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Interfacial Microstructure Formed by Reactive Metal Penetration of Al into Mullite

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Abstract

Microstructures in the reaction interface between molten Al and dense mullite have been studied by transmission electron microscopy to provide insight into mechanisms for forming ceramic-metal composites by reactive metal penetration. The reactions, which have the overall stoichiometry, $3\text{Al}_6\text{Si}_2\text{O}_{13} + (8 + x)\text{Al} \rightarrow 13\text{Al}_2\text{O}_3 + x\text{Al} + 6\text{Si}$, were carried out at temperatures of 900, 1100, and 1200°C for 5 minutes and 60 minutes, and 1400°C for 15 minutes. Observed phases generally were those given in the above reaction, although their proportions and interfacial microstructures differed strongly with reaction temperature. After reaction at 900°C, a thin Al layer separated unreacted mullite from the $\alpha\text{-Al}_2\text{O}_3$ and Al reaction products. No Si phase was found near the reaction front. After 5 minutes at 1100°C, the reaction front contained Si, $\alpha\text{-Al}_2\text{O}_3$, and an aluminum oxide phase with a high concentration of Si. After 60 minutes at 1100°C many of the $\alpha\text{-Al}_2\text{O}_3$ particles were needle-shaped with a preferred orientation. After reaction at 1200°C, the reaction front contained a high density of Si particles that formed a continuous layer over many of the mullite grains. The sample reacted at 1400°C for 15 minutes had a dense $\alpha\text{-Al}_2\text{O}_3$ reaction layer less than 2 μm thick. Some isolated Si particles were present between the $\alpha\text{-Al}_2\text{O}_3$ layer and the unreacted mullite. Using previously measured reaction kinetics data the observed temperature dependence of the interfacial microstructure have been modeled as three sequential steps, each one of which is rate-limiting in a different temperature range.

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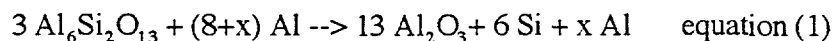
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I. INTRODUCTION

Metal-ceramic reactions at high temperatures are important to the processing and performance of advanced materials in many applications, such as metal-ceramic joining, metal-ceramic composites and electronic packaging[1-5]. Understanding interfacial reactions is central to reliable fabrication and to obtaining the best properties in the products. Because reactions at high temperature are generally very complex, their prediction based on first-principles considerations is often impossible[6]. As a result, the composition and microstructure of the resulting interface is often used to infer the reactions that occurred.

High temperature reactions are being used to make composites by a number of related techniques that are commonly labeled as in-situ methods. Reactive penetration of molten Al into dense mullite to give Al/Al₂O₃ composites is one example[7,8]. In this process, a dense mullite preform is placed in contact with molten aluminum at temperatures above 900°C, which initiates a reaction that converts the preform to a composite of Al₂O₃, Si and Al, according to:



The reaction is a net-shape process, i.e. the composite product has the same shape and size as the ceramic preform[7]. Silicon is generally absent from the resulting product because as the reaction proceeds, it diffuses away from the reaction front into the pool of unreacted Al. The Al content of the composite, represented by the coefficient x in the above reaction, varies over about 15 to 40 vol%, depending on the purity, SiO₂ content, and porosity of the mullite preform[9]. The microstructure of the composite comprises mutually interconnected networks of Al₂O₃ and Al, similar to those reported for Al/Al₂O₃ composites made by other methods[10-12].

Despite the success of making composites using reactive metal penetration, the mechanism that controls the reaction is not well-understood. Two recent studies have reported the kinetics of the reaction between Al and mullite[13,14]. The aluminum

penetration rate (i.e. the reaction layer formation rate) was found to change dramatically with time and temperature[13,14]. Reaction was negligible below 900°C but increased with increasing reaction temperature, reaching a maximum rate around 1150°C. Above 1150°C the penetration rate decreased with increasing reaction temperature. At 1300°C and above, no reaction layer could be detected by optical microscopy[13].

In this paper, we report the results of studies by transmission electron microscopy (TEM) on the microstructure near the reaction front formed by reactive metal penetration of mullite by Al. The interfacial microstructures observed for different reaction temperatures (900-1400°C) and times (5-60 minutes) are used in combination with earlier kinetic data[13] to develop a reaction model for composite formation.

II. EXPERIMENTAL

Mullite preforms used in the study were prepared by sintering isostatically pressed compacts of high-purity mullite powder at 1700°C for 3 h. The preforms had densities greater than 99 percent of the theoretical density of mullite, 3.16 g/cm³, and an average grain size of about 1 μm. Details for preparing mullite preforms have been reported elsewhere[8].

The Al and mullite reactions were carried out for 5 minutes and 60 minutes at 900°C, 1100°C and 1200°C, and for 15 minutes at 1400°C. Mullite preforms for the 5 minute reactions were cut into discs of about 2 cm in diameter and 1 mm in thickness, and then were polished with successively finer abrasive grits, finishing with 1 μm Al₂O₃ particles. Al metal sheets with purity greater than 99.99% were placed on the polished mullite discs at the center of a graphite-heated resistance furnace inside a high-vacuum system. The samples were heated to the desired temperature under an atmosphere of flowing Ar and maintained there for 5 minutes. After 5 minutes the power to the furnace

was turned off and the sample cooled to room temperature at an initial rate of about 100°C/min.

Experiments at longer times were done slightly differently. For the 15 and 60 minute reactions, the sintered mullite preforms were in the form of cubes about 2x2x2 cm fixed to the end of an alumina support rod. Reaction was initiated by immersing the preform in molten Al contained in high-purity Al₂O₃ crucibles maintained at the desired reaction temperature in a tube furnace under an atmosphere of flowing Ar. Prior to immersion, the preform was allowed to equilibrate to the furnace temperature to lessen the thermal shock on being suddenly immersed in the high temperature Al. After reaction, the specimen was immediately removed from the furnace and allowed to cool rapidly to room temperature. It is estimated that the specimen cooled from the reaction temperature to less than 600°C in 5 minutes. The thickness of the reacted layer was about 0.3, 5.0 and 1.5 mm for samples reacted for 60 minutes at 900, 1100 and 1200°C, respectively. The reacted layer for the sample that was heated for 15 minutes at 1400°C was not detectable by optical microscopy.

Microstructures near the reaction front between the reacted and unreacted mullite were examined in cross-section by TEM. The cross-section TEM samples were prepared by the following steps: (1) mechanically polishing the mullite side of the sample parallel to the reaction interface to reduce the thickness of unreacted mullite to about 20 μm; (2) gluing the polished surface to a piece of a Si single crystal; (3) cutting the sample in cross-section into slides of 0.5 mm in thickness; (4) mechanically polishing the cross-section sample to a thickness of less than 5 μm; and (5) ion-milling the sample to perforation at 4 keV and at an incident angle of about 6°. Step (4) is the most critical and was completed by using a tri-polisher with the sample thickness monitored by observing the color of light transmitted through the Si. The technique used in the sample preparation ensures that the damage to the interface, such as that due to preferential removal of the materials by ion-milling, is

minimized. To reduce charging in the microscope, the samples were coated with a thin layer of amorphous carbon (<10 nm).

