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Preparation of Laminated Composites Using Mullite Refractories and Aluminum

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Abstract: Ceramic/metal composites were fabricated by using mullite refractory plate and Al foil, and their mechanical properties were investigated. Al_2O_3/(Al–Si) composite was formed in the mullite refractories by the reaction between Al and the mullite and silica glassy phases in the refractories. This reaction joined Al metal with the refractory plate. Si formed by the reaction dissolved in the molten Al and precipitated in the Al–Si layer after processing. The Al–Si layer remained almost same thickness after heating at 900°C, but at 800°C and 1000°C, thin Al–Si and Al_2O_3/(Al–Si) composite layers and cavities were observed between the refractory plates. Three types of characteristic fracture behaviour were observed. The bending strength of the mullite refractories/(Al_2O_3/Al–Si)/(Al–Si) laminates with thick Al–Si layers was lower than that of the laminates with thin reaction layers, but the former laminates showed fracture tailing and the plateau of deformation in the load/displacement curve compared with the brittle fracture of the latter laminate. The lower strength of the former laminates may be attributed to the Si phase formed in the Al–Si layer.

1 INTRODUCTION

Laminated composites of ceramic/metal or intermetallic/metal have been investigated due to their superior strength and fracture toughness.[1-3] Especially, the laminate shows high damage-tolerance since the ductile metal in this laminar structure prevents the sudden fracture of the brittle materials. On the other hand, the laminates of ferroelectric ceramic and metal are focused for high capacity condenser in small size.[4]

These laminates are usually fabricated by sintering layers, stacked alternately, of ceramic and metal powders. In order to improve the properties of the laminates, a hot-pressing technique is used for sintering. On the other hand, some unique techniques have recently been applied for fabricating laminates. For example, a plasma spraying process[5] was used for Y_2O_3/Nb laminate and self-propagating high-temperature synthesis (SHS)[6] for Fe_xAl/Fe, Ni_xAl/Ni and Ti_xAl/Ti laminates. The former process is simple and has an industrial application capability, and the latter is low cost.

The authors have investigated the formation of Al_2O_3/(Al–Si) composite by the reaction between commercial mullite refractories and Al. This process could improve the mechanical properties of the refractories by a factor greater than two. By applying this process for the fabrication of ceramic/metal laminate, the following additional benefits will be expected; (i) a strong contact between metal and ceramics due to their reaction and (ii) the increase of mechanical properties of the laminates due to the formation of Al_2O_3/(Al–Si) composite. This paper describes the fabrication of the laminates using the reaction between mullite refractory plate and Al foil and the fracture behaviour of the resulting laminates.

2 EXPERIMENTAL PROCEDURES

The schematic drawing for preparing laminated composites is depicted in Fig. 1. The mullite plate (Nikkato, Japan) used in this work is a commercial refractory and contains mullite phase and silica glass (SiO_2/Al_2O_3 = 1·23 (in mol)). Four pieces of

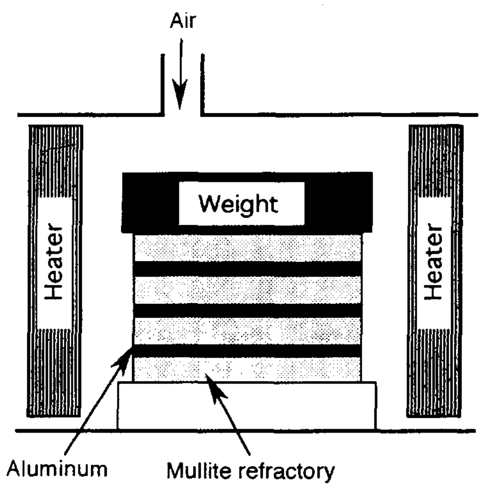

Fig. 1. Schematic drawing for preparation of laminated composites.

the mullite plate of 1·1 mm × 9 mm × 50 mm and three pieces of aluminum foil (purity 99·6%, Nilaco, Japan) of 0·3 mm (or 0·025, 0·1 mm in thickness) × 8 mm × 48 mm were stacked alternately. Here, the Al foil was smaller in size than the mullite plate to prevent the exudation of Al after melting. The stacked samples were placed in the furnace under a weight of 20g/cm^2, heated to 800–1000°C at 200°C/h and held for 30 and 60 min under air flow. If less than 20g/cm^2 was applied, insufficient contact occurred between refractories and Al and cavities appeared.

