Effects of AlN and rare earth fluorides on the thermal conductivity of SiC ceramics with impedance spectroscopy analysis

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Abstract: Dense silicon carbide (SiC) ceramics were fabricated through hot-pressing with an innovative additive combination of AlN and rare earth fluorides (ReF3, Re= La, Nd and Gd). Effects of these additives on the microstructure, phase composition and thermal conductivity of SiC ceramics were evaluated. All samples showed compact microstructures, high densities and clean grain boundaries without visible secondary phases. Sample sintered with 4 wt%AlN and 1 wt%NdF3 (4A1Nd sample) exhibited the highest thermal conductivity (152.3W/mꞏK) amongst all. Impedance spectroscopy analysis was employed to associate with the thermal conductivity variations in different samples by analyzing defects and impurities. 4A1Nd sample exhibited the highest fitting grain and grain boundary resistances among all samples, indicated its lowest concentration of vacancies and impurities, which suggested the best impurity purifying ability of AlN and NdF3 combination. On the contrary, the sample sintered with 4 wt%AlN (4A sample) exhibited a higher concentration of defects than other ReF3 added samples. Therefore, the AlN-ReF3 additive combinations are promising in both tailoring and improving the thermal conductivity of SiC ceramics.

1. Introduction
Silicon carbide (SiC) ceramic is a potential substrate and package material that possesses variety of advantages such as high thermal conductivity, promising mechanical properties and outstanding heat resistance [1-3]. However, pure SiC ceramic is difficult to sinter due to its strong covalent bonding wurzite structure. In pursuit of full densification, the sintering temperature of SiC ceramic is generally over 2200°C [4,5]. The existence of liquid phase during sintering can promote the densification and sinterability, lower the sintering temperature and thus lead to finer microstructure and improved mechanical properties of the SiC ceramics [6]. Therefore, the fabrication of SiC ceramics through liquid phase sintering to achieve a higher densification at lower temperature has becoming a focus in recent decades. Various sinter additives have been utilized to obtain liquid phases during sintering. T.Y. Cho et al. [7] fabricated SiC ceramic with AlN-Y2O3-Sc2O3 additive combination through pressureless sintering and yielded decent thermal conductivity and bending strength of 110 W/(mꞏK) and 520 MPa respectively. A.C. Santos and S. Ribeiro [8] observed the mechanical properties of SiC ceramics sintered with AlN and Yb2O3, obtained high fracture toughness and bending strength of 3.39 MPa m1/2 and 638 MPa respectively.
Unfortunately, $\text{ReF}_3$ additives were seldom employed despite their promising properties of improving the ceramic sinterability. Compared to conventional metal oxide additives, $\text{ReF}_3$ can form liquid phases with $\text{SiO}_2$ at further lower temperature, $\text{AlN}$ can form solid solution (2H$_\text{ss}$ phase) with $\text{SiC}$ and promote the sinterability of ceramics [9]. Moreover, the introduction of $\text{AlN}$ and $\text{ReF}_3$ can also prevent the extra introduction of oxygen impurity. In addition, in-depth studies referring to the effects of impurity and defect on thermal conductivity of $\text{SiC}$ ceramics are still lacking.

In this report, effects of different $\text{AlN-ReF}_3$ (Re= La, Nd, Gd) additive combinations on densification, microstructure development and thermal conductivity of $\text{SiC}$ ceramics were investigated. The impedance spectroscopy analysis was utilized to further associate with the variations in thermal conductivity and defects in different samples.

2. Materials and Methods
Commercially available sub-micron $\alpha$-SiC (H.C. Starck, Germany) with an average particle size of 0.5μm was used as the raw material. $\text{ReF}_3$ (Re= La, Nd, Gd) powders (99.99% purity) and $\text{AlN}$ powder (98% purity, Toyo Aluminium, Japan) were added to the SiC raw material as sintering additives.

Mixing ratio of the powder mixtures are 95 wt%$\text{SiC}$-4 wt%$\text{AlN}$-1 wt%$\text{ReF}_3$ (4A1Re samples) and 96 wt%$\text{SiC}$-4 wt%$\text{AlN}$ (4A sample) respectively. Firstly, the powder mixtures were milled using a planetary ball mill in ethanol for 24 hours at a speed of 350 rpm. Secondly, the resulting mixtures were dried at 80°C for 12 hours. Thirdly, the mixtures were crushed and sieved (100 mesh) and finally hot-pressed at 1950°C with flowing argon atmosphere. Ambient was kept still at a constant pressure of 40MPa for 2 hours and then cooled to room temperature.

Density of specimens were measured using the Archimedes method with an immersion medium of deionized water and calculated from the theoretical density of raw materials by the rules of mixture (neglecting interaction of mixtures), while the relative density is calculated by comparing the bulk density to theoretical density.

The thermal conductivities of all samples were acquired by measuring their thermal diffusivity through laser flash method at room temperature (Nanoflash Model LFA467, Netzsch, Germany). Specimens used to measure thermal diffusivity were prepared into disk shape (φ12.7×2mm). An average diffusivity value of three samples was taken as the final thermal diffusivity.