TEM samples were examined in a JEOL-2010EX high-resolution electron microscope operated at 200keV. The microscope was equipped with an energy dispersive X-ray spectroscopy (EDS) detector with an ultra-thin window. The minimum electron probe size available for the analysis is about 10 nm in diameter.

III. RESULTS

A. Samples reacted at 900°C

Fig.1a is a TEM micrograph for the sampled reacted at 900°C for 5 minutes, showing the reaction front formed between the reacted and unreacted mullite. The unreacted mullite, labeled M, is at the upper-left part of the micrograph and has an average grain size about 1 μm . The reacted mullite, which is at the bottom-right in the micrograph, consists of $\alpha\text{-Al}_2\text{O}_3$ and Al phases with grain sizes typically of 200 nm. The $\alpha\text{-Al}_2\text{O}_3$ phase was identified by EDS analysis and by its electron diffraction pattern.

A thin layer of Al was found to be present at the reaction front that separates the reacted area from the unreacted area in the 900°C/5 min specimens. The EDS spectra from the mullite, Al layer, and $\alpha\text{-Al}_2\text{O}_3$ are shown in Figs.1b, 1c and 1d, respectively. The small O peak in Fig.1c is due to interference from the neighboring $\alpha\text{-Al}_2\text{O}_3$ particles. The Al phase is present at all the interfaces observed. The layer varies in thickness from area to area between a few nm and about 100nm. No Si phase, however, was observed near the interfaces in the reacted mullite. EDS analysis of the reacted area away from the reaction front (>2 μm) indicated that the reacted area contains a negligible amount of Si (<2 vol %) after the reaction.

Fig. 2 is a TEM micrograph of the reaction front for the sample reacted at 900°C for 60 minutes. Again, a thin layer of Al is present at the reaction front. In addition, Al channels between the elongated Al_2O_3 particles are apparent in Fig.2. These channels are connected to each other and appear to be continuous with the Al layer at the reaction front and the external Al pool. The observation suggests that the Al supply to the reaction front is provided by macroscopic flow of the molten Al through these channels rather than by atomic-scale lattice and grain boundary diffusion.

Fig.3 shows a TEM micrograph of a 900°C specimen in which a grain boundary, marked as G, intercepts the reaction front. The Al layer covering the reaction front is clearly visible in the micrograph. No further penetration of Al metal at the grain boundary is observed, indicating that the grain boundary plays a minor role, at best, in the reaction.

B. Samples reacted at 1100°C

Fig.4 shows a TEM micrograph of an interface formed by reaction at 1100°C for 5 minutes. The reaction front is much rougher than those formed at 900°C. The large grain with relatively light contrast labeled M in the figure is mullite. The reaction product consists of grains ranging in size from a few nm to about 500 nm.

A different distribution of phases was observed near the 1100°C reaction front as compared to those formed at 900°C. Examples of two 1100°C reaction fronts are given in Figs.5 and 6. The phases observed in the reacted area include Si, $\alpha\text{-Al}_2\text{O}_3$ and an aluminum oxide phase with a high concentration of Si, which we term Si-rich aluminum oxide (SAO). The EDS spectrum in Fig.6 is from such a SAO particle. Very few Al particles were observed near the reaction front, and particularly, no Al was observed in direct contact with the mullite. The Si particles in Fig.5 are triangular in cross-section and appear to be in contact with mullite and between the $\alpha\text{-Al}_2\text{O}_3$ particles. The average size of the $\alpha\text{-Al}_2\text{O}_3$ particles is about 250 nm. The SAO particles were found always to be in direct

contact with the mullite. Fig.6 shows where the reaction front has penetrated into a mullite grain. The phase at the reaction front is the SAO particle and the Al_2O_3 particle has grown right behind the SAO phase. The geometry shown in Fig.6 was observed frequently at many areas of the reaction front. The SAO particles were found to have a range of Si compositions, indicating that they might be a non-stoichiometric, intermediate reaction product. No other penetration of the reaction front is observed at the grain boundary labeled G in Fig.6.

For samples reacted at 1100°C for 60 minutes, the phase distribution near the reaction front generally seems to be quite similar to that of samples reacted for 5 min, although, as discussed below, there are differences in microstructure. Fig.7 is a TEM micrograph of one region of the interface produced by reaction for 60 minutes at 1100°C , along with EDS spectra from three indicated areas. The reaction front penetrates deeply into the mullite, similar to the situation shown in Fig.6. The particle at the reaction tip is SAO, as indicated by its EDS spectrum. The particle behind the SAO is $\alpha\text{-Al}_2\text{O}_3$. The small Si peak in the EDS spectrum for the $\alpha\text{-Al}_2\text{O}_3$ is due to interference from its neighboring particles. The particle parallel to the Al_2O_3 phase with lighter contrast is another SAO particle. This particle has a Si content higher than that of mullite but smaller than that of the SAO phase at the tip. Overall, the microstructure of Fig.7 is similar to that in Fig.6.

Other sections of reaction interfaces of specimens reacted at 1100°C for 60 minutes, however, were often found to have a different microstructure from that shown in Fig.7. In many regions there is a microstructure containing long needles with a preferred orientation. An example of such microstructure with the oriented needles is shown in Fig.8a. The selected area electron diffraction patterns from the mullite and from an area that includes many needles are shown in Figs.8b and 8c, respectively. The needle-shape particles are $\alpha\text{-Al}_2\text{O}_3$, as determined by EDS and electron diffraction. The diameter of the needles ranges from 5 nm to 20 nm. The needle tips contacting the mullite often have a phase

distribution similar to that shown in Fig.6 and Fig.7, indicating the structure in Figs.6 and 7 is the initial stage of the needle development. Most of the needles appear to have an axis parallel to the C-axis of the α - Al_2O_3 structure, as shown from the pattern in Fig.8c. The needles, however, are not specially oriented with respect to the mullite grains, as shown by comparing the patterns in Figs. 8b and 8c.

C. Samples reacted at 1200°C

The reaction front formed at 1200°C for 5 minutes is shown in Fig.9. Unlike the samples reacted at 900 and 1100°C, the 1200C specimens have a reaction front with a Si layer or a high density of Si particles between the mullite and the α - Al_2O_3 . Such a Si layer is clearly visible in Fig.9. The Al is about 1 μm away from the reaction front between the α - Al_2O_3 particles. The Al channel close to the reaction front in Fig.9, however, is filled by Si particles. The average grain size for the α - Al_2O_3 particles is about 500nm, about twice the size of those formed at 1100°C.