Microstructures of the resulting laminates were observed with SEM and a metallurgical microscope. Before the observation, the specimens were cut using a diamond blade and ground by SiC abrasive papers (#1000, 1500), followed by polishing

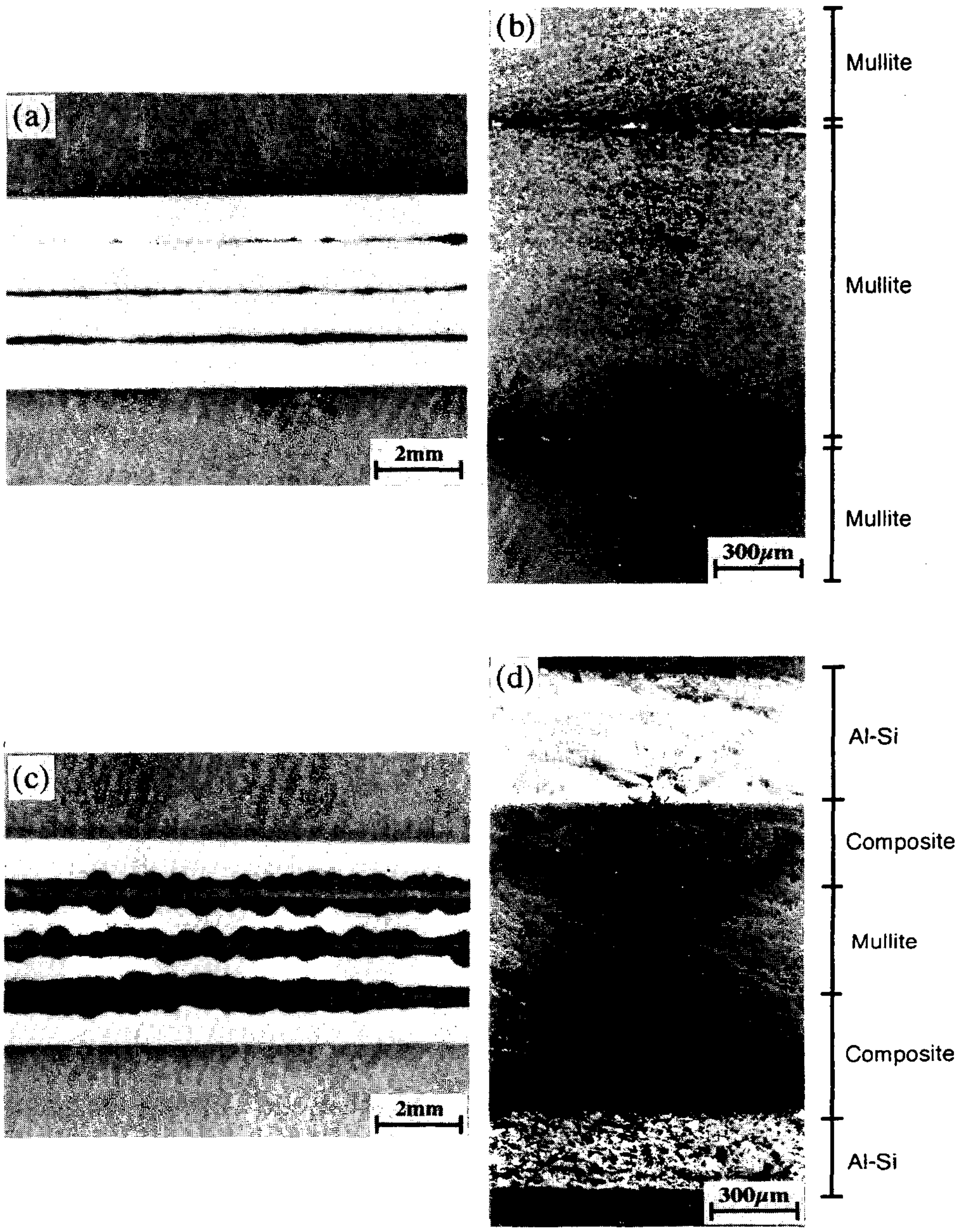

Fig. 2. Sectional view of laminated composites after being heated at 800°C ((a), (b)) and 900°C ((c), (d)) for 30 min.

with diamond suspension (4 μm). The phases and the components in the reaction zone were determined with micro-area XRD and EPMA, respectively. The bending strength of the laminates of 5 mm × 6·5 mm × 36 mm were measured by three-point bending test with a lower span of 30 mm under a crosshead speed of 0·5 mm/min after cutting with a diamond blade and polishing with SiC abrasive paper (#1000).

