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REACTION MECHANISMS AND MICROSTRUCTURES OF CERAMIC-METAL COMPOSITES MADE BY REACTIVE METAL PENETRATION

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ABSTRACT

Ceramic-metal composites can be made by reactive penetration of molten metals into dense ceramic preforms. The metal penetration is driven by a large negative Gibbs energy for reaction, which is different from the more common physical infiltration of porous media. Reactions involving Al can be written generally as $(x+2)Al + (3/y)MO_y \rightarrow Al_2O_3 + M_{3/y}Al_x$, where MO_y is an oxide that is wet by molten Al. In low P_{O_2} atmospheres and at temperatures above about 900°C, molten Al reduces mullite to produce Al_2O_3 and Si. The Al/mullite reaction has a $\Delta G_r°(1200K)$ of -1014 kJ/mol and, if the mullite is fully dense, the theoretical volume change on reaction is less than 1%. A microstructure of mutually-interpenetrating metal and ceramic phases generally is obtained.

Penetration rate increases with increasing reaction temperature from 900 to 1150°C, and the reaction layer thickness increases linearly with time. Reaction rate is a maximum at 1150°C; above that temperature the reaction slows and stops after a relatively short period of linear growth. At 1300°C and above, no reaction layer is detected by optical microscopy. Observations of the reaction front by TEM show only Al and Al_2O_3 after reaction at 900°C, but Si is present in increasing amounts as the reaction temperature increases to 1100°C and above. The kinetic and microstructural data suggest that the deviation from linear growth kinetics at higher reaction temperatures and longer times is due to Si build-up and saturation at the reaction front. The activation energy for short reaction times at 900 to 1150°C varies from ~90 to ~200 kJ/mole, depending on the type of mullite precursor.

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DISCLAIMER

INTRODUCTION

Ceramic-metal composites are being developed because they exhibit combinations of properties that are unobtainable in single phase materials, for example, high stiffness, high toughness and oxidation resistance.[1,2] A number of processing methods are being studied, including physical mixing of ceramic powders or whiskers in molten metals[2], metal infiltration of fibrous or porous ceramic preforms[3,4], and reaction routes such as directed oxidation of molten metals[5-9], in-situ displacement reactions[10-13], and reactive metal penetration of dense ceramics[14-18]. The reactive techniques have a number of advantages, including the prospect of near-net shape forming. In this paper we review and summarize work we have done over the past several years to understand and control the synthesis and properties of composite formation by reactive metal penetration (RMP). Key to this control is our emerging understanding of reaction mechanisms, which is also presented.

BACKGROUND ON REACTIVE METAL PENETRATION

Results on different ceramic and metal compositions show that the RMP process is applicable to a variety of systems and in most of them parts are produced to near net shape[14-18]. Two requirements for RMP are that the molten metal must wet the ceramic (i.e., the contact angle $\theta < 90°$) and that the Gibbs energy for reaction must be negative[14]. For composites made from Al and oxide preforms reactions can be written in general as,

$$(2 + x)\,\mathrm{Al} + (3/y)\,\mathrm{MO_y} \rightarrow \mathrm{Al_2O_3} + \mathrm{Al_xM_{3/y}} \qquad (1)$$

where $\mathrm{MO_y}$ is an oxide and $\mathrm{Al_xM_{3/y}}$ is the residual metal phase.

Most of our work has been on the Al/mullite system in which molten Al reduces mullite to produce alumina and elemental Si according to the reaction,

$$3\,\mathrm{Al_6Si_2O_{13}} + (8 + x)\,\mathrm{Al} \rightarrow 13\,\mathrm{Al_2O_3} + 6\,\mathrm{Si} + x\,\mathrm{Al} \qquad (2)$$

For the reaction with $x=0$, $\Delta G_r(1200\mathrm{K}) = -1014$ kJ and $\Delta G_r(1600\mathrm{K}) = -828$ kJ[19-21]. For excess Al (i.e., $x > 0$), a composite of alumina, Si, and Al is formed. When the mullite preform is in contact with a large external source of molten Al, the Si produced from the reaction diffuses outward into the Al source, as shown in Figure 1, leaving only a small amount in the composite. Thus, the process naturally avoids leaving significant concentrations of Si that could embrittle the composite.

The change in volume, ΔV, on reaction can be calculated from the molar volumes, V_m, of reactants and products in Reaction 2 [16]. In the Al/mullite system, the relevant values in cm^3/mol are: $\mathrm{Al_6Si_2O_{13}}$ (135.26), Al (9.99), $\mathrm{Al_2O_3}$ (25.62), and Si (12.00). For Reaction 2, assuming $x = 0$ and a dense mullite preform, the predicted volume change, ΔV, after Al penetration is -0.72 cm^3/mole. The calculated fractional volume change on reaction is -0.0018 as shown by:

$$\frac{\Delta V}{3\,V_m(\mathrm{Al_6Si_2O_{13}})} = \frac{13\,V_m(\mathrm{Al_2O_3}) + 6\,V_m(\mathrm{Si}) - 3\,V_m(\mathrm{Al_6Si_2O_{13}})}{3\,V_m(\mathrm{Al_6Si_2O_{13}})} = -0.0018 \;.$$

Figure 1. The interface between the reacted composite (left) and contacting aluminum bath (right) showing Si precipitates in the Al after cooling to room temperature. The composite was reacted for 60 min at 1100°C.