Similar microstructures were also observed from the sample reacted at 1200°C for 60 minutes, as shown in Fig.10. In Fig.10a, a number of large Si particles (~300nm) are visible at the reaction front and the Si layer does not appear to be continuous. In Fig.10b, which was obtained from a different area, a thin layer Si(~50nm) is visible between the Al_2O_3 and mullite. The Si phase also occupies the space (or channel) between the Al_2O_3 particles near the reaction front. The Al_2O_3 crystals with needle-shaped microstructures found in the 1100°C specimens (Fig.8a) were not observed in those reacted at 1200°C.

D. Samples reacted at 1400°C

Fig.11 shows the microstructure formed by the reaction at 1400°C for 15 minutes. The thin dark layer present between the Al and mullite is α - Al_2O_3 . The thickness of the

layer is between about 1 and 2 μm and varies from area to area. The $\alpha\text{-Al}_2\text{O}_3$ layer is continuous and very dense. Some isolated Si particles are present between the $\alpha\text{-Al}_2\text{O}_3$ layer and the mullite.

IV. DISCUSSION

The microstructural data discussed here can be combined with previously published reaction kinetics studies [13,14] to develop a microscopic model of the reaction. The kinetic data [13,14] can be summarized as follows. The reaction layer thickness increases linearly with time for reaction temperatures between 900°C and about 1150°C , for times as long as 250 minutes. Above 1200°C the reaction kinetics exhibit two different time dependences—an initial linear regime, followed by a regime that exhibits $t^{1/2}$ kinetics. The transition from linear to $t^{1/2}$ kinetics occurs sooner, the higher the temperature (e.g., the transition occurs at 0.6 min at 1250°C [13]). This behavior is shown schematically in Fig. 12. The penetration rate in the linear time regime increases with increasing reaction temperature. However, for practical experimental reasons the linear regime is observable only between about 900°C and 1200°C . (Below 900°C reaction is inhibited by a passivating oxide layer on the Al. Above 1200°C the reaction shuts off so quickly that it is difficult to get any reliable thickness measurements.) Kinetics in the $t^{1/2}$ regime are so slow at 1300°C and above that essentially no reaction layer is detectable at the scale observable by optical microscopy. Further details on these results are provided in references 13 and 14.

Explaining reactive penetration of mullite by molten Al requires relating thermodynamics, macroscopic kinetics, and evolution of microstructure. The overall thermodynamics are described by equation 1, which has a $\Delta G_r^\circ = -1014$ kJ at 1200K for $x=0$ [7]. The reaction involves several sequential steps, including: (a) transport of molten Al to the reaction front; (b) reduction of the mullite by molten Al at the reaction front, leading to formation of Al_2O_3 and Si (equation 1); and (c) transport of Si to the external Al

pool. The overall reaction rate will be determined by the slowest of these sequential steps. The possibilities are that the overall reaction rate is determined by the rate of the interface reaction (process (b)), or by diffusion of a species to or from the reaction front (process (a) or (c)). If the rates of any of the steps are comparable then there could be some sort of mixed control. The rate of process (b) is also the rate of Si and Al_2O_3 production at the reaction front.

The relatively large Al channels observed in the reacted layer (Fig.2 and references 12 and 13), suggest that transport of molten Al will be by liquid diffusion or flow rather than by atomic-scale diffusion through the lattice and grain boundaries. Al and Si transport may operate simultaneously since the Si is highly soluble in the molten Al (about 37, 56, 67, and 96(wt%) at 900, 1100, 1200 and 1400°C, respectively), so that the path for liquid Al transport is also the path for Si counter-diffusion. All three processes a, b, and c should be thermally activated and exhibit Arrhenius behavior. However, the activation energies for the processes are expected to differ, which could lead to different rate controlling steps in different temperature regions.

Note that transport of oxygen through the molten Al to the reaction front is not required because reaction between Al and mullite is thermodynamically favored and oxygen comes directly from the mullite. Significant oxygen transport through the molten Al in the present case is unlikely in any event because oxygen and Al are so reactive that they would form a dense Al_2O_3 coating on the Al surface, which would act as a barrier to further oxygen diffusion.

Based on the observed microstructures and available kinetic data [13,14], we propose three rate controlling steps that operate in three different temperature regions. At lower temperatures (from 900°C to less than 1100°C), the overall reaction rate is limited by the rate of interfacial reaction between the Al and mullite (process a). Interface control is supported both by the observed microstructures and by the kinetic data [13, 14]. The microstructure formed at 900°C (Figs. 1 and 2) showed that an Al layer was present at that

reaction front, separating the mullite from the reacted area, and that no Si particles were present near the reaction front. This microstructure suggests that Al and Si transport were much faster than the rate of Si and Al_2O_3 production. The overall reaction rate, therefore, must be controlled by the interface reaction. The linear dependence of the reaction layer thickness with time in this temperature range [13, 14] requires rapid transport of reactants and products, uninhibited by any diffusion through a reaction layer, which is consistent with an interfacial reaction controlled mechanism.

Interfacial microstructures depicted in Figs. 9-11 indicate that at temperatures of 1200°C and higher the rate of the overall reaction is controlled by the rate of Si diffusion away from the reaction front. The microstructures in Figs. 9 and 10 show a significant Si built-up at the reaction front at 1200°C , suggesting that the rate of Si production is greater than the rate of silicon transport away from the interface. This conclusion is supported by published estimates of the rates of Si production and transport for the reaction given by equation 1 [13]. At 1200°C the rate of formation of Si at the interface is calculated as $9.0 \times 10^{-5} \text{ g cm}^{-2} \text{ sec}^{-1}$ and the rate of Si transport in a narrow channel of molten Al was estimated to be $7.5 \times 10^{-5} \text{ g cm}^{-2} \text{ sec}^{-1}$ [13]. Because the temperature dependence is steeper for Si formation than transport [13], the difference in rates is even greater at higher temperatures. As the reaction proceeds, the Si concentration builds up rapidly at the interface. Solid Si should precipitate when the Al becomes saturated with Si at the reaction front. This Si built-up slows down the reaction and eventually stops it by creating a Si diffusion barrier. Further reaction requires either Al diffusion through solid Si or for the Si layer to be gradually dissolved into the molten Al and to be transported away from the reaction front. The observed microstructures (Figs. 9 and 10) suggest that Si transport is rate limiting at 1200°C . The microstructures observed for specimens reacted at 1400°C (Fig. 11) provide evidence for a second rate limiting step at higher temperatures in which a dense, continuous $\alpha\text{-Al}_2\text{O}_3$ layer forms at the interface. This $\alpha\text{-Al}_2\text{O}_3$ layer should be a stable diffusion barrier to Al and Si transport, which should reduce the reaction rate even further. Thus, at 1400°C

the Si and α - Al_2O_3 layer buildup at the reaction front are so rapid that the reaction is very limited and almost no reaction zone is observed (Fig.11).

