range between 1473 K and 1723 K, and was compared with the reported rates between molten Al and mullite. A maximum growth rate was obtained at 1623 K, above which the rate decreased and the reaction halted with formation of an initial thin layer. The same phenomenon had been reported for the reaction between Al and mullite, however, temperatures of the maximum reaction rate were lower than the present (SiO$_2$) case.

According to the observation of microstructures in the reacted layer, gradient of Si concentration became larger as an increase of the reaction temperature up to 1573 K, and closure of the Al phase occurred at 1723 K. Growth rate of the reaction layer was large at 1573 K, however, the residual Si concentration in the reacted layer was also large, indicating that the growth rate is not determined by the rate of Si transport hindrance at the reaction front. There are no reports on the rate above 1673 K, and no reports on the halt of the reaction (eq. (1)) so far. It is of interest to observe what will happen in this reaction system at the higher temperature range above 1573 K in order to confirm that the similar phenomena of the rate decrease and of the reaction halt occur. Microstructural observation of the reacted layer is performed in order to discuss the causes of the reaction rate changes.

1. Introduction

Vitreous silica (SiO$_2$) reacts with molten Al and the reaction product is a composite body consisting of interwoven Al$_2$O$_3$ and Al (containing a little amount of Si) phases, according to the following substitutional reaction:

$$3\text{SiO}_2(s) + 4\text{Al}(l) = 2\text{Al}_2\text{O}_3(s) + 3\text{Si} \text{ (in Al)}$$ (1)

This reaction is also known to occur in silica-containing ceramics, such as mullite, as expressed in eq. (2) the reaction product is also a composite body similar to the above case, with larger volume fraction of Al$_2$O$_3$.

$$3\text{Al}_6\text{Si}_2\text{O}_{13} + (8 + x)\text{Al} = 13\text{Al}_2\text{O}_3 + 6\text{Si} + x\text{Al}$$ (2)

Much attention has been paid for these reactions, because these reaction processes can be applied to fabricate composite materials. In the both processes, the reactions proceed with little changes in shape and size from the original SiO$_2$ or mullite bodies. There are some studies concerning on this material and their applications.1–4)

Kinetic studies of the reaction between Al and mullite (eq. (2)) have been reported.5,6) The shown data5) with a broken line in Fig. 17) indicate an interesting feature that the rate has a maximum at 1423 K and then decreases rapidly above the temperature. It has been reported that the reaction halted after formation of an initial thin layer. They attributed the reason to be due to closure of the Al channels in the Al$_2$O$_3$ networks as the increase of reaction temperature,5) and due to the Si transport hindrance at the reaction front.5) There are no data of the reaction (eq. (2)) below 1173 K, because the rate is very low.

On the other hand, kinetic studies of the reaction (eq. (1)) have also been reported. First, there are old reports on the low temperature below 1073 K.5,8) Data above 1073 K are also reported.10–14) The authors observed the decrease of the rate in the temperature range between 1073 and 1273 K, which is consistent with the other reports,10–12) as shown in Fig. 1, and the reason was attributed to transition of the produced Al$_2$O$_3$ phase.13) However, the rate increased with temperature again above 1273 K up to 1573 K. In the temperature region between 1073 and 1273 K, the growth rate is low, however, the layer growth occurred steadily and the reaction does not halt. There are no reports on the rate above 1673 K, and no reports on the halt of the reaction (eq. (1)) so far. It is of interest to observe what will happen in this reaction system at the higher temperature. This study attempts to investigate the growth rate of the reaction layer between SiO$_2$ and molten Al in the higher temperature range above 1573 K in order to confirm that the similar phenomena of the rate decrease and of the reaction halt occur.

2. Experimental

The raw materials used for the experiments were vitreous...
silica rods (Toshiba Ceramics, T1030), having diameter of five to fifteen milli-meters, and an aluminum ingot having three nines in purity. There are other silica rods’ product (Toshiba Ceramics, T2030), which has lower concentration of OH (high quality). However, it was confirmed that no considerable differences in the growth rates have been found. Thus the T1030 was utilized in this study because of the better availability. Before the reaction, SiO$_2$ rods were cleansed with an alcohol by application of ultrasonic agitation. The Al lumps were etched with 0.1HCl aqueous solution, and cleansed with water for about 10 min. They were melted in an alumina crucible (Nikkato, CP-4) using a high frequency induction furnace (FRT-30-380H, Fuji Denpa Inc.) in an Ar atmosphere. Temperature was measured with platinum thermo-couple, together with confirmation by optical pyrometer. The silica rods were heated in advance, and were immersed into the molten Al. After the reaction procedure, specimens were quenched into water. The detailed descriptions on the procedures can be found in the other reports.