The volume change on reacting Al with commercial mullite-SiO_2 ceramics can be calculated in a similar way by assuming that the molar volumes of the mullite and silica phases in the preform are additive.

With excess Al (i.e., $x > 0$), reactive metal penetration produces a composite of Al_2O_3, Al, and Si whose molar volume depends on the x value in Reaction 2. Net-shape composites also can be obtained with $x > 0$ compositions by adjusting the porosity of the ceramic preform to accommodate the increased volume of Al present in the composite after reaction. For x excess moles of Al, the relative density of the mullite preform required for no volume change on reaction is given by the ratio

$$\frac{3V_m(Al_6Si_2O_{13})}{13V_m(Al_2O_3) + 6V_m(Si) - xV_m(Al)} = \frac{40.62}{40.55 + x}$$

Understanding and controlling RMP allows physical properties to be optimized for particular applications. For composites in the Al_2O_3/Al/Si system, improvements in Young's modulus, fracture strength, density, hardness, fracture toughness, and specific modulus are apparent, compared with the unreacted mullite preform, as shown[14] in Table 1. The fracture toughness of reactively-formed ceramic-metal composites increases with increasing Al concentration, while modulus and density remain relatively constant, making it possible to make materials that are both tough and have a high specific modulus (i.e., high modulus/density).

Table 1. Properties of Ceramic-Metal Composites Formed by Reactive Metal Penetration Compared to the Properties of the Ceramic Preform[14]

Property	Mullite	Al_2O_3-Al-Si Composite
Bend Strength(MPa)	180	250-320
Hardness (GPa)	11.2	10-11
Toughness (MPa • √m)	1.7	6-9
Density (g/cc)	3.16	3.6
Young's Modulus (GPa)	200	274
Specific Modulus(GPa•cm^3/g)	63	76-86

Measurements of physical properties and microstructures show that a three-dimensional skeleton of alumina is formed during reactive penetration[14]. If the Al concentration is high enough that phase also is continuous, resulting in a composite with mutually-interpenetrating metal and ceramic phases. Our measurements show that, relative to the ceramic preform, the composites are more flaw tolerant; that is, the strength degradation from crack formation and propagation appears to be less severe in the ceramic-metal composite than in the original mullite preform[14].

EXPERIMENTAL

Ceramic preforms for most of our studies have been made by sintering mullite powders (Chichibu MP40, Scimarec Ltd. Tokyo, Japan or MULCR, Baikowski International Corp., Charlotte, NC), kaolin (EPK, Feldspar Corp., Edgar, FL) , or mixtures of mullite and SiO_2 (Corning Inc., Corning, NY) to >90% theoretical density by heating in air at 1200 - 1600°C. Some porous ceramic specimens were made by sintering at lower temperatures and for shorter times. In some experiments commercial mullite tubes (MV 30, Vesuvius McDanel, Beaver Falls, PA) or blocks (Ceraten, SA, Getafe, Spain) were used as preforms. Both pure Al (99.9%, Johnson Matthey, Ward Hill, MA), commercial Al alloys (6061 and 5052, Alcoa, Pittsburgh, PA), and synthesized alloys of Al and varying concentrations of Si have been used as the reactive metal.

Wetting and reactive penetration of Al on different ceramics were studied by melting small cubes of metal on polished ceramic disks at fixed temperatures between 900 and 1500°C in a resistance-heated, high vacuum furnace in an atmosphere of flowing, gettered Ar. The furnace has a viewing port that allowed the contact angle of the molten metal to be measured optically. Kinetics and mechanisms of composite formation were studied on samples made in another furnace in which ceramic preforms were dipped in molten Al at a fixed temperature from 900 to 1400°C for up to 250 min. and then removed. The thickness of composite layers was determined by optical microscopic measurements on polished cross sections of reacted specimens. The rate of composite formation was determined from the measured reaction thicknesses. Other specimens were prepared for examination by scanning and transmission electron microscopy using standard techniques. Still others were sectioned into bars that were used for measurement of mechanical properties. Some specimens were made by hot pressing reactive mixtures of ceramic and metal powders in graphite dies in the processing range: 900 - 1100°C, 5 - 60 min., 1000 - 4000 psi. Reaction to produce the composite occurred in the graphite die, which also prevented the Si from diffusing out of the composite.

RESULTS

Contact angles of Al on aluminosilicate ceramics such as mullite[14] or fired kaolin decrease with increasing temperature and with time at fixed temperatures of 900°C and above. The steady decrease in Al contact angle with time at temperature is evidence of an on-going chemical reaction. The molten Al drop decreases in volume during a typical experiment as it reacts with and penetrates the ceramic. Wetting of mullite by Al generally is not observed at 900°C (i.e., $\theta > 90°$) and Al wets mullite only after ~30 minutes at 1000°C. Sessile drop experiments conducted on nominally 100%, 99.5%, and 99% pure, dense mullite (with the remainder SiO_2) at 1100°C reveal no significant differences in wetting behavior with minor variations in silica content of the ceramic preform[14]. Aluminum-magnesium alloys readily wet mullite but do not react with it. Al alloys saturated with Si at the reaction temperature also do not react with mullite or mullite-SiO_2 ceramics. X-ray diffraction analysis shows reacted specimens contain Al_2O_3, Al, and Si, in accord with Reaction (2) above. Both Al and Al_2O_3 are present in specimens formed by reactive hot pressing of mixed powders or by penetration of Al into dense ceramics. However, little or no Si is found in samples made by ceramic-molten Al reaction. In them, much of the Si produced in Reaction 2 is found as precipitates in the Al source after cooling to room temperature.

