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Effect of in-situ formed $MoSi_2$ on phase transformation and thermal diffusivity of spark plasma sintered silicon nitride

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ABSTRACT

Dense silicon nitride - Molybdenum disilicide (Si_3N_4-$MoSi_2$) was prepared by spark plasma sintering (SPS) of the Si_3N_4 and Mo powder mixture with 7 mol% CeO_2 sintering additives. The sintering time and sintering temperature were optimized, and the effect of in-situ formed $MoSi_2$ on the microstructure, phase transformation and thermal diffusivity of Si_3N_4 ceramic was investigated. The $\alpha - \beta$ transformation ratio and the thermal diffusivity of Si_3N_4 ceramic composites were both higher than the monolithic Si_3N_4 that had a β:α ratio of 84.3:15.7 and the thermal diffusivity of 10.24 mm^2/s. Furthermore, the Si_3N_4 ceramic composites densified by two-stage SPS exhibited 100% β phase ratio of Si_3N_4, and the highest thermal diffusivity of the composites was 23.17 mm^2/s when the content of Mo particles was under 6 wt%. The in-situ synthesis of $MoSi_2$ is proposed as explaining the improvement of α to β-phase transformation and thermal diffusivity of Si_3N_4 ceramic composites, due to the enhanced SPS process.

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1. Introduction

Silicon nitride ceramics present high strength and toughness due to the specific interlocking microstructure formed by large elongate β-Si_3N_4 grains [1,2]. Haggerty et al. [3] have estimated that the theoretical thermal conductivity of Si_3N_4 crystal can be 200 W/(m·K) or higher, and, in recent papers, the major approach for enhancing thermal conductivity of silicon nitride ceramics is the pure large elongate β-Si_3N_4 grains obtained by the solution-reprecipitation mechanism during a long time sintering at a temperature higher than 1850 °C [4–7]. However, as an effective rapid sintering technique, the SPS technique is typically characterised by a higher heating rate associated with the electric current passing through the die and the powder sample (if the latter is conductive) [8,9]. And the α to β phase transformation of Si_3N_4 has been always incomplete due to the much higher activation energy for phase transformation for SPS than that for conventional sintering (CS) techniques such as pressureless sintering (PS), hot pressing (HP) or hot isostatic pressing (HIP) [10]. Thus, Si_3N_4 composites sintered by SPS technique have been widely studied for enhancing the mechanical properties or thermal conductivities with addition of

conductive second phase such as TiN [11],TiB_2 [12], TaN [13], TiC [14], $MoSi_2$ [15], WC [16], and carbon nanostructures [17–20]. Nevertheless, the conductive second phase has hindered the α to β phase transformation of Si_3N_4, and reduced the thermal conductivity of Si_3N_4 composites due to the retention of α phase while promoting the sintering process [21].

Nygren's group [22,23] has proposed that the solution-reprecipitation process involving the α to β phase transformation could be accelerated by the dynamic ripening mechanism, due to the rapid heating rate during SPS process of Si_3N_4. Furthermore, the rapid densification resulting from an enhanced solution-reprecipitation process is a major factor of the retention of α phase. In order to utilise the solution-reprecipitation mechanism sufficiently during SPS of Si_3N_4, the second phase that should prevent high α phase retention while enhancing the sintering, is required. Krishnarao et al. [24] have showed that $MoSi_2$ can be formed by the reaction of Mo and Si_3N_4 at a temperature of 1400 °C, that is, between the temperature of the liquid phase formation and the temperature of the α to β phase transformation during the SPS of Si_3N_4. Hence, it should be able to promote phase transformation of Si_3N_4 through the short-range diffusion of silicon and nitrogen by adding Mo as the second phase into Si_3N_4 matrix during SPS process, aimed at enhancing the β phase ratio.

The goal of the present work is to investigate the influence of in-situ formed $MoSi_2$ on the SPS process of Si_3N_4 and the resulting α to

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β phase transformation. The microstructure, the phase composition and thermal diffusivity of Si₃N₄-MoSi₂ composites were studied.

2. Material and methods

The starting materials were commercially available powders: α-Si₃N₄ (SN-E10, UBE Corp., Japan), Mo (purity >99%, Sinopharm Chemical Reagent Co.Ltd, China) and the sintering additive CeO₂ (purity >99.99%, Baotou, China).

Pure α-Si₃N₄ powders and mixtures of α-Si₃N₄ powders and 15 wt% Mo particles prepared by a planetary ball milling, denoted as powder P1 and powder P2, were fabricated without additions. Sample P1 and P2 were placed in a covered BN graphite crucible, and pressure-less sintered at 1500 °C for 30 min in a flowing nitrogen atmosphere.

Three Si₃N₄ mixed powders, SN, 6M-SN and 12M-SN, were prepared for SPS. The content of Mo was 0 wt%, 6 wt% and 12 wt% related to the mass of Si₃N₄/CeO₂ mixture in which the molar ratio of Si₃N₄:CeO₂ was 93:7. The mixed powders were subjected to a planetary milling in ethanol for 16 h, using Si₃N₄ milling media in a polythene jar. The slurries of ceramic powder mixtures were dried in a rotary evaporator at 90 °C in a vacuum and thereafter passed through a 100-mesh nylon sieve. The samples based on ceramic powder mixtures were processed by SPS (HP D250-1, FCT Systems GmbH, Germany) under an axial pressure of 30 MPa in a vacuum with the heating rate of 100 °C/min. The SPS schedules carried out for the samples and corresponding densities are shown in Table 1. The sample SN without Mo addition was prepared by heating at 1850 °C for 1 h in order to densify fully as control.