Reacted specimen rods were cut perpendicular to the longitudinal direction, they were mounted in resin and wet-polished with SiC abrasive paper, finished by polishing with alumina powder of 1 $\mu$m in size. Thickness of the reacted layer was measured directly with a venier or by observing with an optical microscope (OM, Olympus, BX60). Compositional distributions in the reacted layer were obtained in a scale of several hundred microns by means of energy dispersive X-ray microanalyzer attached to a scanning electron microscope (SEM/EDX, Hitachi S-6501). Specimens for SEM/EDX observation were coated with carbon to prevent charge-up due to irradiation of an electron beam.

### 3. Results

#### 3.1 Growth Rate of the Reaction Layer

Relationships between the layer thickness and the reaction time at high temperature range (1473–1723 K) are plotted for silica case (eq. (1)) in Fig. 2. At 1623 K or 1573 K, the specimens having diameter of 15 mm were almost completely reacted within 30 min. However, the reaction thickness decreased at 1673 K. At 1723 K, an initial reaction layer was formed, but the change in its thickness was not observed any more, namely, the reaction virtually halted after 15 min.

Variation of the growth rates with the reaction temperature is plotted in Fig. 1, in which the rates are compared with the mullite reaction cases. The silica rate data in our previous report are also plotted (973–1373 K). It was demonstrated that the rate had a maximum at 1623 K and the rate decreased above 1673 K. This is a similar phenomenon as the mullite reaction case, however the reaction halt temperature was shifted higher by 200 degrees in silica case.

#### 3.2 Microstructural observation

Microstructures of the reacted layer at different reaction temperatures were observed. The layers are compared in the etched states in Fig. 3 (1373, 1573 K), where Al is dissolved out and the only remained Al$_2$O$_3$ skeleton networks are seen. Scale of the Al$_2$O$_3$ network at 1573 K became larger than that at 1373 K.

Compositional analysis was performed by means of EDX. The Si concentration gradient was present in the reacted layer as shown in Fig. 4, where the Si concentration is normalized with respect to that of SiO$_2$ and is plotted with respect to the normalized distance of the reaction layer. A tendency was observed that Si concentration gradient increased as an increase of the reaction temperature between 1373 and 1573 K. Here, it has to be noted that the large growth rate (at 1573 K) was obtained under a condition of large macroscopic Si concentration gradient. The Si concentration is low when reaction temperature is below 1373 K.
Fig. 5  SEM photograph and EDX compositional profiles in the reaction interface area. The specimen obtained by reaction at 1723 K for 15 min.

A thin reacted layer formed at the beginning stage of the reaction at 1723 K, and it was observed by means of SEM/EDX. The obtained photograph with the analyzed concentration profiles are shown in Fig. 5. There are some areas in which a fraction of oxygen is low and that of Aluminum is high, which correspond to the Al portion in the composite body. From this photograph, it is clear that these Al portions are closed and isolated, thus supply of Al (the reactant) to the reaction front is hindered.

4. Discussion

The reaction proceeds by steady supply of liquid aluminum to the reaction front (interface between SiO$_2$ and the reacted layer) and by simultaneous steady removal of Si to the outer Al bath. Thus, progress of the reaction has to be discussed, considering the observed phenomena, namely the changes in Si concentration distributions and the changes in the Al channels or Al$_2$O$_3$ network structures.

4.1 Rate of Si transport

Halt of the mullite reaction was discussed in terms of the Si transport in microscopic area at the reaction interface. In this study, the obtained macroscopic Si concentration gradient are discussed considering the transport rate of Si as follows: The Si concentration distributions in the reacted layers are formed as a result of the competition between the production rate of Si at the interface and the rate of transport to the outer bath. The transport occurred through diffusion of Si in liquid aluminum to the opposite direction of the Al transport. The Al flows through the channel in the porous Al$_2$O$_3$ product, (a flow in a porous body driven by the capillary force). Diffusion coefficient of Si in liquid Al is extrapolated, using values of activation energy and pre-exponential factor at 1073 K. The diffusion distances (d) are compared with the moving distance (d) of the reaction interface for a given time. The diffusion distance is estimated by the following relation:

$$d_1 = \sqrt{2 \cdot D \cdot t}, \quad D = D_0 \exp(-E/RT),$$

where \(D_0 = 2 \times 10^{-7} \text{m}^2\text{s}^{-1}\), \(E = 21.8 \text{kJ mol}^{-1}\)

The moving distance of the interface was taken from that of the experimentally measured. They are compared in Table 1. The diffusion distance is larger than that of the interface movement. Difference in two distances decreases as an increase of the reaction time (1800 s). It is necessary to take into consideration that the effective diffusion constant is smaller than the above equation, because of the volume factor (Al: 0.2–0.3) and complexity of the Al channels, namely the diffusion distance (d) must be lower than the estimated values in Table 1. Therefore, it is expected that the Si diffusion at the final reaction stage cannot keep up the movement of the reaction interface. The observed macroscopic Si concentration gradient was formed as a result of the competition of these processes. However, the reaction rate had a maximum at 1573–1623 K, indicating that the reaction is possible to proceed without sufficient removal of Si (reaction product).