The RMP reaction forms composites with other aluminosilicate ceramics than mullite. One example is kaolin, $Al_2Si_2O_5(OH)_4 \cdot 2H_2O$, which dehydrates to meta-kaolin, $Al_2Si_2O_7$, when heated to 800°C. At typical kaolin processing temperatures of 1600-1700°C crystalline mullite, $Al_6Si_2O_{13}$, nucleates and grows within a glassy matrix. Thus, fired kaolin is similar to mullite but with a continuous glassy grain boundary phase. Reactions 3 and 4 illustrate the sequential conversion of kaolin to meta-kaolin and then to mullite/silica ceramics.

$$Al_2Si_2O_5(OH)_4 \cdot 2H_2O \rightarrow Al_2Si_2O_7 + 4\ H_2O \qquad (3)$$

$$3\ Al_2Si_2O_7 \rightarrow Al_6Si_2O_{13} + 4\ SiO_2 \qquad (4)$$

As with the Al/mullite reaction, initiating the Al/kaolin reaction depends on first forming a ceramic-metal interface. Recent results, as shown in Figure 2, suggest that Al wets dense kaolin better than mullite, as indicated by a reduced contact angle. The lower contact angle should produce a more uniform ceramic-metal interface and, therefore, a more stable reaction front as the metal reacts with and penetrates into the preform.

Aluminum reacts with fired kaolin preforms in much the same way as it does with phase-pure mullite. The reaction is near-net-shape and Si diffuses away from the reaction front and out of the developing composite, to produce an Al_2O_3/Al composite. Due to the higher silica content of the preform, composites prepared from kaolin preforms contain more Al than those prepared from mullite. The Al/kaolin reaction can be represented as the reaction of Al separately with mullite and silica:

$$(8 + x)\ Al + Al_6Si_2O_{13} + 4\ SiO_2 \rightarrow 7\ Al_2O_3 + 6\ Si + x\ Al \qquad (5)$$

Figure 2. The contact angle of molten Al on fired kaolin substrates as a function of time at the indicated temperatures.

Mass and volume balance calculations show that stoichiometric reaction of dense kaolin with Al produces a composite that contains approximately 30 vol.% Al and 70 vol.% Al_2O_3. This corresponds to an x value of ~ 7 in Reaction 5. The predicted composite density is 3.62 g/cm^3. The Al/kaolin reaction seems to be more favorable than Al reaction with mullite as suggested by the observation that complex shapes are more easily formed from kaolin preforms than from mullite.

Samples made by immersing dense mullite preforms in molten Al or Al-Si alloys unsaturated in Si exhibited identical penetration rates for temperatures of 1000-1150°C. There is an induction period of about 5 min. where no reaction occurs, after which the rate increases with temperature and is linearly proportional to time between 1000 and 1150°C. Composite formation rate reaches a maximum of ~6 mm/hour at 1150°C and then decreases with increasing temperature above 1150°C. Closer examination of growth kinetics at 1150°C and above shows that reaction layer formation slows or stops after a relatively short period of linear growth. The duration of linear growth decreases from 25 minutes at 1150°C to less than a minute at 1250°C. At 1300°C and above, no reaction layer is detected by optical microscopy.

Figure 3. Aluminum penetration depth as a function of time for the reaction of aluminum and Ceraten mullite at 1000, 1050, and 1100°C.

Figure 4. The penetration rate of aluminum into MP40 mullite as a function of temperature calculated from the aluminum penetration depth measured after a 15 minute reaction.

Transmission electron microscopic analysis of specimens quenched from the growth temperature shows that the reaction front contains little or no silicon after reaction at 900°C, but that silicon is present at the Al-mullite interface after reaction at 1100°C. The amount of Si at the interface increases with reaction temperature. As shown in Figure 5, at the growth front there is a lamellar microstructure of alternating layers of Al_2O_3 and Al with Si precipitates at the end of the Al_2O_3 lamella for the higher reaction temperatures. The kinetic data and microstructural information suggest that the deviation from linear growth kinetics at higher reaction temperatures and longer times is due to silicon build-up and saturation at the reaction front.

Figure 5. Transmission electron micrographs of the reaction interface for MP40 mullite reacted with pure aluminum at 900°C for 10 minutes and 1100°C for 10 minutes.

Formation rates exhibit Arrhenius behavior up to 1150°C with activation energies between 90 and 200 kJ/mol that seem to depend on the composition of the mullite preform. The reason for the variation in activation energy is still under investigation, but it may be related to the fact that ceraten mullite contains a small amount (<<1%) of a finely dispersed phase that is high in zirconium.

Figure 6. The activation energy for the reaction of Ceraten, Baikowski, and MP40 mullite preforms with aluminum

DISCUSSION

We have proposed a mechanism for reactive metal penetration of Al into mullite that accounts for the experimental observations described above:

(1) Al does not wet mullite below about 1000°C, which inhibits the reaction;

(2) when the molten Al contacts the mullite surface there is an induction period of about 5 min. before reaction starts;

(3) the kinetics of composite layer formation are linear from 1000 to 1150°C;

(4) the reaction rate increases with temperature to a maximum at about 1150°C and decreases at higher temperatures; and

(5) the reaction front shows a buildup of Si for temperatures above 1150°C.