3 RESULTS AND DISCUSSION

3.1 Formation of mullite/(Al_2O_3/Al–Si)/(Al–Si) laminates

Mullite and glassy phases in the mullite refractories reacted with Al foil, forming alumina and silicon as in the following equations:

$$3(3Al_2O_3 \cdot 2SiO_2)(s) + 8Al(l) \rightarrow 13Al_2O_3(s) + 6Si(s) \quad (1)$$

$$3SiO_2(s) + 4Al(l) \rightarrow 2\ Al_2O_3\ (s) + 3Si(s) \quad (2)$$

The molten Al dissolved the resulting silicon and penetrated into the product. Finally, the mullite plate changed to Al_2O_3/(Al–Si) composite. This process increased the bending strength and fracture toughness of the plate from 170–210 MPa to 330–420 MPa and 1·3–1·8 MPa·$m^{1/2}$ to 5·2–5·9 MPa·$m^{1/2}$, respectively. The details will be described elsewhere.[7]

In the present work on mullite refractories/Al laminate, Al foil of 0·27 mm thickness is required to convert the refractory plate of 1·1 mm thickness completely to Al_2O_3/(Al–Si) composite based on the composition and the above eqns (1) and (2). Therefore, the thickness of the composite produced by the reactions can be varied by changing the thickness of the Al foil. However, the laminated products prepared with Al foils of 0·025 mm and 0·1 mm in thickness showed inhomogeneous reaction and large cavities. The Al foil of 0·3 mm was satisfactory for preparing the laminates without cavities and was used in the following experiments.

The photographs of the sectional view of the laminated composites heated at 800°C and 900°C are shown in Fig. 2. The XRD pattern (Fig. 3) from the black-coloured product in Fig. 2(c) shows the formation of Al_2O_3/(Al–Si) composite in the mullite refractories after eqns (1) and (2). The resulting Si was partly dissolved into molten Al as mentioned above. Since the reaction between the refractory plate and Al foil was slow at 800°C, the molten Al exuded from the laminates, resulting in a thin reaction layer (Fig. 2(a)). In high magnification of this specimen (Fig. 2(b)), there are also small cavities and a thin Al–Si layer

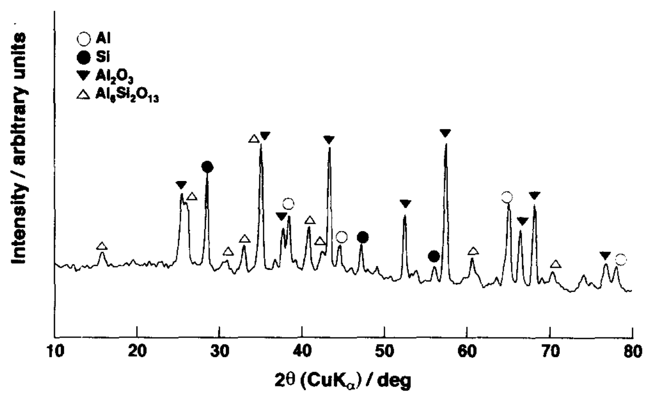

Fig. 3. Micro-area XRD analysis in composite layer of laminated composite reacted at 900°C.

between the mullite refractories. The same feature was observed in the laminate fabricated at 1000°C owing to the exudation of molten Al at low viscosity. On the other hand, Al reacted with the refractory plate easily at 900°C, forming a thick reaction product of Al_2O_3/(Al–Si) and the remaining Al–Si layer. The reaction and the high viscosity of Al prevents the exudation of molten Al. The resulting specimen became the mullite refractories/(Al_2O_3/Al–Si)/(Al–Si) laminate, but the formation rate of the composite varied with its position and the advancing line of the composite was wavy as shown in Fig. 2(c). Also, the lower Al layer of the composite in Fig. 2(c) reacted with the mullite refractory more than the upper one, becoming thin. There is no cavity between the Al–Si layer and the resulting Al_2O_3/(Al–Si) composite nor between the composite and the mullite. On heating the raw laminate for longer time of 60 min, large cavities were produced between the resulting Al_2O_3/(Al–Si) composites due to consumption of Al metal. Large grains were observed in the Al–Si layer (Fig. 2(d), Fig. 4(a)). To determine the composition of the grains, the layer was analyzed by EPMA. The resulting maps withAl-Kα and Si-Kα lines are shown in Fig. 4(b) and (c), respectively. Silicon precipitated in Al–Si alloy during processing or cooling and some large grains were formed. The Si grain showed a Vickers hardness of 1030 and brittle cracks from the edges of the indented rectangle. The hardness of Al–Si alloy was 55 and higher than that of pure Al.