At temperatures between these two extremes (from about 1100°C to about 1200°C), the rates of Si production and transport are comparable and the rate of reaction appears to be under mixed control. The observed microstructures suggest that the reaction between molten Al and mullite at 1100°C is relatively fast so that any molten Al in direct contact with the mullite is consumed immediately, which leads to formation of the SAO, Si, and Al_2O_3 particles shown in Figs.5 and 6. As a result, many Si particles and very few Al particles are present near the reaction front. The kinetic data also showed the macroscopic reaction rate was a maximum between 1100 and 1200°C[13,14]. All these results imply that the rate of Si production and the rate of Si transport away from the reaction front (i.e. rate of process (b)) are comparable, and that the Si concentration at the reaction front does not reach saturation, at least for times up to 250 min [14]. The rate of reaction, therefore, is under mixed control.

This proposed reaction model can also explain other observed microstructural features. Fig.13 shows schematically the microstructure frequently developed at the reaction zone for temperatures from about 1100°C to about 1200°C. The schematic microstructure is representative of that observed in the specimens reacted at 1100°C for 60 minutes(Fig.8a). The reaction zone in these specimens contains many α - Al_2O_3 needles of nearly the same orientation with Si/Al channels between the needles. Where the Al_2O_3 needles contact the mullite, one can observe the SAO particles, which are a non-stoichiometric and intermediate reaction product. Further reaction of SAO particles would lead to growth of the Al_2O_3 needles and production of Si near the channel tips. At the temperatures where the rate of reaction is under mixed control, the reaction zone microstructure shown in Fig.13 is clearly preferred because it provides effective paths both for the supply of molten Al and for Si removal to the external Al pool. The highest reaction

rate is observed in the temperature range where the α - Al_2O_3 needles are most evident[13,14]. It is also expected the structure shown in Fig.8a and schematically in Fig.13 would become more and more dominant with increasing reaction time. In fact, the structure is observed at the reaction front over a very limited length scale for the 1100°C/5 minute reaction(Fig.6), and is a dominate feature for the 1100°C/60 minute reaction(Fig.8a). The needle (or channel) orientation was found to be nearly parallel to the direction of Al supply, and there was no specific orientation between the mullite grain being consumed and the needles being produced (Figs.8b and 8c). This observation indicates that the channels were oriented for most favorable Si and Al transport. As for why the needle growth axis is parallel to the c-axis of the Al_2O_3 structure, it is very likely that the c-axis is the faster growth direction under these conditions.

V. SUMMARY AND CONCLUSIONS

We have studied by TEM the microstructures of the interface formed by reacting molten Al with dense mullite at 900, 1100, 1200 and 1400°C for periods from 5 to 60 minutes. Quite different microstructures were observed at the reaction front for the four temperatures. For reaction at 900°C, a thin Al layer was found that separates the unreacted mullite from the α - Al_2O_3 product. No Si phase was found near the interface. For reaction at 1100°C, Si, Al_2O_3 , and a SAO phase were found at the interface. The SAO, which has a high concentration of Si, is likely to be an intermediate, nonstoichiometric reaction product. No Al phases were found to be in contact with the mullite. Reaction fronts formed at 1100°C for 60 minutes often exhibited a structure of high aspect ratio α - Al_2O_3 needles with a preferred orientation. For samples reacted at 1200°C, a high density of Si particles was found at the reaction front. The Si particles formed a continuous layer in some regions. For specimens reacted at 1400°C for 15 minutes, the reaction layer was less than 2 μm .

The layer was made of α - Al_2O_3 particles, and was dense and continuous. Some isolated Si particles were found between the α - Al_2O_3 layer and mullite.

We have identified three possible rate-limiting steps that operate in three different reaction temperature regions, based on the observed interfacial microstructures and published kinetic data [13,14]. In the low temperature region from 900°C to about 1100°C, the rate of reaction is limited by interfacial reaction between the molten Al and mullite. In the intermediate to high temperature region from about 1100°C to about 1200°C, two processes with comparable rates control the overall reaction rate. In this temperature range the reaction rate at the Al-mullite interface is comparable to that of molten Al transport to the reaction front, or that of Si transport from the reaction front to the external Al source. In the high temperature region above 1200°C, the rate of reaction is limited either by transport of molten Al from the external Al source to the reaction front or by Si transport from the reaction front to the external Al pool. The TEM observations show that, above 1200°C, continuous layers of Si or Al_2O_3 are found between the unreacted mullite grains and the Al reactant. Closer to 1200°C the Si layer is more evident, whereas at 1400°C layers of Al_2O_3 are more common. Either layer could act as a barrier to further reaction and inhibit the processes that give the linear kinetics observed at lower temperatures.

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Figure captions

- Fig.1. (a) TEM micrograph showing the reaction front formed by Al and mullite reaction at 900°C for 5 minutes; and (b), (c) and (d) EDS spectra taken from the mullite, Al layer and Al₂O₃ particles, respectively. The dashed line in (a) indicates the macroscopic orientation of reacted mullite and the mullite interface.
- Fig.2. TEM micrograph of the reaction front formed by Al and mullite reaction at 900°C for 60 minutes. The dashed line indicates the macroscopic orientation of reacted mullite and the mullite interface.
- Fig.3. TEM micrograph of the reaction front formed by Al and mullite reaction at 900°C for 5 minutes, showing the Al layer at the front is not affected by grain boundaries (marked by G). The dashed line indicates the macroscopic orientation of reacted mullite and the mullite interface.
- Fig.4. TEM micrograph showing the rough reaction front formed by Al and mullite reaction at 1100°C for 5 minutes. The dashed line indicates the macroscopic orientation of reacted mullite and the mullite interface.
- Fig.5. The reaction front formed by Al and mullite reaction at 1100°C for 5 minutes. The dashed line indicates the macroscopic orientation of reacted mullite and the mullite interface.
- Fig.6. TEM micrograph showing penetration of the reaction front into mullite at 1100°C, along with the EDS spectrum from the SAO particle. The dashed line indicates the macroscopic orientation of reacted mullite and the mullite interface.
- Fig.7. TEM micrograph showing the reaction front formed at 1100°C for 60 minutes, along with the EDS spectra taken from three areas as indicated. The dashed line indicates the macroscopic orientation of reacted mullite and the mullite interface.

Fig.8. (a) The reaction front with oriented α - Al_2O_3 needles formed at 1100°C for 60 minutes; and (b) and (c) selected area electron diffraction patterns from the mullite and the Al_2O_3 needles, respectively. The dashed line in (a) indicates the macroscopic orientation of reacted mullite and the mullite interface.

Fig.9. TEM micrograph showing the reaction front formed by Al and mullite reaction at 1200°C for 5 minutes. The dashed line indicates the macroscopic orientation of reacted mullite and the mullite interface.

Fig.10. The reaction front formed at 1200°C for 60 minutes showing (a) Si particles; and (b) a Si layer at the reaction front. The dashed line indicates the macroscopic orientation of reacted mullite and the mullite interface.

Fig.11. The reaction front formed by Al and mullite reaction at 1400°C for 15 minutes, showing a continuous and dense α - Al_2O_3 layer separating the Al from the mullite.