The lack of wetting by Al is explained by its strong tendency to form a thin surface oxide coating when melted even in low Po_2 atmospheres. Although Al melts at 660°C, it does not initially react or spread readily on surfaces because the oxide coating forms a cohesive, passivating layer. At higher temperatures (≈ 1000°C) the oxide tends to be removed by vaporization so Al is able to wet surfaces such as mullite and reaction can proceed.

There is a strong thermodynamic driving force for Reaction (2), for which $\Delta G_r = -1014$ kJ at 1200K. The Gibbs energy for reaction between Al and atmospheric oxygen to form Al_2O_3 is also strongly negative with $\Delta G_r = -1163$ kJ/mole at 1200K[19-21]. The Ellingham diagram for Al/Al_2O_3 indicates that Al and alumina are in equilibrium at a P_{O_2} of $10^{-28.5}$ atm. at 1200K. Thus, to promote Al-mullite reaction and to reduce competition from atmospheric oxidation of Al, the system P_{O_2} should be as low as possible, although obtaining a P_{O_2} below $10^{-28.5}$ atm. in the overall reaction atmosphere is extremely difficult.

The induction period for reaction is explained by the time it takes for parts of the Al-mullite interface that are isolated by the molten Al locally to reach the equilibrium P_{O_2}, which makes conditions favorable for wetting and reaction.

The linear growth kinetics below 1150°C for the reactive penetration of mullite by Al is similar to the linear growth behavior found for directed metal oxidation of Al and other liquid-solid displacement reactions.[5-9] The metal layers seen in at the reaction front of RMP composites, as illustrated in Figure 5, form channels that allow macroscopic flow of molten Al to the reaction front rather than atomic-scale diffusion through narrow grain boundaries. The observed linear growth kinetics suggest that transport of Al from the molten source to the reaction front is not rate-limiting below 1150°C because if it were, the increase in thickness of the reaction layer would be proportion to the square root of time. Below 1150°C silicon diffusion away from the reaction front also cannot be rate-limiting because that would increase the concentration of Si at the reaction front, which would shut down the reaction as it does at the higher temperatures, as discussed below. However, the rate-limiting step in the linear growth regime has not been determined. Potential candidates are the rate of Reaction 2 itself or, less likely, the rate of Al transport through a transitional zone (of constant thickness) near the reaction front.

Because RMP is thermodynamically driven, the decrease in reaction rate with temperature above 1150°C is unexpected. The reaction rate maximum at 1150°C suggests two different mechanisms with different temperature dependences are operative, one being dominant below 1150°C and the other dominant above. TEM analysis of reaction couples heated at different temperatures (Figure 5) show Si precipitates in the reaction zone at 1100°C, with larger amounts at higher temperatures. These results suggest a mechanism where Si production in Reaction 2 increases faster with temperature than the rate of Si transport away from the reaction front. The buildup of Si progressively slows the reaction and eventually stops it when the interface becomes saturated with Si and it begins to precipitate. Because silicon does not react with aluminum, it forms a stable diffusion barrier that prevents further reaction. This proposed mechanism is illustrated schematically in Figure 7.

Figure 7. Schematic of reaction mechanism in formation of composites by reactive metal penetration.

CONCLUSIONS

Al reacts with dense mullite to form ceramic-metal composites according to the reaction: $3Al_6Si_2O_{13} + (8 + x)Al \rightarrow 13Al_2O_3 + 6Si + x\ Al$. Reaction between Al and fired, calcined kaolin can be represented as separate reactions with mullite and silica according to $(8 + x)\ Al + Al_6Si_2O_{13} + 4\ SiO_2 \rightarrow 7\ Al_2O_3 + 6\ Si + x\ Al$. The resulting composites have better properties than the ceramics from which they are made. For reaction between Al and mullite or mullite-SiO_2 ceramics the volumes of reactants and products differ by less than 2%, resulting in a net-shape process. Below 900°C reaction is inhibited by a passivating oxide layer on the molten Al. The penetration rate increases with temperature from 900 to 1150°C, reaching a maximum of ~6 mm/hour at 1150°C. Above 1150°C, the penetration rate slows or stops after a relatively short period of linear growth. The reaction produces Si as a by-product, which must diffuse away from the reaction front in order for reaction to continue. The results suggest that the rate of Si production has a steeper temperature dependence than does its rate of diffusion away from the reaction front. As the temperature increases above 1150°C, Si formation is faster than its transport and Si saturates the reaction front, which causes the reaction to slow drastically. At 1300°C and above, no noticeable reaction occurs.

