

Effects of a carbothermal reduction reaction on the microstructure of nano-silicon nitride ceramics

Horng-Hwa Lu^{a,*}, Yi-Chi Huang^b, Alex C. Lee^b, Jow-Lay Huang^{b,c}

^aDepartment of Mechanical Engineering, National Chin-Yi University of Technology, Taiping, Taichung 41170, Taiwan, ROC

^bDepartment of Materials Science and Engineering, National Cheng Kung University, Tainan 701, Taiwan, ROC

^cDepartment of Chemical and Materials Engineering, National University of Kaohsiung, Kaohsiung 81148, Taiwan, ROC

Received 1 May 2014; accepted 3 June 2014

Available online 16 June 2014

Abstract

In this study, using amorphous nano-Si₃N₄ as the starting powder, the oxides on the Si₃N₄ powder surface were removed by carbothermal reduction to prevent the formation of the O'-sialon phase in the sintered product. The results indicate that carbothermal reduction can be effectively induced at 1250 °C and produce single-phase Si₃N₄. However, as the temperature increased, the liquid phase that formed during Si₃N₄ sintering began to impede the carbothermal reduction. Analysis revealed that when the temperature exceeded 1350 °C, the reaction gradually shifted from that of carbothermal reduction to that of decomposition, and residual carbon and O'-sialon phase were observed in the sintered product.

© 2014 Elsevier Ltd and Techna Group S.r.l. All rights reserved.

Keywords: Hot pressing; Si₃N₄; Carbothermal reduction reaction; Microstructure

1. Introduction

Si₃N₄ ceramics are characterized by lightness, high hardness, superior thermal shock resistance, and excellent corrosion resistance. Additionally, Si₃N₄ ceramics possess exceptional thermal and mechanical properties at both room and high temperature. This structural ceramic material thus possesses high developmental potential and is often applied in functional components, including ceramic turbine engines, internal combustion engines, cutting tools, bearings, and fire-resistant materials [1,2]. One of the disadvantages of this material, however, is its poor toughness due to the brittle fracture behavior inherent to ceramic materials, which limits the scope of the material's engineering applicability. Thus, numerous research efforts have aimed at improving the fracture toughness of Si₃N₄ ceramics to enhance their applicability.

A number of studies have indicated that the use of a nano-powder as the starting material can effectively reduce the sintering

temperature, enabling the sintered products to achieve the desired theoretical density and nano-sized microstructure. A nanostructure can increase the strength, wear resistance, and superplasticity of specimens [3,4]. However, the excessively high specific surface area of nano-Si₃N₄ powder leads to the formation of excessive residual oxygen on the powder surface, thus forming SiO₂. According to Dogan et al. [5], excessive SiO₂ on the surface of nano-Si₃N₄ powders can react with Si₃N₄ at high temperatures and produce a secondary phase, such as Si₂N₂O, further affecting the mechanical properties of Si₃N₄.

Kim et al. proposed a method that effectively eliminates the oxygen adsorbed by the nano-Si₃N₄ surface, preventing the formation of secondary-phase Si₂N₂O [6]. This method involves employing the CO or CO₂ formed by SiO₂ on the Si₃N₄ powder surface using a carbon source. However, the mechanisms underlying the Si₃N₄ reactions initiated using carbon sources and subsequent changes in microstructure require further research.

In this study, nano-Si₃N₄ powder was submitted to hot-press sintering. The possible reactions initiated by the thermal

*Corresponding author. Tel.: +886 4 23924505; fax: +886 4 23930681.

E-mail address: hhl@ncut.edu.tw (H.-H. Lu).

process were examined using thermogravimetric analysis-mass spectrometry (TG-MS) and electron spectroscopy for chemical analysis (ESCA); furthermore, the carbothermal reduction mechanism and microstructural development were also investigated.

2. Experimental procedures

Amorphous nano-silicon nitride powder coated with 6 wt% Y_2O_3 and 8 wt% Al_2O_3 (PCT Ltd., 30 nm) as additives was mixed with carbon black (30 nm) as the carbon source, then ball-milled in a PE bottle with high-purity silicon nitride balls and ethanol for 24 h. The slurry was dried in a rotary evaporator and then dried in a vacuum oven at 120 °C for 24 h to remove the ethanol. The powders were then subjected to a carbothermal reduction reaction in an alumina tube furnace at 1150–1450 °C for 10 h under a nitrogen gas flow of 200 sccm to obtain the starting powders. The starting powders were subsequently pulverized by a high-energy mixer mill and screened through a 200-mesh screen to pulverize the aggregates. Samples were hot pressed with 25 MPa of mechanical pressure under 10 atm of nitrogen pressure at 1600–1800 °C for 1 h in a graphite furnace.