Fig.12. The schematic diagram showing the reaction kinetics at different temperatures T_1 , T_2 and T_3 ($T_1 < T_2 < T_3$). The reaction kinetics has two different time dependencies: an initial linear regime, and a regime that exhibits $t^{1/2}$ kinetics. The transition from the linear to the $t^{1/2}$ kinetics occurs sooner at the higher temperature (i.e. $t_1 > t_2 > t_3$).

Fig.13. The schematic model showing the microstructure at the reaction zone developed for temperatures from about 1100°C to about 1200°C .

Fig.1

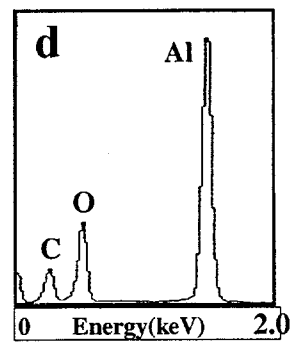
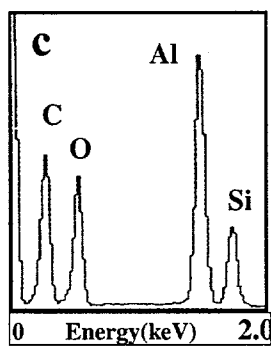
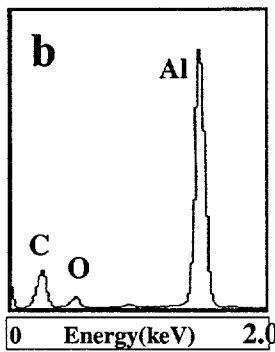
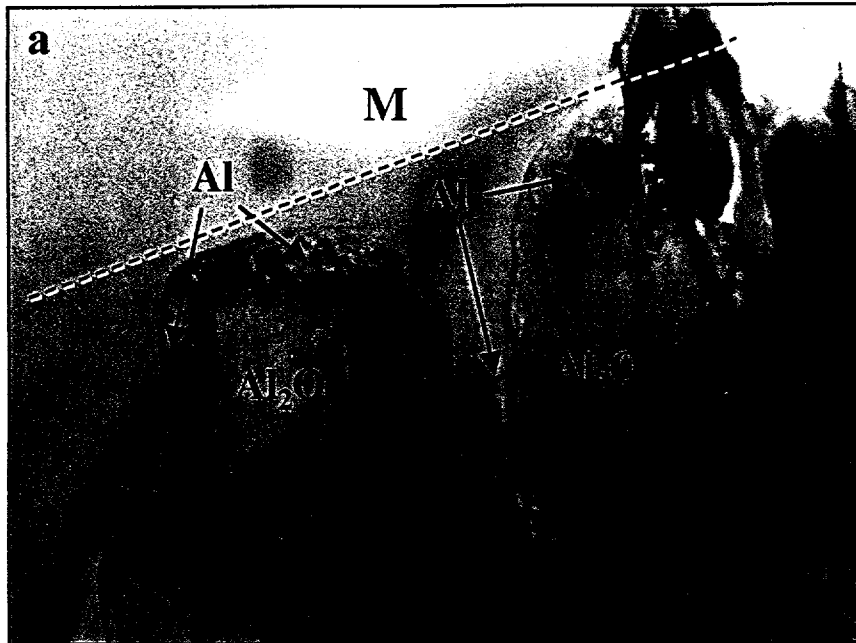