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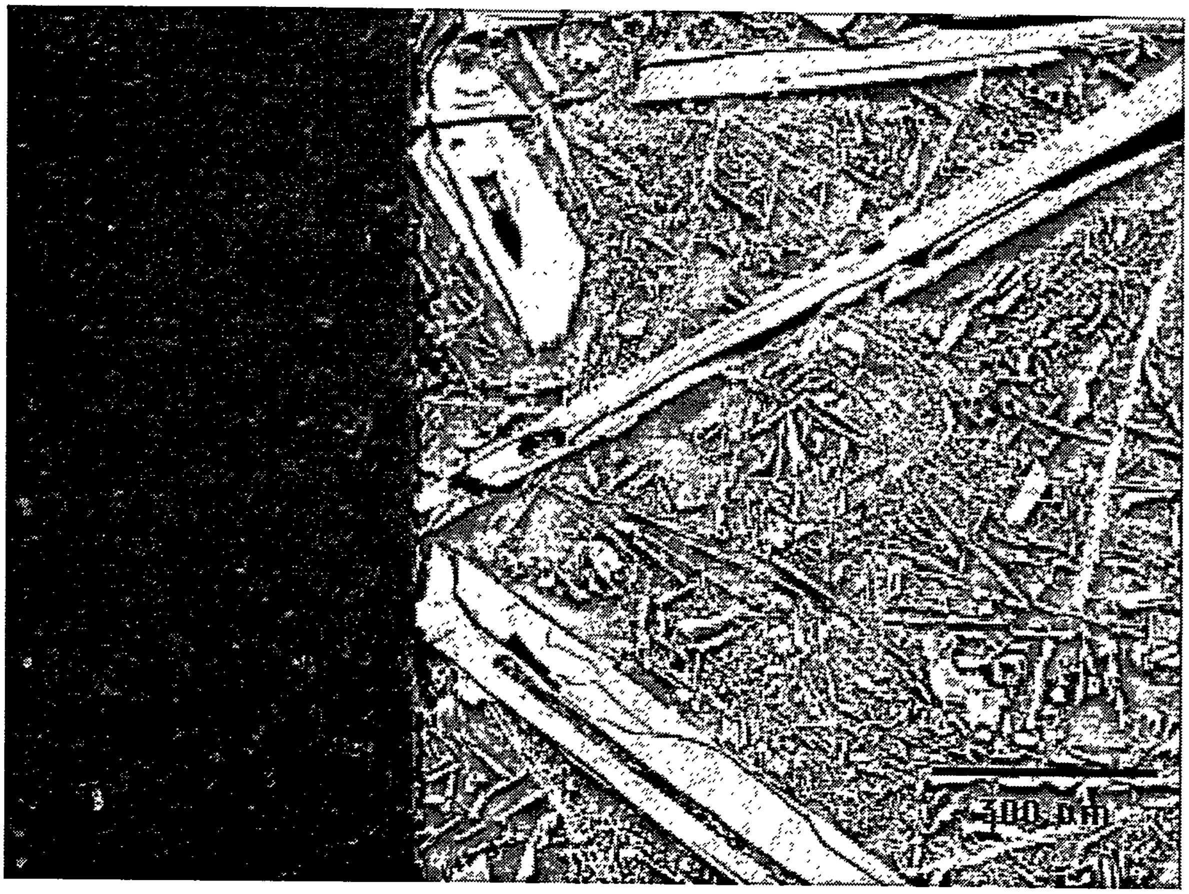


Figure 1. Interface betweenthe reacted composite (left) and the contacting aluminum bath (right)showing Si precipitates in the Al after cooling to room temperature. The composite was reacted for 60 min, at 1100°C.