3.2 Fracture behaviour of laminated composites

Figure 5 shows the load/displacement curves observed in the laminated composites with thin reaction layers ((a)) and thick Al–Si and Al_2O_3/(Al–Si) layers ((b),(c)), and the views of the

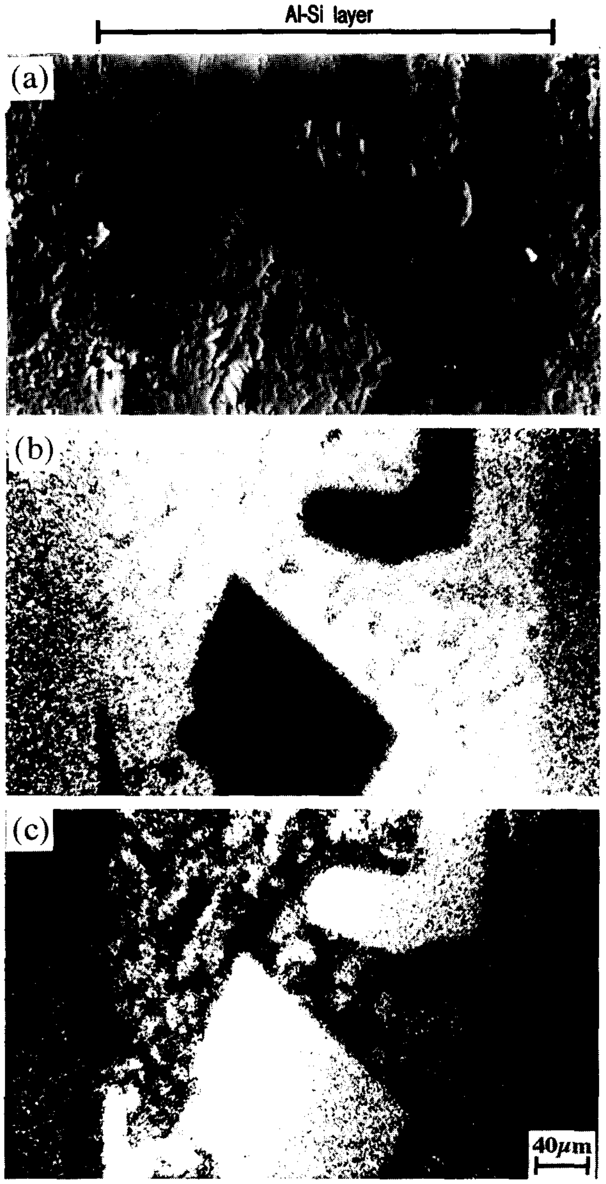

Fig. 4. SEM (a) and EPMA analyses of (b) Al-Kα and (c) Si-Kα in Al–Si layer.

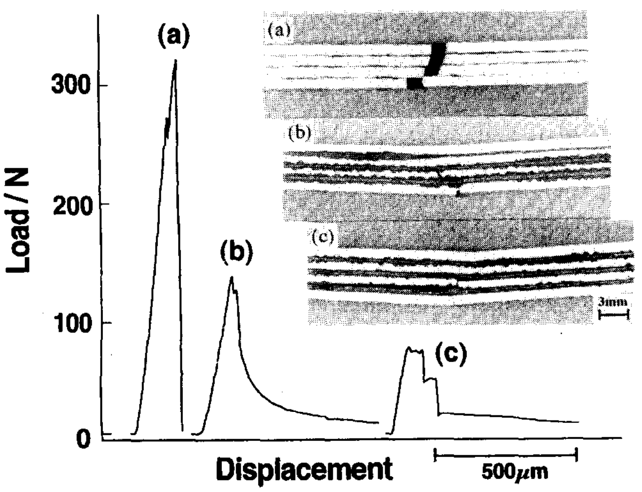

Fig. 5. Load–displacement curves and micrographs of laminates fabricated at 800°C (a) and 900°C ((b), (c)).

