Fabrication and microstructure characterization of dense and porous SiC–Si₃N₄/AlN composites using multi-pass extrusion process

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Novel dense and porous SiC–Si₃N₄/AlN composites were fabricated using a multi-pass extrusion process. In the 2nd and 3rd pass dense composites, the diameter of AlN fibers in the SiC–Si₃N₄ matrix was about 170 µm and 30 µm, respectively. The AlN fibers were refined in the SiC–Si₃N₄ composites with the increase of extrusion pass number. However, in the porous SiC–Si₃N₄/AlN composites, the thin layer of AlN was well coated on the continuous pore surface of the porous SiC–Si₃N₄ matrix. The thickness of the AlN layers in the porous composite was about 40 µm. The detailed microstructures and material properties of the dense and porous SiC–Si₃N₄/AlN composites were investigated using OM, SEM, XRD, TEM and HRTEM techniques.

Key-words : Multi-pass extrusion, Structural material, Composite, Microstructure, Material properties

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1. Introduction

Silicon carbide (SiC) and aluminium nitride (AlN) are attractive candidate materials for various high-temperature and electrical applications because of some rare properties embedded in them. SiC has some noteworthy properties such as good oxidation, corrosion resistance, relatively high thermal conductivity, thermal shock resistance and excellent creep resistance. However, strength, reliability and fracture toughness of SiC, still limit its use for some applications. To overcome these disadvantages, there have been some efforts going on to fabricate SiC composites, specially with AlN. AlN has relatively high thermal conductivity, high electrical resistivity and good chemical resistance properties. On the other hand, reaction bonded Si₃N₄ has also some notable properties such as high temperature strength, thermal shock resistance, good chemical stability at elevated temperature and excellent creep resistance which is why it finds uses in gas turbine engines and other high temperature structural applications.

Thus a dense composite of SiC, AlN and Si₃N₄ could be more useful instead of single phase SiC, AlN and Si₃N₄ in high temperature structural, refractory and substrate applications. However, there have been some reports that the reaction bonded porous Si₃N₄ can be used as a material for filtering air and water. Hence, incorporating the favorable properties of AlN, a porous composite of SiC, AlN and Si₃N₄ could be used as an environmental filter in severe conditions.

In this work, we have fabricated SiC–Si₃N₄/AlN composites using multi-pass extrusion process. The goal of this work was two fold: (a) to fabricate dense SiC–Si₃N₄/AlN composites for high temperature structural, refractory and substrate applications and (b) to fabricate continuous porous SiC–Si₃N₄/AlN composites for use as an environmental filter. The detailed microstructure of both the dense and porous composites was investigated using optical micrograph, SEM, XRD, TEM and HRTEM techniques while the material properties such as bending strength and relative density were also evaluated.

2. Experimental procedure

2.1 Dense SiC–Si₃N₄/AlN composites

First of all, waste SiC powder, Si (H. Starck, average size: 7 µm) and sintering additives (6% Y₂O₃, Daejung Chemicals & Metal Co., Siheung-City, Gyeonggi-do, Korea–2% Al₂O₃, Sumitomo Chemical Co., Osaka, Japan) were mixed by ball-milling in a liquid media of ethanol with Al₂O₃ ball for 12 h. At the same time AlN powder (Aldrich Chemical Company, St. Louis, MO, USA, < 10 Micron, > 98 %) and sintering additives (6% Y₂O₃–2% Al₂O₃) were mixed by ball-milling in a liquid media of ethanol with Al₂O₃ ball for another plastic jar for 12 h. Next, both the SiC and AlN powders were dried by heating on a hot plate. The dried SiC and AlN powders were mixed separately with ethylene vinyl acetate (EVA) (ELVAX 210 and ELVAX 250, Dupont, Wilmington, DE, USA) and stearic acid (CH₃(CH₂)₁₇COOH, Daejung Chemicals & Metals Co., Korea), maintaining a volume ratio of 45/48/7 in each case by using a shear mixer (Shina Platec, Co., Korea). After shear mixing for 30 min at 120°C, the homogeneous shear mixed mass of SiC was used to make two tubes by warm pressing and the mass of AlN was extruded as a rod. The two tubes and rod were assembled together to prepare the feed roll and subsequently the feed roll was extruded to make the 1st pass filaments with a diameter of 3.5 mm. The first pass filaments resulted in a core–shell structure in which the core part was of AlN and the tube/shell part was of SiC. The 2nd and 3rd pass filaments were produced by extruding
the bundle of 1st pass and 2nd pass filaments, respectively.

### 2.2 Porous SiC–Si₃N₄/AlN composites

In case of porous SiC–Si₃N₄/AlN composites, a pore forming agent (Carbon, Aldrich Chemical Company, St. Louis, MO, USA), polymer, and CH₃(CH₂)₁₆COOH were shear mixed with a volume ratio of 50/40/10 and the mixture was extruded as a rod having a diameter of 29 mm. A total of two shell of SiC (containing 15 mass% Si) and AlN each, were prepared by warm pressing the shear mixed mass of SiC and AlN, respectively. The shell of AlN (outside dia 29.5 mm) was assembled inside the shell of SiC (outside dia 30.5 mm). Finally, the carbon rod was inserted to prepare the feed roll and was extruded to make the 1st pass filaments with a diameter of 3.5 mm. The 1st pass filament had a core–shell structure in which the core part was the pore forming agent and the shell part was of two alternative layers of SiC and AlN. The inside layer was of AlN and the outside layer was of SiC. The 2nd and 3rd pass filaments were produced by extruding the bundle of 1st pass and 2nd pass filaments respectively.