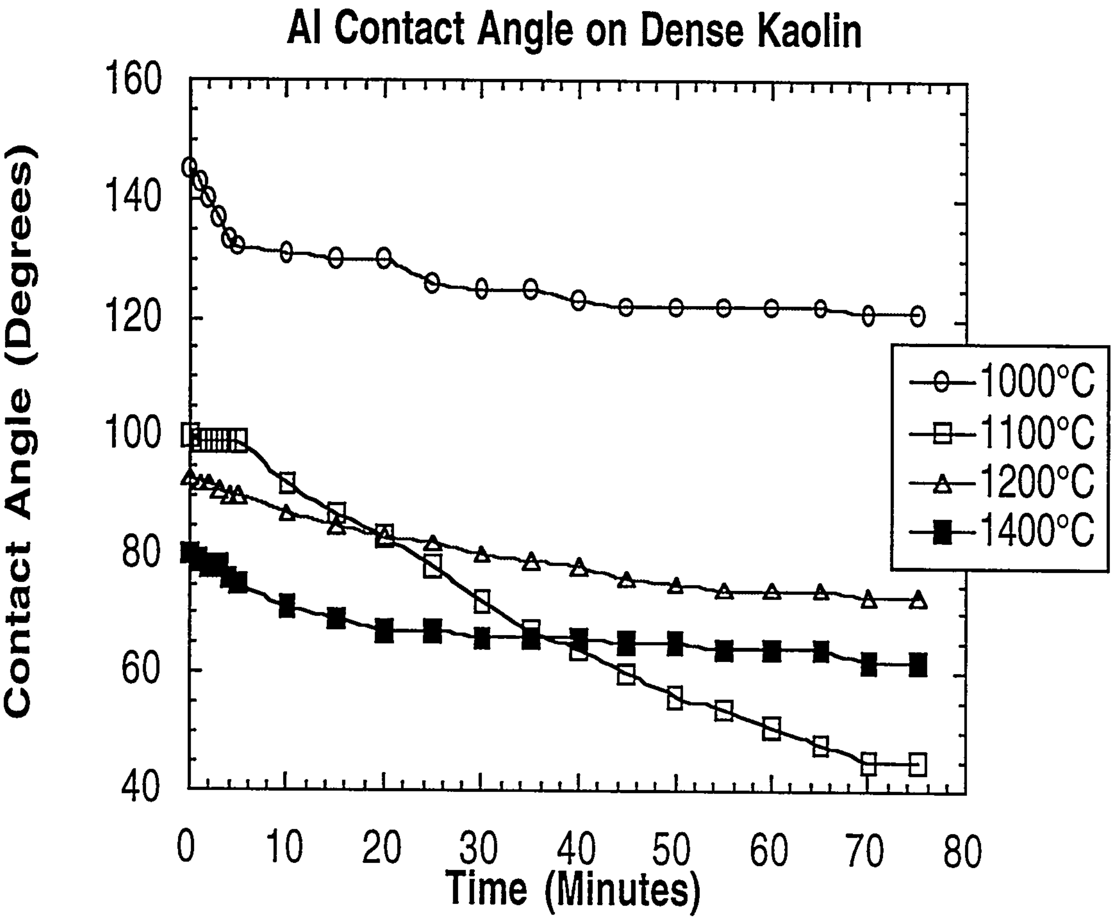


Figure 2. Contact angle of aluminum on dense kaolin as a function of time at the indicated temperatures.

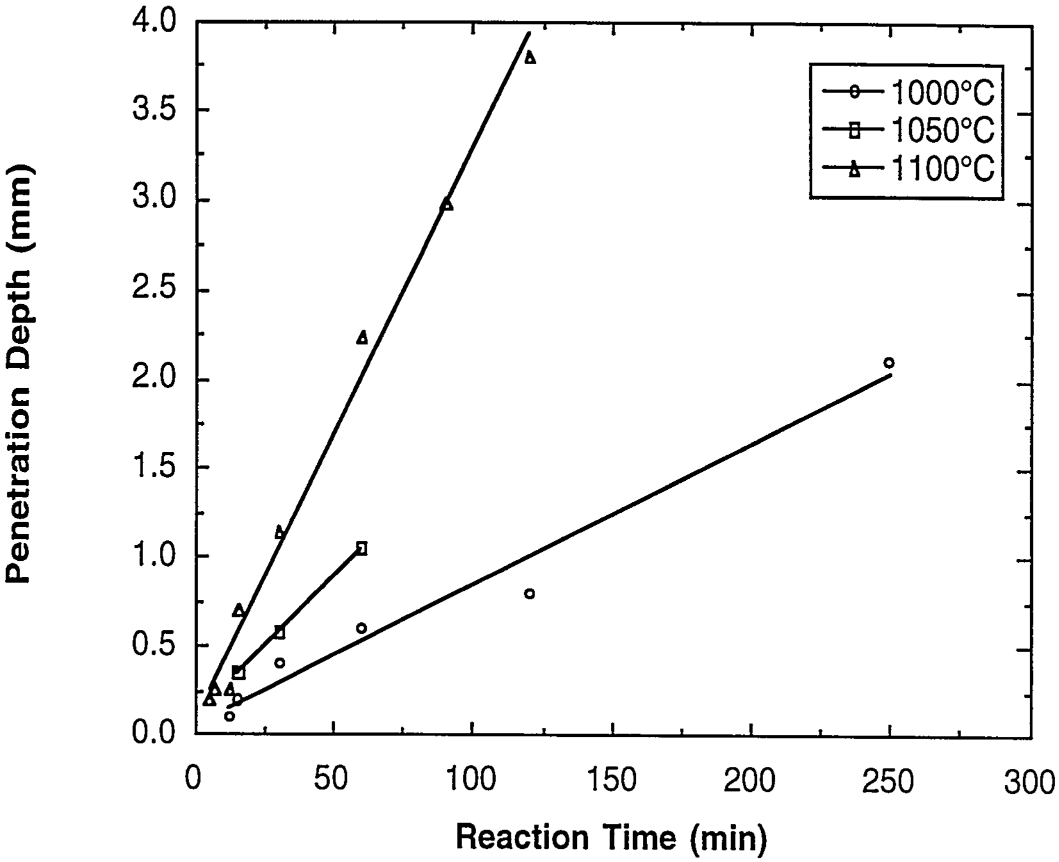


Figure 3. Aluminum penetration depth as a function of time for the reaction of aluminum and Ceraten mullite at 1000, 1050, and 1100°C.