Fig.2

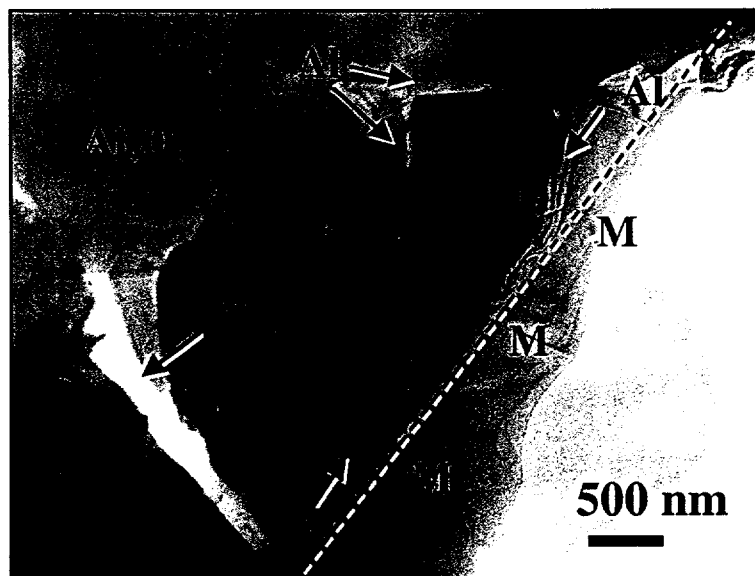


Fig.3

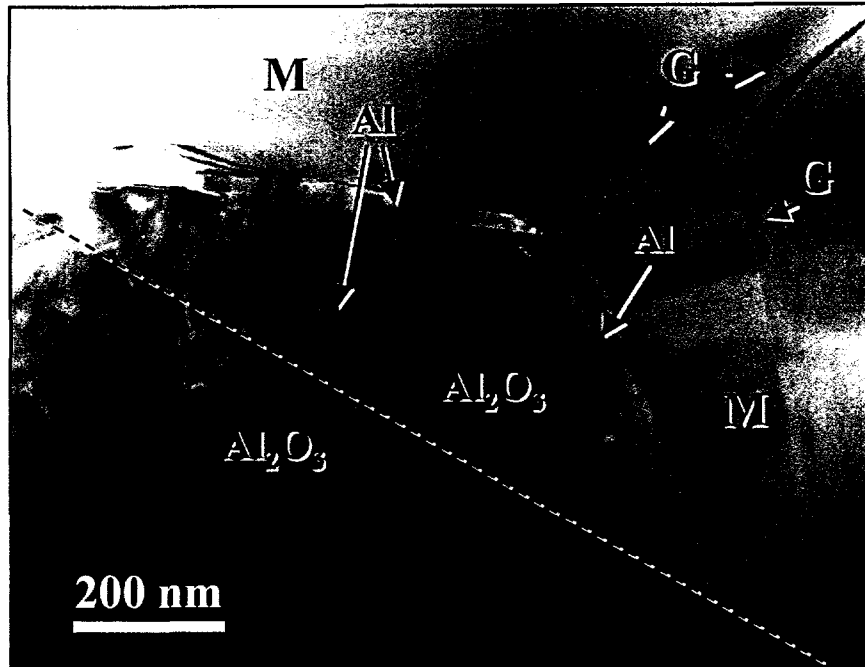


Fig.4

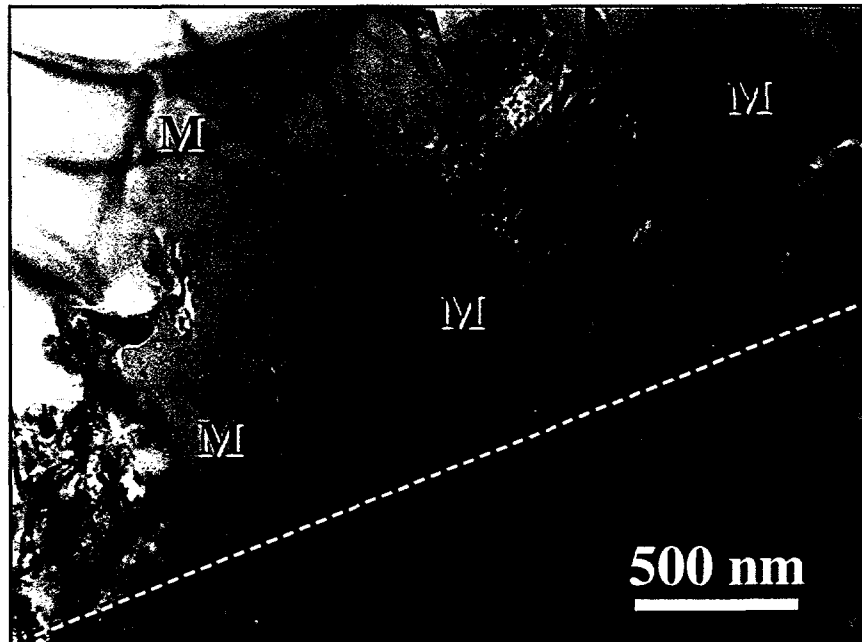


Fig.5

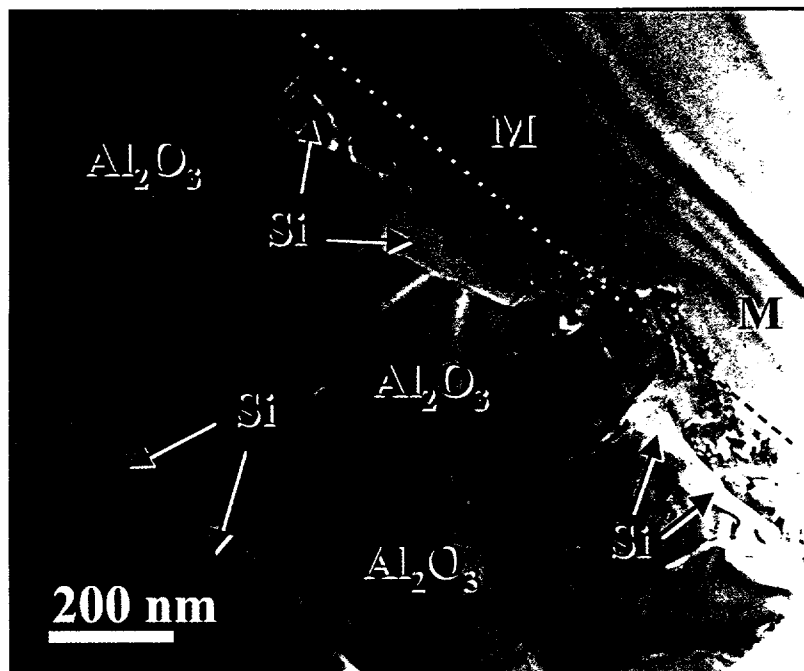


Fig.6