Microstructural development and morphology of $\text{SiC}$ ceramics were examined by performing scanning electron microscopy (SEM; EM-30 Plus, COXEM CO., LTD, Korea) on their fractured surfaces. The linear intercept method was employed to calculate the average grain sizes of all samples from SEM images. Phase composition of specimens was characterized by X-ray diffraction (XRD; MAXima_X XRD-7000, SHIMADZU, Japan) with Cu-K$_\alpha$ radiation at a step width of 0.02° from 20-80°.

Polished and silver coated SiC ceramic disks (φ12.7×2mm) were prepared for the impedance spectroscopy analysis. Impedance spectroscopy was measured at 550°C using an impedance analyzer (6500B, Wayne Kerr, UK) and a temperature change measurement system (VDMS-2000, Partulab, China).

3. Results and Discussions
Fig.1 shows the XRD patterns of all samples after hot press sintering. The XRD analysis suggest that $\text{SiC}$ is the main phase in all samples, among which 4H-$\text{SiC}$, 6H-$\text{SiC}$ and 2H$_{\text{ss}}$ phases are the primary constitutions, none secondary phases were detected from any resultant ceramics.
Fig. 1 XRD patterns of SiC ceramics hot-pressed with AlN-ReF$_3$ additive combinations, (a)=4A1La, (b)=4A1Nd, (c)=4A1Gd, (d)=4A

It looks to us that a sintering temperature of 1950°C is relatively high, these secondary phases (from the reactions between ReF$_3$ and SiO$_2$ in raw material) tend to volatilize during 2 hours sintering, especially when applied to hot-press method with external pressure.

Fig. 2 Typical fractured surfaces of all samples. (a)=4A1La, (b)=4A1Nd, (c)=4A1Gd, (d)=4A

Fig. 2 (a)-(d) shows the SEM micrographs of typical fractured surface of SiC ceramics sintered with different additives. All samples exhibit contiguous microstructure, equiaxed grains and clean grain boundaries with no visible secondary phases. Differences in their microstructures are apparent, 4A1La sample shows the largest average grain size amongst all, while 4A sample exhibits the most refined microstructure. The relative density and average grain size of all samples are listed in Table 1.

The relative densities of all samples were over 97%, 4A samples exhibited a lower relative density than 4AlRe samples, which suggested that the ReF$_3$ additives can evidently improve the densification and sinterability of SiC ceramics.

Such microstructure differences were mainly due to the radius difference among various rare earth cations: La$^{3+}$(106.1pm) possesses larger cation radius than Nd$^{3+}$(99.5pm) and Gd$^{3+}$(93.8pm). The cationic field strength (CFS) of liquid phase is given by:

$$CFS = \frac{Z}{r^2}$$

(1)

Where $Z$ is the valence of corresponding rare earth cation in liquid phase, $r$ is the cation radius.
Accordingly, as the viscosity of resultant liquid phase increases with increasing CFS, it also increases with decreasing cation radius [10]. Thus the viscosity of liquid phases in 4A1La sample was the lowest amongst all samples, which made the sinterability and grain growth of 4A1La sample obviously outstripped others. 4A sample produced very limited liquid phases during sintering, hence yielded the finest grains.

Table 1 Average grain sizes and relative densities of all samples

| Samples    | Grain size (μm) | Relative density (%) |
|------------|----------------|----------------------|
| 4A1La      | 3.411 (±0.092) | 98.3                 |
| 4A1Nd      | 2.739 (±0.058) | 98.7                 |
| 4A1Gd      | 2.168 (±0.060) | 99.2                 |
| 4A         | 1.991 (±0.079) | 97.5                 |

Fig.3 shows the thermal conductivity of all samples, 4A1Nd and 4A obtained the highest (152.3 W/m·K) and lowest (122.4 W/m·K) thermal conductivity respectively. It is well known that the mean free path of phonon inside SiC grains is highly responsible for the thermal conductivity value. Larger average grain size leads to further reduced phonon scattering and higher thermal conductivity due to fewer scattering grain boundaries per unit volume [11].

As listed in Table 1, the average grain size of 4A1La sample is 24% larger than that of 4A1Nd sample, 56% and 71% larger than those of 4A1Gd and 4A sample respectively. Such an advantage of grain size contributed a lot to a high thermal conductivity of 4A1La sample.

However, the 4A1Nd possessed an even higher thermal conductivity despite its distinctively smaller grains than 4A1La sample, which indicated that the average grain size is hardly the sole decisive factor of thermal conductivity in SiC ceramics.