samples after measurement. The initial displacement increased linearly with the load in all specimens, but the apparent elastic slopes of samples (b) and (c) were about one-third of that of sample (a). This lower slope cannot be explained by the Young's modulus from the literature: 71 GPa for Al–Si (5 wt%) alloy,[8] 69 GPa for the mullite refractories,[9] and 231 GPa for Al_2O_3/(Al–Si) composite.[10] That is to say, the elastic slopes of samples (b) and (c) should be larger than that of sample (a), since the Young's modulus of the composite should locate between those of the components of the composite.[11] The reason for the unexpected behaviour is unexplained. The sample (a) shows two peaks in the fracture curve. The first peak corresponds to the crack formation of the lowest refractory plate, to which was applied the maximum tensile load in the test, but this crack was arrested by the first bonding layer and the unbroken refractory plate. The second peak showed brittle fracture in the following three refractory plates. The maximum rupture stress of the sample (a), 138 MPa, was close to that of monolithic refractory plate, 149 MPa. This indicates that, in this specimen, the bonding between refractory plates is enough even though there are cavities in it. On the other hand, the fracture behaviours of samples (b) and (c) are complicated. The maximum rupture stresses of samples (b) and (c) are 43 and 24 MPa, respectively, and these values are much smaller than that of sample (a). However, the former specimens showed semistable fracture behaviour, that is, the fracture tailing in sample (b) and the stepwise fracture with a quasi-plateau of deformation in sample (c). In the case of the fracture behaviour of sample (b), the lowest refractory plate and composite layer initially cracked and the crack arrested temporarily at the Al–Si layer. However, as shown in Fig. 6, the Al–Si layer did not show a plasticity, which was observed in the fracture of Al_2O_3/Al composite without Si phase in Al layer,[12] due to the existence of Si grains. Furthermore, the large Si grain acts as a fracture origin in the Al–Si layer

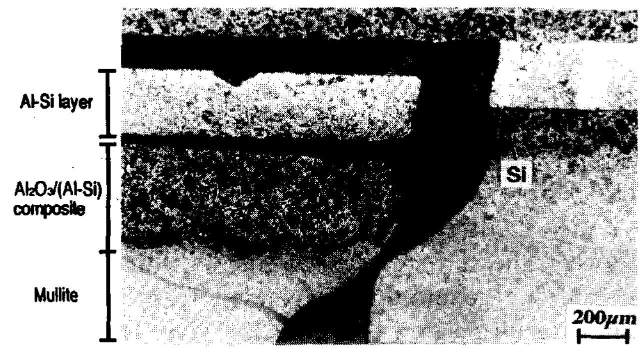

Fig. 6. Micrographs showing delamination cracking in the laminate fabricated at 900°C.

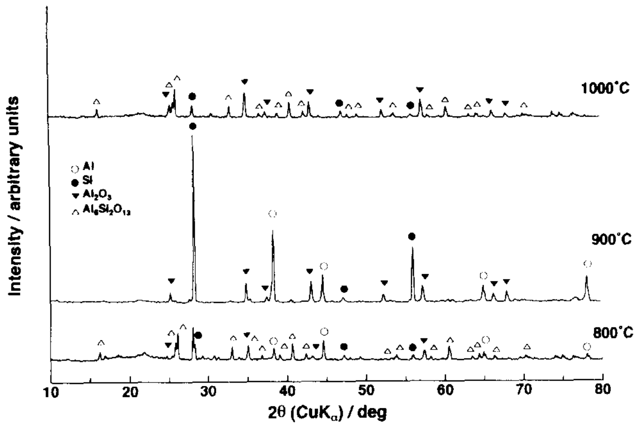

Fig. 7. XRD patterns of delaminated composite layers fabricated at 800°C, 900°C and 1000°C.

(Fig. 6). Finally, the fracture of the second refractory plate occurred and followed delamination cracking at the interface as shown in (b) in Figs 5 and 6, resulting in the tailing in the load/displacement curve. In the case of sample (c), the abrupt decrease in the load corresponds to the fracture of the refractory plate and the quasi-plateau of deformation to the occurrence of delamination between Al_2O_3/(Al–Si) composite and Al–Si layer.

The surface of the delaminated interface of the refractory plates fired at 800°C, 900°C and 1000°C were analyzed using XRD as demonstrated in Fig. 7. Mullite components were observed at the interface under the reaction at 800°C and 1000°C because the exudation of molten Al caused incomplete reaction. Although silicon had been found at all interfaces of the three temperature regions, the amount of Si in the composite heated at 900°C was much higher than that at 800°C or 1000°C. The brittle Si phase caused delamination cracking at the interface.

4 CONCLUSIONS

The microstructure and fracture behaviours of the ceramic/metal laminates fabricated using the reaction between mullite refractory plate and Al foil were studied and the results are summarized below.

(1) Al_2O_3/(Al–Si) composite was well grown into the refractory plate by heating the refractories/Al laminates at 900°C for 30 min. Si was formed by the reaction and precipitated in the Al–Si layer, partially as large grains.

(2) The bending strength of the laminate with a thin Al–Si layer was higher than that of the laminate with thick Al–Si and composite layers. The latter laminate showed a fracture tailing behaviour and delamination cracking occurred due to the formation of Si at the interface and Al–Si layer.

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