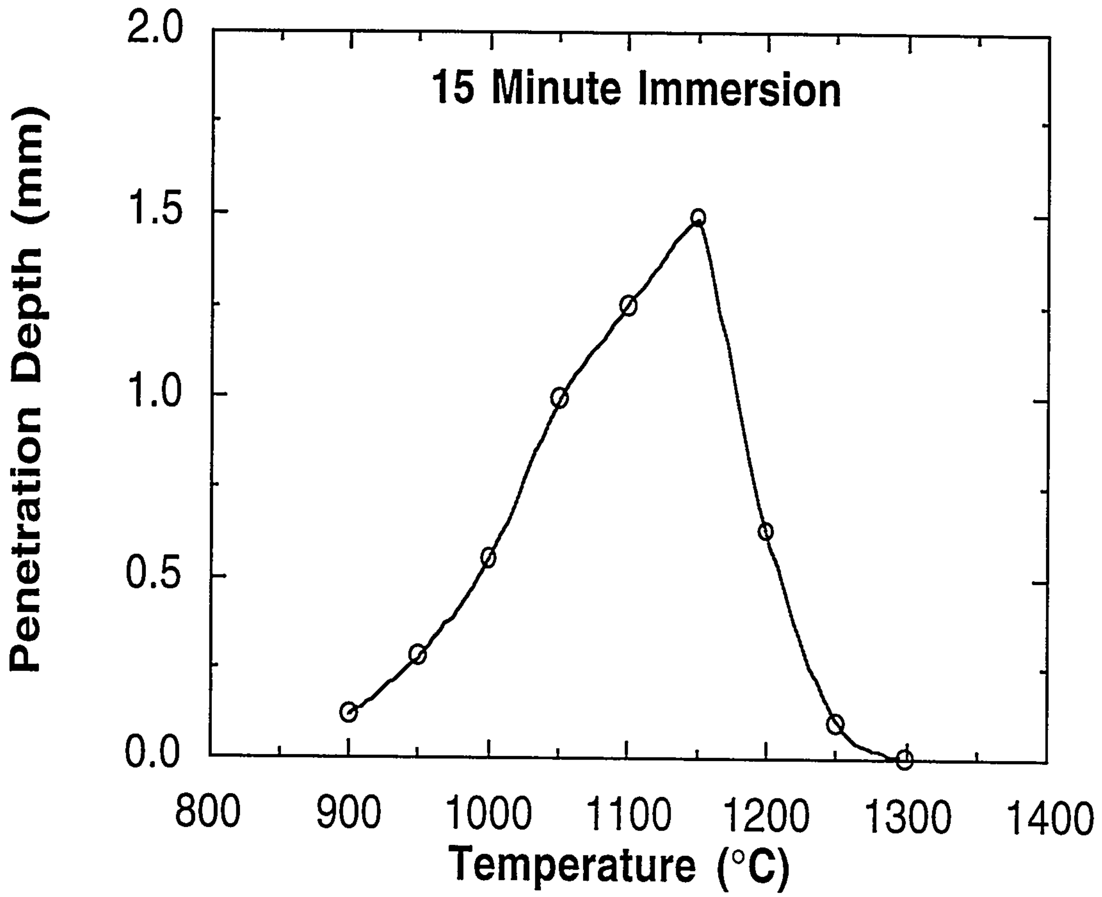
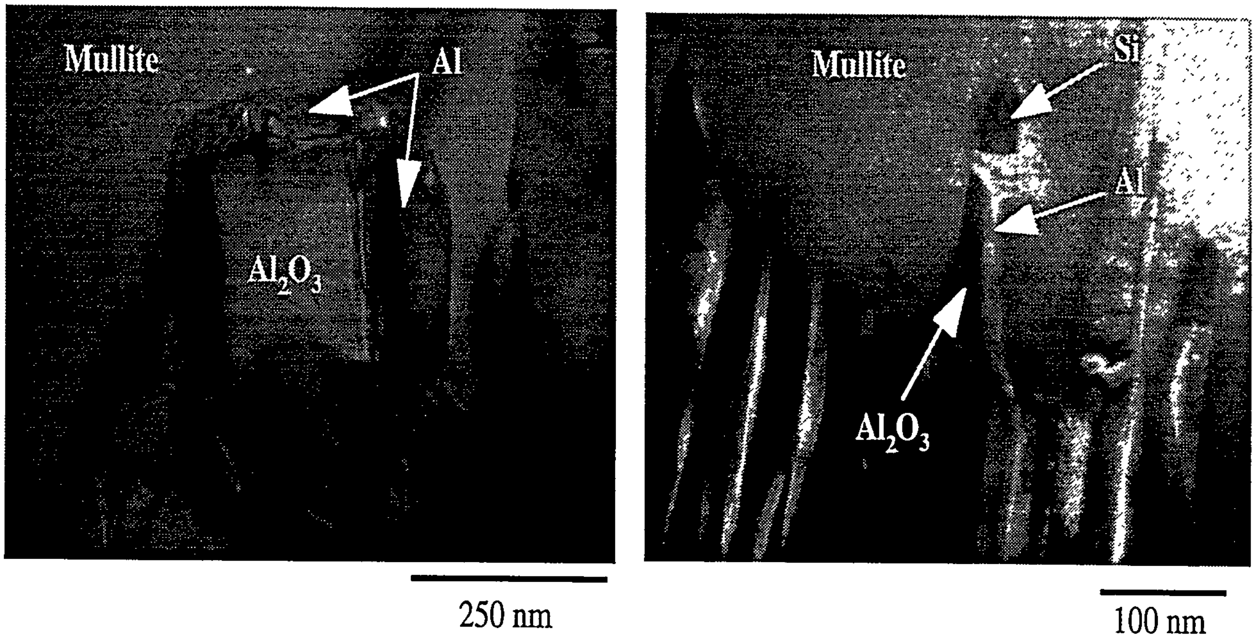


Figure 4. The penetration rate of aluminum into MP40 mullite as a function of temperature calculated from the aluminum penetration depth measured after a 15 minute reaction.



900°C for 10 min

1100°C for 10 min

Figure 5. Transmission electron micrographs of the reaction interface for MP40 mullite reacted with pure aluminum at 900°C for 10 min. and 1100°C for 10 min.