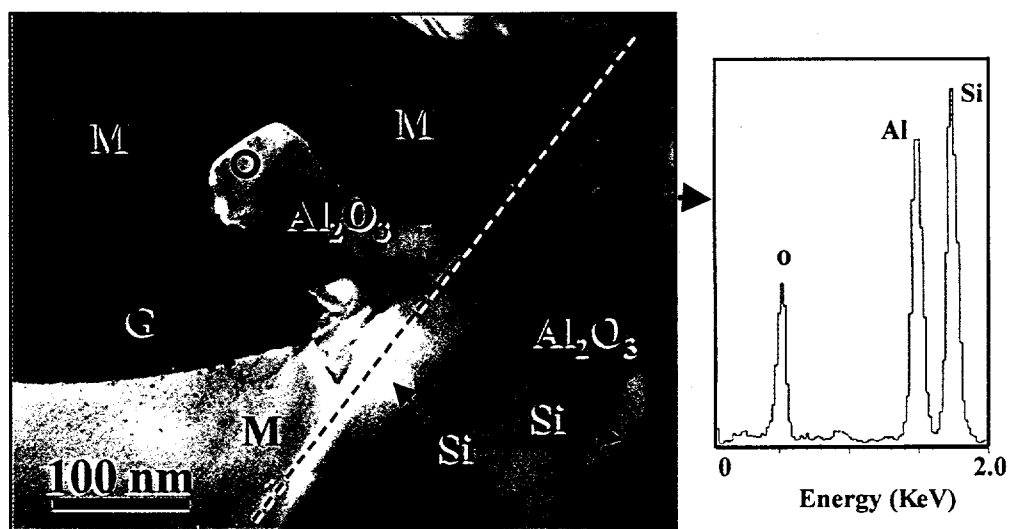


Fig.7

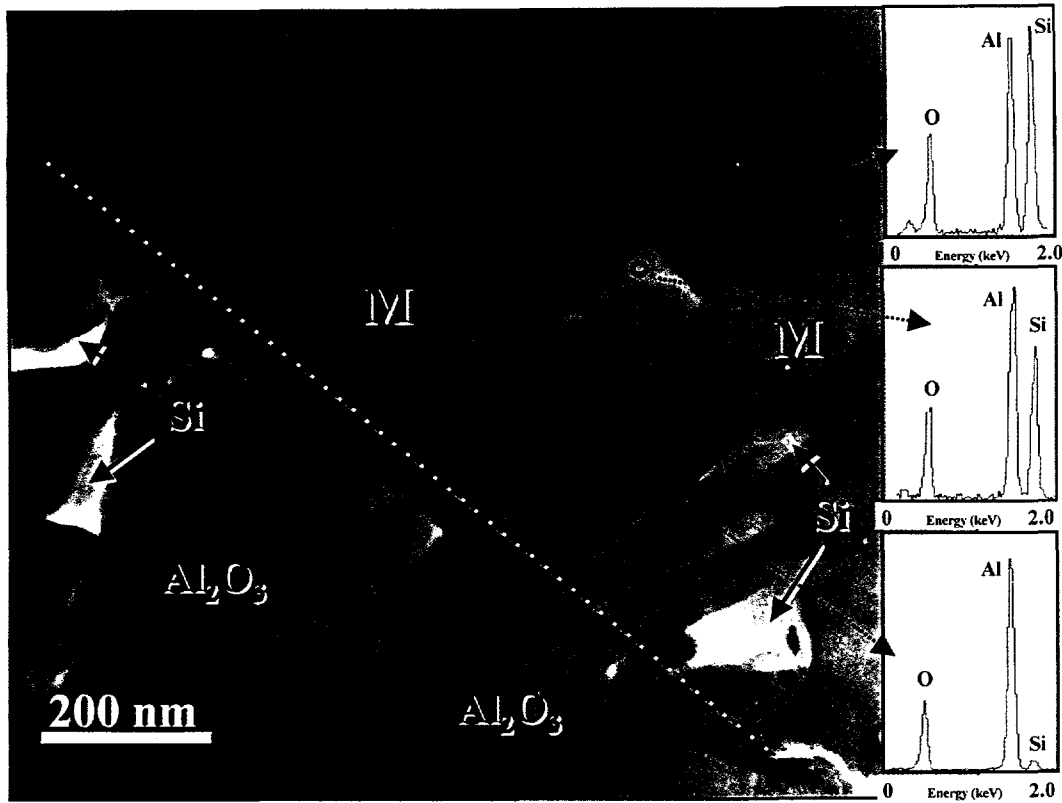


Fig.8

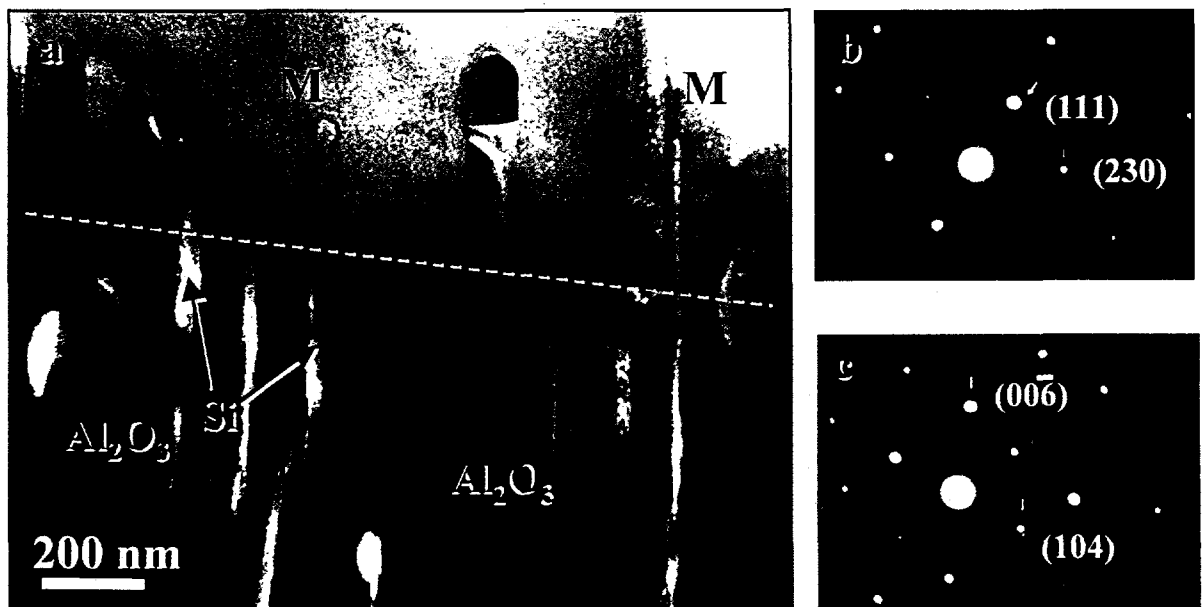


Fig.9

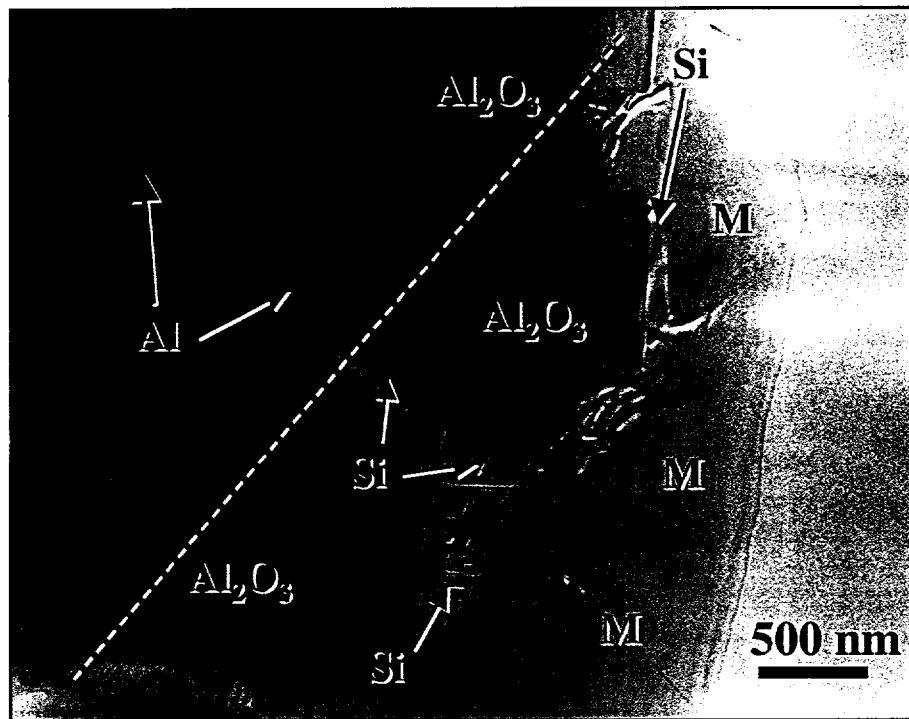


Fig.10

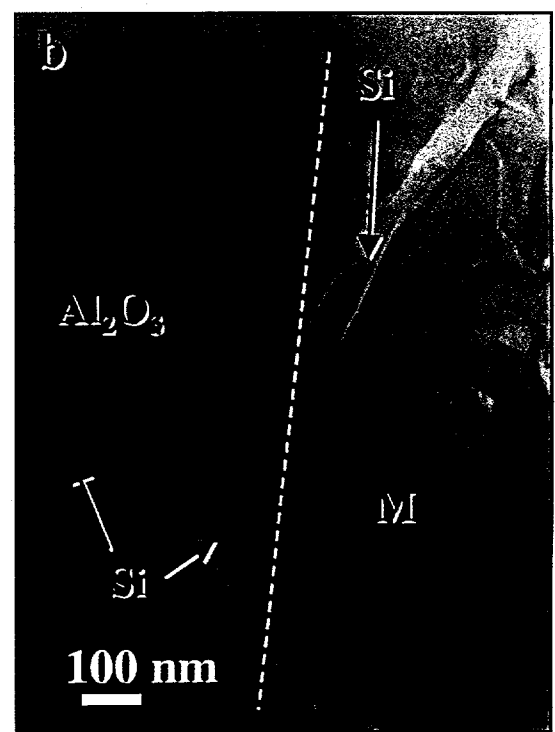