After extrusion, polymer binder was burnt out in a tube furnace at 700°C in flowing N₂ gas condition for both dense and porous composites. Then, a second burn out process was carried out at 1000°C to make the porous composites by removing the carbon. Finally, nitridation was performed at 1400°C in flowing (N₂ + 10% H₂) gas for 6 h. Next, the samples were crushed into powders and were analyzed to identify the phase composition by X-ray diffraction (XRD). The microstructure of the dense and porous composites, pore size and pore distribution of the porous composites were analyzed by scanning electron microscope (SEM) with Pt coating. The bending strength was measured by a Universal Testing Machine (UnitechTM, R&B, Daejeon, Korea) with a cross head speed 0.5 mm/min. The relative density of the composites was measured by the Archimedes method with an immersion medium of water.

### 3. Results

**Figure 1** shows the cross-sectional (a, b, c, g) and longitudinal (d, e, f, h) optical micrographs of extruded bodies of 1st pass (a, d), 2nd pass (b, e), 3rd pass (c, f) dense and 2nd pass (g, h) porous SiC–Si₃N₄/AlN composites. After the first pass extrusion a core–shell structure was obtained in which the core part was of AlN and the shell part was of SiC/Si which is shown in Fig. 1(a). The shell containing SiC/Si converts to SiC–Si₃N₄ after nitridation at 1400°C. The outer diameter of the 1st pass extruded dense body was 3.5 mm and the thickness of the SiC/ Si shell was about 560 μm. After extruding a bundle of 1st pass filaments (61 unit), the 2nd pass (b, e) composites were obtained. The outer diameter of the second pass extruded dense body was also 3.5 mm. The 3rd pass filament (c, f) was similarly obtained by re-extruding the bundle of 2nd pass filaments. Figure 1(g, h) shows the 2nd pass extruded bodies for porous SiC–Si₃N₄/AlN composites in which the light dark contrast, the white contrast and the deep dark contrast represent SiC/Si, AlN layer and the carbon rod, respectively. It is evident from the micrographs that the integrity and the homogeneity of the structure were maintained throughout the extrusion and re-extrusion process.

**Figure 2** shows the XRD profiles of the SiC–Si₃N₄/AlN composites after (a) second burnout (1000°C) in presence of air and (b) nitridation of the composites in flowing (N₂ + 10% H₂) gas for 6 h. Apart from SiC, Y₂O₃, AlN and Si peaks, a noticeable peak of Al₂O₃ was also appeared after 2nd burnout of the composites. This was due to the oxidation of AlN to Al₂O₃ during the 2nd burnout process which was carried out at 1000°C in presence of air. After nitridation of the composites in flowing N₂ gas at 1400°C for 6 h, silicon was converted to (α/β) Si₃N₄. The new peak of the solid solution of SiC–AlN also appeared at this stage as silicon carbide diffused to aluminum nitride at this high temperature.

**Figure 3** shows the SEM micrographs of the 2nd and 3rd pass nitrided dense composites. The white circles indicated by the arrow heads in Fig. 3(a) shows the AlN layer which is homogeneously dispersed in the SiC–Si₃N₄ matrix. The diameter of the AlN layer in the 2nd pass SiC–Si₃N₄ matrix was about 170 μm. The white contrast corresponds to the AlN layer while the relatively dark contrast corresponds to the SiC–Si₃N₄ matrix in Fig.
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3(a, b). Figure 3(c) shows the cross-sectional micrograph of the 3rd pass dense SiC–Si₃N₄/AlN composites. With the increase of extrusion pass number, AlN layer was refined in the SiC–Si₃N₄ matrix and a fibrous structure was obtained as can be seen in Fig. 3(d). The refined AlN layers in the 3rd pass composite had a diameter of about 30 μm.

Figure 4 shows the SEM micrographs of the 2nd pass porous composites. The pore region resulted due to the burning of carbon rod at 1000°C as shown in Fig. 4(a). The longitudinal image in Fig. 4(b) confirms that the AlN layer was successfully laminated throughout the continuous pore surface of the SiC–Si₃N₄ matrix. A distinct laminated layer of AlN in the pore region of the SiC–Si₃N₄ matrix, can be seen in the enlarged images of Fig. 4(c, d). The thickness of the laminated AlN layer in the SiC–Si₃N₄ matrix was about 40 μm.

Figure 5 shows the relative density (a) and bending strength (b) of the dense and porous SiC–Si₃N₄/AlN composites.

4. Discussion

Dense and continuous porous SiC–Si₃N₄/AlN composites were fabricated using a multi-pass extrusion process. In case of the dense SiC–Si₃N₄/AlN composites, a core–shell structure was obtained where the core was of AlN and the matrix was of SiC–Si₃N₄. The AlN layer was refined with the increase of extrusion pass number. In the 2nd pass dense composites, the AlN layer had a thickness of about 170 μm and in the third pass, the diameter reduced to 30 μm. The bending strength increased from 58.05 MPa (2nd pass) to 64.16 MPa (3rd pass) for the dense composites while the relative density increase from 62.3% to 70.47%, respectively. In case of the 2nd pass porous SiC–Si₃N₄/AlN composites, the AlN fiber in the SiC–Si₃N₄ composites, the bending strength can be increased further. The increase of bending strength was consistent as the relative density of the composite also increased with the increase of extrusion pass number.
5. Conclusion

In summary, using a multi-pass extrusion process, dense and porous composites of SiC–Si₃N₄/AlN were fabricated from raw SiC, Si and AlN commercial powder. The Si powder converted to (α/β) Si₃N₄ after nitridation at 1400°C. During nitridation, SiC also diffused into AlN to form a 2H solid solution of SiC–AlN. The relative density and the bending strength of the composites increased with the increase of the extrusion pass number due to the refinement of the AlN layer in the SiC–Si₃N₄ matrix.

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