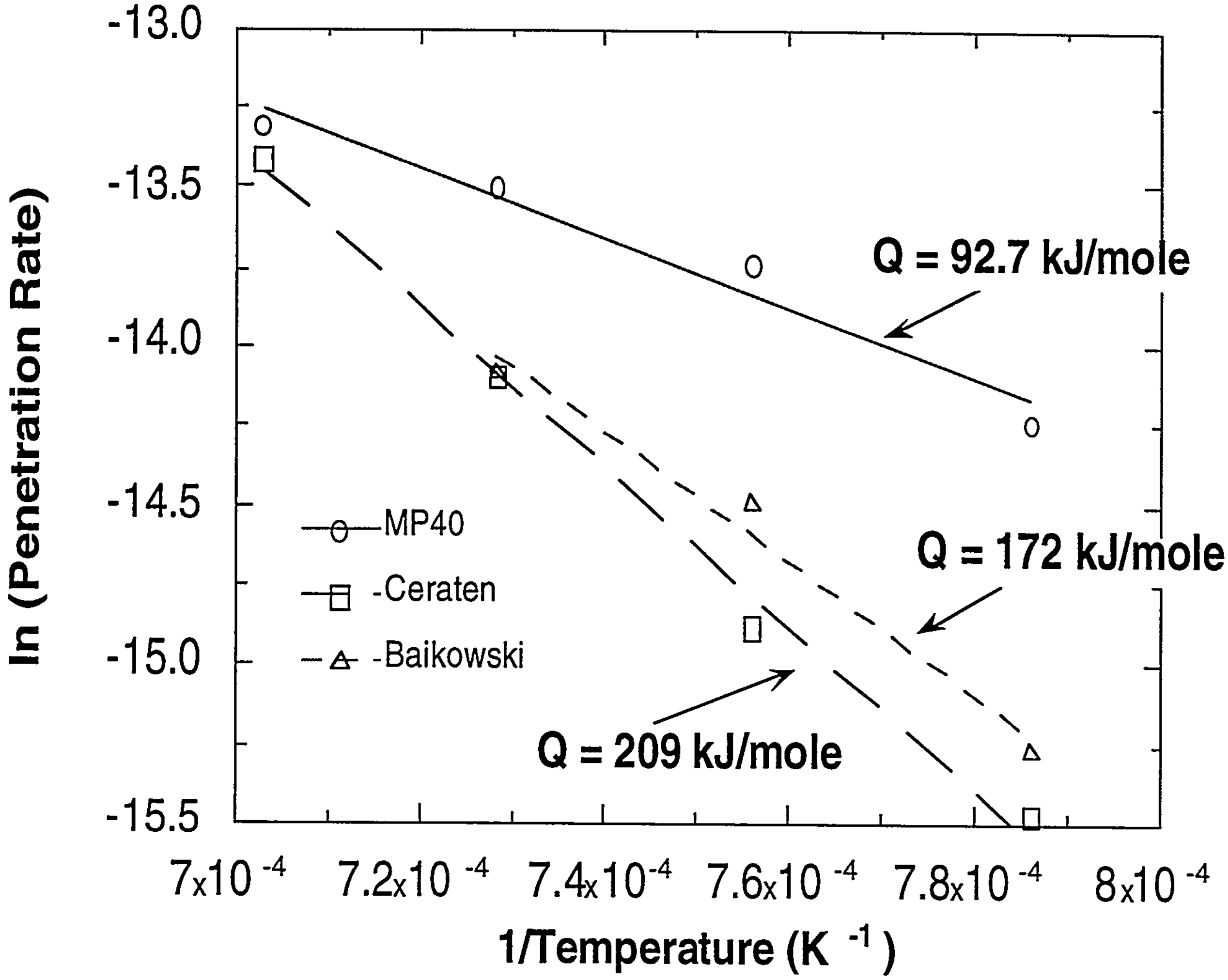


Figure 6. The activation energies for the reaction of Ceraten, Baikowski, and MP40 mullite preforms with aluminum.

In the Reaction Zone:

$$3Al_6Si_2O_{13} + (8+x)Al \rightarrow 13Al_2O_3 + 6Si + xAl$$

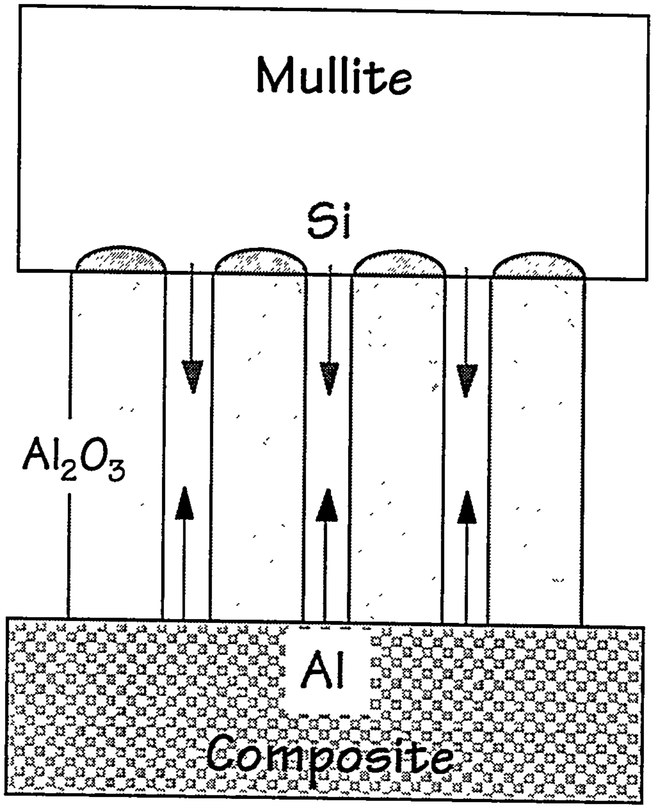


Figure 7. Schematic of the reaction mechanism proposed for formation of composites by reactive metal penetration.