The thermal properties of the test powders were investigated using a TG-MS system (STA409CD-Skimmer-Mass, Netzsch, Germany). The sample was set in a platinum crucible to be introduced into the furnace of the TG-MS and then heated to 1400 °C at a rate of 10 °C min^{-1} under nitrogen flow. Alumina powder was used as the reference material. The gaseous products formed by pyrolysis were identified using a mass spectrometer. Bulk densities were measured by the Archimedes method. The theoretical density was calculated by the rule of mixtures. X-ray diffraction (XRD) analysis was conducted to identify the main crystalline phases and measure the phase ratio using the relative intensities of selected XRD peaks. An FIB-SEM system (AURIGA, Carl Zeiss, Germany) was used to examine the microstructure of the samples. Samples were plasma etched for 2 min in a gas mixture of CF_4 and O_2 with a flow ratio of 93:7 and then ultrasonically cleaned prior to examination by SEM. An X-ray photoelectron spectroscopy instrument (XPS; VG ESCA Scientific Theta Probe, United Kingdom) with an Al $\text{K}\alpha$ X-ray source (1486.6 eV) was used to investigate the chemical state of the specimens.

3. Results and discussion

Fig. 1(a) shows a TG-MS analysis diagram of nano- Si_3N_4 powders, which indicates that the powder without carbon black experienced minimal weight loss from 350 °C to 1400 °C, whereas that with carbon black exhibited a significant and continuous reduction in weight beginning at 1200 °C. In addition, the gas that vaporized during the MS detection experiment had a molecular weight of 44 and was possibly SiO or CO_2 . According to Chollon [7], although SiO is the main reactant in carbothermal reduction, because of its metastability, it can only be detected using MS with a rapid reduction in temperature. The results thus suggest that the

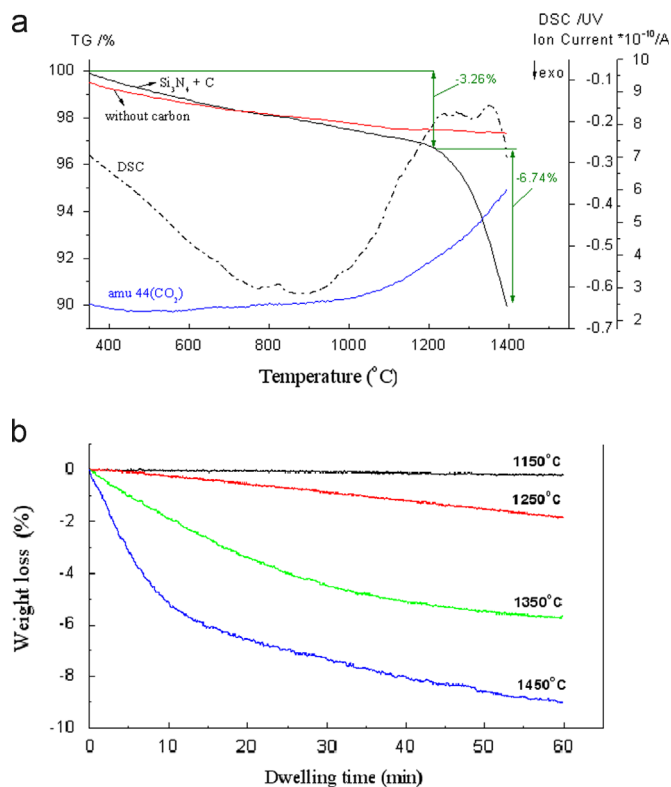


Fig. 1. (a) TG-MS data of Si_3N_4 powders under CRN at temperatures ranging from 350 °C to 1400 °C and (b) TGA data of powders submitted to CRN at different calcination temperatures for 1 h in N_2 atmosphere.

weight loss that occurred above 1200 °C was primarily caused by the reaction of carbon black with SiO_2 , which produced CO_2 . The reaction equation for this process is as follows:



If the temperature continues to increase, nitridation will occur as SiO reacts with nitrogen and then produces Si_3N_4 . The reaction equation for this process is as follows:



The reaction was further examined at various heat-treatment temperatures, with the resulting variations that occurred over 1 h of thermogravimetric (TG) measurement shown in Fig. 1 (b). This figure shows insignificant specimen weight loss at a heat-treatment temperature of 1150 °C. However, above 1250 °C, consistent weight loss was observed, accounting for 2% of the overall weight. When the temperature was increased to 1350 °C, significant weight loss was observed, and the rate of weight loss could be separated into two stages. This behavior was observed because the sintering additive used for Si_3N_4 sintering transformed into a liquid phase in the specimen, facilitating sintering when it reached its eutectic point at approximately 1350 °C [8]. The formation of the liquid phase also facilitated the carbothermal reduction of carbon black, leading to massive weight loss. In addition, Fig. 1(a) shows endothermic peaks in the differential scanning calorimetry (DSC) curve at 1248–1320 °C. The endothermic

Download English Version:

<https://daneshyari.com/en/article/10625046>

Download Persian Version:

<https://daneshyari.com/article/10625046>

[Daneshyari.com](https://daneshyari.com)