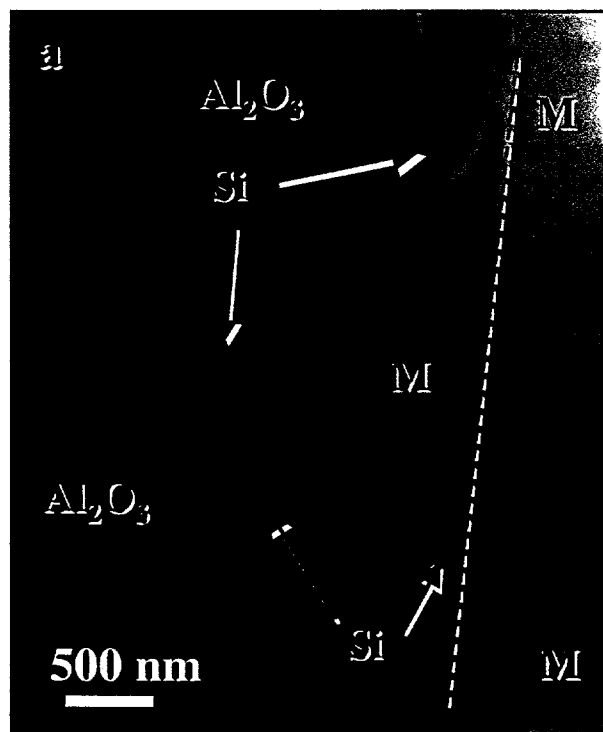
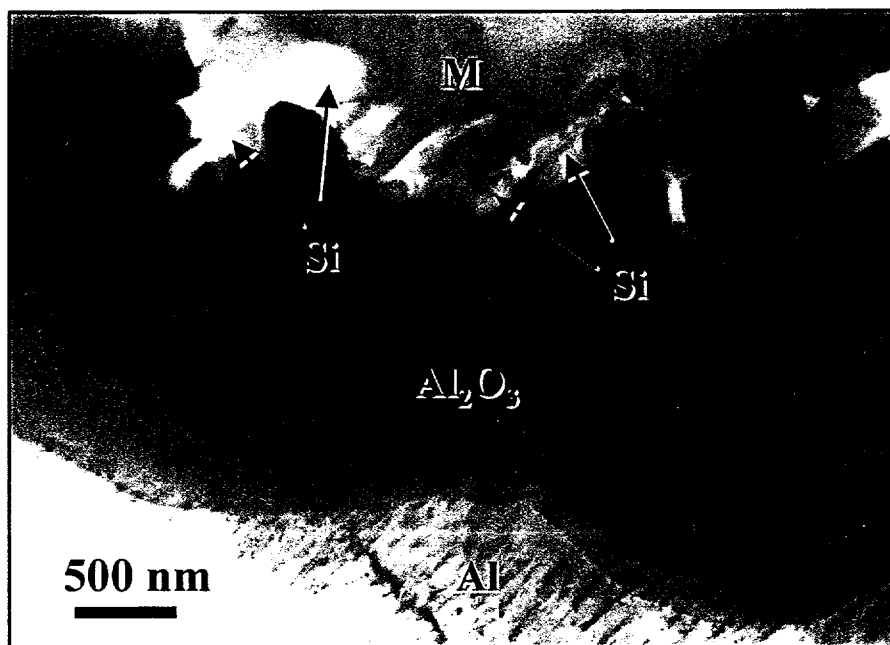


Fig.11



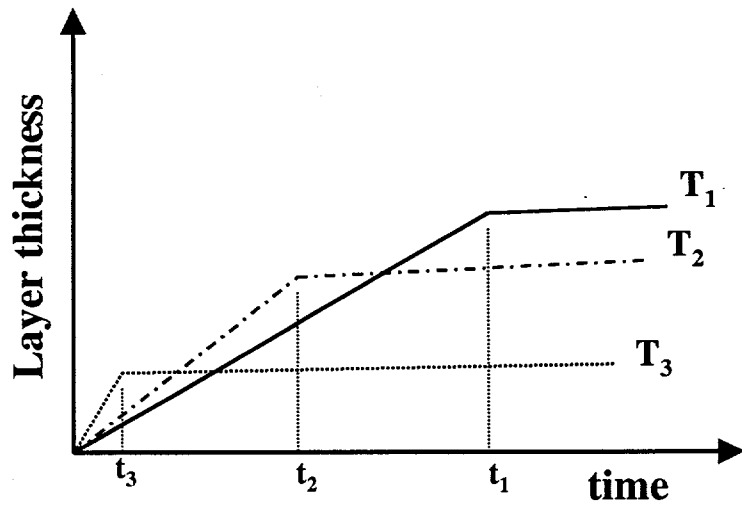


Fig.12

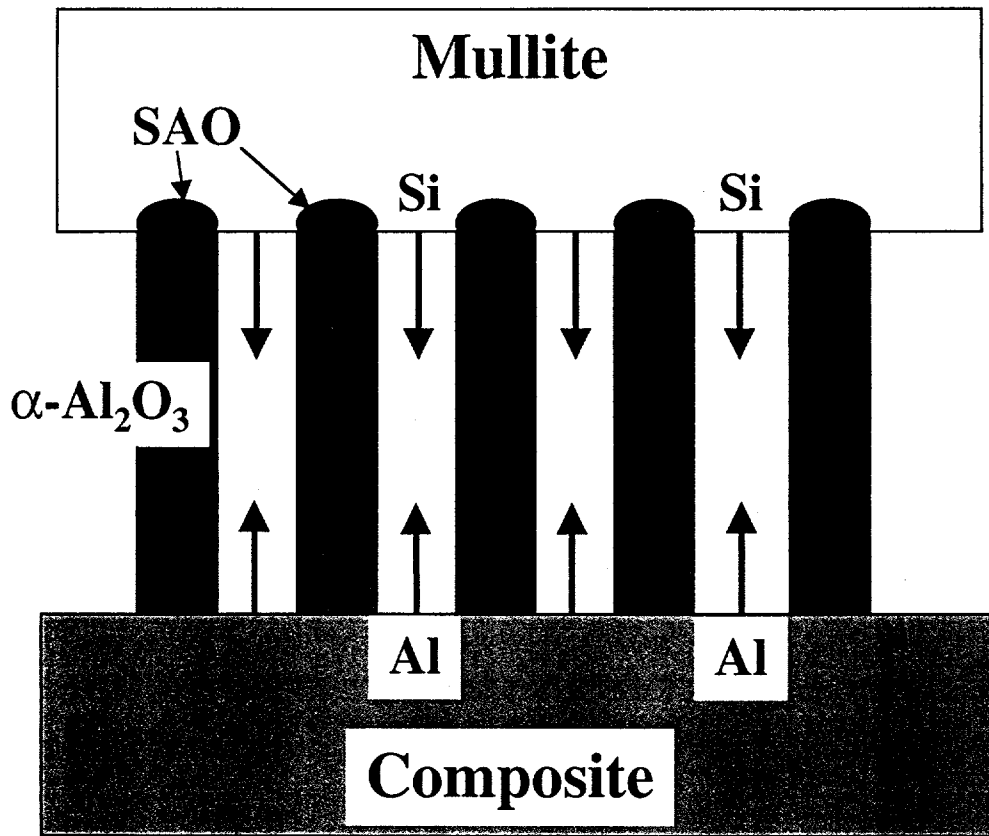


Fig.13