4.2 Change in the Al$_2$O$_3$ network structure

In mullite case, it has been reported that Al$_2$O$_3$ networks become dense and formed closed portions by a phenomenon similar to sintering. In the closed portion, liquid Al is confined, thus Al liquid is not supplied to the reaction interface and the reaction halted at 1573 K.

On the other hand, in SiO$_2$ reaction (eq. (1)), width of Al$_2$O$_3$ networks increased as an increase of temperature between 1373 K and 1673 K (Fig. 3). SEM photograph in Fig. 5 shows that the Al$_2$O$_3$ layer with isolated Al portions existed in the vicinity of the interface, which reveals the confinement of Al phase.

As for the differences in Al$_2$O$_3$ structure in the two composite bodies, the following fundamental mechanisms are proposed: In both (mullite and SiO$_2$) reactions, it is considered that Al$_2$O$_3$ thin layer is formed, through which solid state diffusion of Al into mullite or SiO$_2$ occurs. The layer is fragmented due to molar volume difference between SiO$_2$ (or mullite) and the produced Al$_2$O$_3$. The Al$_2$O$_3$ fragments are interconnected, thus Al$_2$O$_3$ networks and Al

<table>
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<th>Temperature (K)</th>
<th>t = 180 s</th>
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<tr>
<td>1373</td>
<td>$3.26 \times 10^{-3}$</td>
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<tr>
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<tr>
<td>1573</td>
<td>$3.69 \times 10^{-3}$</td>
<td>$6.48 \times 10^{-4}$</td>
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channels are formed, simultaneously. Scale of the fragments changes from nano size to micron size drastically at about 1200 K, because of the transition of the Al<sub>2</sub>O<sub>3</sub> phase (from γ, θ to α phase), and due to the molar volume change. The fragment scale increases gradually above 1200 K, possibly because of increase of the reaction rate. On the other hand, sintering or connection of the fragments is supposed to occur extensively above 1673 K (Al<sub>2</sub>O<sub>3</sub> closure temperature in mullite case). Temperature of 1673 K corresponds to 0.72 of the meting point of Al<sub>2</sub>O<sub>3</sub> (2323 K). Diffusion of the ions in Al<sub>2</sub>O<sub>3</sub> is supposed to occur extensively, and contribute to the connection of the fragments. There is a competition of the rates between formation of wide clearance of the fragments and their coalescence. When the latter becomes overwhelming, the Al channels are closed.

In SiO<sub>2</sub> case, because of the smaller volume fraction of Al<sub>2</sub>O<sub>3</sub> comparing with mullite, connection (sintering) of the Al<sub>2</sub>O<sub>3</sub> fragments is not easier to occur. Therefore, higher temperature is required for occurrence of the sintering and confinement of Al phase due to enhancement of deformability of the Al<sub>2</sub>O<sub>3</sub> fragments.

Lastly, it is required to discuss these results considering the other factors. Although Si transport rate does not seem to influence the reaction kinetics directly as discussed above, the changes in the Al viscosity with Si content, and Si diffusivity in Al, etc. have to be taken into consideration as the relevant factors to the kinetics.

5. Conclusion

Reaction rate between SiO<sub>2</sub> and molten Al was measured between 1373 and 1723 K, and the microstructural observation of the reacted layer was performed. The following results were obtained:

(1) The reaction rate increased up to 1623 K and then the rate decreased, the reaction halt was observed at 1673, 1723 K.

(2) The reaction halt temperature was compared with the mullite case, and it was found that the temperatures of the maximum rate and the reaction halt were lower in the SiO<sub>2</sub> reaction case by about 200 degrees.

(3) The reaction halted after formation of an initial reaction layer of several hundred microns, the phenomenon was demonstrated to be caused by closure of the Al channel at high reaction temperature through a process similar to sintering.

(4) Si concentration gradient was large at 1573 K, where the reaction rate was high. Formation of the gradient was discussed in comparison of the diffusion distance with the rate of the reaction interface movement.

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REFERENCES

7) The mullite kinetics were obtained by measurement of the thickness divided by the reaction time in some temperature range, and a period of 15–30 min is considered enough for evaluation of the rate. Although the layer thickness did not increase linearly increased with the reaction time in some temperature range, value of the layer thickness divided by the reaction time was plotted in the graph in order to compare all the rate data in a wide temperature range.