Phonon scattering by the defects inside SiC grains is another dominating factor that greatly affects the thermal conductivity of SiC ceramics. The scattering cross section $\Gamma$, which representing the phonon scattering by lattice defects is given by the equation below [12]:

$$\Gamma = X_c (1 - X_c) \left[ (\Delta M / M)^2 + \varepsilon (\Delta \delta / \delta)^2 \right]$$

Where $X_c$ is the solute concentration, $\varepsilon$ is a dimensionless parameter, $\Delta M/M$ and $\Delta \delta/\delta$ represent mass and strain misfit (mainly between Si and $V_{\text{Si}}''''$ in this study) respectively. Higher $\Gamma$ leads to lower thermal conductivity. Since the mass of vacancies are zero, the $V_{\text{Si}}''''$ vacancy possesses a larger cross section value, hence the decrease of $V_{\text{Si}}''''$ concentration will lead to the thermal conductivity improvement in SiC ceramics.

Oxygen is the major impurity in SiC ceramics, which can produce $V_{\text{Si}}''''$ by infiltrating into the SiC lattice, leading to the decline of thermal conductivity by enhancing the phonon scattering effect both
from vacancies and oxygen [13]. The formation of liquid phases during sintering can be beneficial to the removal of oxygen impurity from SiC lattice [14]. In order to further investigate the effects of such oxygen extraction mechanism on the thermal conductivity of SiC ceramics sintered with different AlN-ReF₃ additives, impedance spectroscopy analyses were performed at a frequency range from 100Hz to 10Mhz at 550°C for all samples, the Cole-Cole circle plot was established to analyze the data.

The summary of all analyses (from 4A1La, 4A1Nd, 4A1Gd and 4A samples) are shown in Fig. 4. Different RC elements were assigned to specific regions of certain sample, a simplified model with two parallel R/CPE and one CPE was adopted to fit the measure data in Fig.4, R/CPE and CPE represent different responses like SiC grains, grain boundaries or electrodes [15], the fitting parameters are shown in Table 2.

The impedance of CPE (Z_{CPE}) is introduced to accurately response the behaviors of grain and grain boundary section by fixing the non-ideal behavior of capacitance, which is given by:

\[
Z = \frac{1}{[(j\omega)^n Y_0]}
\]

Where n is an empirical exponent, for an ideal capacitor n=1, for an ideal resistor n=0.

From the fitting parameters in Table 2, the grain resistances (R_g) and grain boundary resistances (R_{gb}) of all samples are diversified: the R_{gb} and R_g of 4A sample is comparably low, indicating its high concentration of vacancies and impurities both at grain boundaries and inside grains. Analogically, since the R_{gb} and R_g of 4A1Nd sample are both higher than that of other samples, the vacancies and impurity concentration in 4A1Nd sample are the lowest amongst all, which suggested the best oxygen cleansing ability. In other words, the thermal conductivity improvement from AlN and NdF₃ additives is optimal. In addition, the fitting resistances of 4A1Nd and 4A1Gd sample are higher than those of 4A and 4A1La sample, in our explanation, a finer microstructure of ceramic can be more favourable to the extraction process of oxygen impurity due to shorter route from grain to the grain boundary.

| samples  | grain boundary | grain | electrodes |
|----------|----------------|-------|------------|
|          | R_{gb}/Ω | Y_0/pF  | n  | R_g/Ω | Y_0/pF  | n  | Y_0/nF  | n  |
| 4A1La    | 1787   | 18510  | 0.79 | 556   | 1324    | 0.97 | 3514    | 0.76 |
| 4A1Nd    | 6115   | 3054   | 0.82 | 1762  | 187     | 0.99 | 2375    | 0.64 |
| 4A1Gd    | 4111   | 3542   | 0.76 | 1184  | 222     | 0.96 | 2748    | 0.63 |
| 4A       | 440    | 23430  | 0.83 | 152   | 1471    | 0.92 | 6823    | 0.72 |

Generally speaking, all the AlN-ReF₃ (Re= La, Nd, Gd) additive combinations can contribute to the reduce of oxygen impurity content in SiC lattice, decreasing the concentration of V'\text{Si}'''' and improving the thermal conductivity of SiC ceramics.
4. Conclusion
Dense SiC ceramics with high thermal conductivity were fabricated through hot-pressing method with AlN and rare earth fluorides (LaF₃, NdF₃ and GdF₃). Effects of different additive combinations on microstructure, morphology and thermal conductivity were studied. All samples exhibited compact microstructures with high relative densities, indicated that such additive combinations can effectively improve the sinterability of SiC ceramics. Sample sintered with 4 wt%AlN and 1 wt%NdF₃ additives showed a higher thermal conductivity (152.3 W/m·K) than other samples. Impedance spectroscopy analysis was utilized to associate with the variations in thermal conductivity and defect concentration in different samples. From the fitting results, 4A1Nd sample showed both the highest grain boundary resistance (R_{gb}) and bulk grain resistance (R_g), which testified its lowest concentration of vacancies after sintering. On the contrary, 4A sample exhibited the lowest R_{gb} and R_g, represented the limited ability of extracting oxygen by AlN as the sole additive. In summary, the present study suggest that AlN-ReF₃ additive combinations are effective in tailoring the thermal conductivity by affecting the morphology and defect concentration of SiC ceramics.

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