The simultaneous thermogravimetric and differential scanning analysis was carried out by NETZSCH STA 449C, from room temperature to 1500 °C at a heating rate of 10 °C/min in a nitrogen atmosphere. Characterisation of sintered samples involved X-ray diffraction (XRD) for phase identification, X-ray photoelectron spectroscopy (XPS, ESCLAB 250Xi, Thermo Fisher Scientific) for chemical bond analysis and field emission scanning electron microscopy (FESEM, Nanolab600i, FEI) combined with Energy Dispersive Spectroscopy (EDS) system for microstructural observations. The thermal diffusivity was measured by laser flash analysis (LFA427, Netzsch) in a vacuum.

3. Results

The XRD patterns of the samples P1 and P2, sintered without additives, are presented in Fig. 1. Both the samples were consisted primarily of α-Si₃N₄ grains, and the obvious diffraction peaks of β-Si₃N₄ phase, MoSi₂ phase and Mo₃Si₅ phase of P2 were identified while the initial Mo reactant was not detected in the final composite. The results show that Mo particles have fully reacted with α-Si₃N₄ and led to the transformation of α-Si₃N₄ to β-Si₃N₄ during the sintering, corroborated by the case of P1 where no β-Si₃N₄ phase has been detected. The possible reaction is proposed by the following equation [24]:

Table 1
The SPS schedules carried out for the samples and corresponding densities.

Samples	Mo (wt%)	Sintering conditions (SPS) Sintering temperature/holding time		Density (g/cm³)
SN	0	1850 °C/60min	–	3.25
6M-SN1	6	1850 °C/35min	–	3.41
6M-SN2	6	1600 °C/35min	–	3.45
6M-SN3	6	1600 °C/20min	1850 °C/15min	3.39
12M-SN4	12	1600 °C/20min	1850 °C/15min	3.59

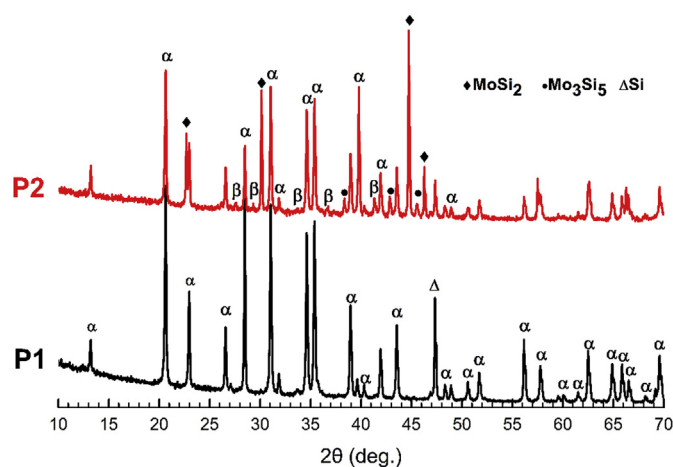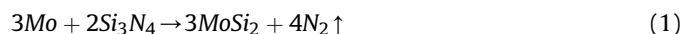**Fig. 1.** The XRD patterns of the samples P1 (α-Si₃N₄ powders sintered without additives) and P2 (α-Si₃N₄ powders sintered with 15 wt% Mo).

$$3Mo + 2Si_3N_4 \rightarrow 3MoSi_2 + 4N_2\uparrow \tag{1}$$

$$5Mo + Si_3N_4 \rightarrow Mo_5Si_3 + 2N_2\uparrow \tag{2}$$

The equations mentioned above indicate that no eutectic liquid phase forms during the reaction of Mo and Si₃N₄. The result obtained from the XRD analysis of P1 and P2 shows that the in-situ formation of MoSi₂ which effectively promotes the transformation of α to β-Si₃N₄, can be occurred at 1500 °C and completely performed within 30 min.

Prior to SPS, in order to identify the effect of Mo particles on the temperature of the liquid phase formation, the simultaneous thermogravimetric and differential scanning analysis of the powders SN and 6M-SN was carried out. The endothermic or exothermic signal of liquid phase formation and α to β phase transformation can be detected by DSC, and the TG/DSC curves of powder SN and 6M-SN are demonstrated in the Fig. 2. The DSC curve of SN (blue dot line) shows a broad sharp endothermic peak at 1210 °C with a small weight loss and two subsequent exothermic peaks at 1365 °C and 1447 °C respectively. The endothermic and the subsequent exothermic event should correspond to the formation of a eutectic liquid resulting from the CeO₂ additions reacting with the Si₃N₄ and SiO₂ originally present on the surface of Si₃N₄ grains, dissolution of α-Si₃N₄ and reaction between Si₃N₄ and CeO₂ additions, respectively. And the last endothermic peak around 1500 °C

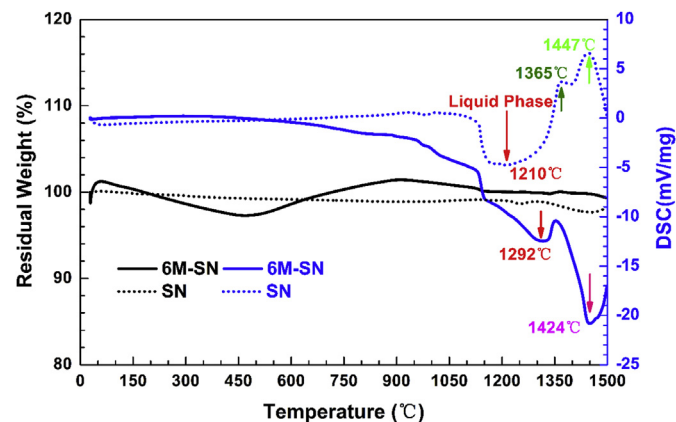**Fig. 2.** The TG/DSC curves of powder SN (dot line) and 6M-SN (solid line).