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Sintering behavior of spark plasma sintered alumina with graphene nanoplatelet reinforcement

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Abstract

Graphene nanoplatelet (GNP) reinforced alumina is synthesized by spark plasma sintering (SPS) using process conditions of 1100–1500 °C, 3–10 min dwell time, and 45–90 MPa in order to investigate the effects of GNP on sintering behavior. High volume fractions of GNP (5–15 vol%) are utilized in order to accentuate effects of GNPs. GNP effects on sintering behavior are assessed by evaluating microstructural evolution, grain growth kinetics, and microhardness. The addition of GNPs is found to suppress grain growth by a grain wrapping mechanism resulting in a 10% increase in activation energy when GNP content is increased beyond 5 vol %. Grain growth suppression partially mitigates a decrease in hardness due to the introduction of the soft GNP phase. Evidence of GNPs serving as a sintering aid are seen at short sintering times (3 min), while densification and grain size are observed to level off with extended sintering time (10 min). The application of higher pressures enhances densification, which enables GNPs to more effectively wrap around grains resulting in enhanced grain growth suppression.

Keywords: A. Sintering; B. Nanocomposite; Graphene; SPS

1. Introduction

Graphene has recently garnered significant interest as a reinforcing phase in composite materials because of its excellent electrical [1–4], thermal [1,5], and mechanical properties [1,3,6–8]. Graphene nanoplatelets (GNPs) in particular have attracted much interest as reinforcements for ceramic matrix composites. GNPs are particles consisting of 30–40 layers of graphene and retain many of the excellent properties of single layer graphene [4]. GNPs have been found to have intrinsic energy dissipating mechanisms such as sheet bending and sliding that enable them to enhance the toughness of ceramic matrix composites [9]. GNPs have been utilized mostly in Al_2O_3 [10–19] and Si_3N_4 [20–31] ceramics; however other ceramic systems of technological interest such as hydroxyapatite [32,33], TiO_2 [34,35], SiO_2 [36,37], SiC [38], TaC [39–41], and ZrB_2 [42] have also been utilized. The addition of GNPs has been shown to improve the fracture toughness and wear resistance of Si_3N_4-GNP composites by up to 235% [20] and 56% [29], respectively, as well as the flexural strength of Al_2O_3 by up to 30%. GNPs have also enhanced electronic properties including a 25% improvement in photocatalytic property activity in TiO_2-GNP composites [35], and the attainment of a conductive Al_2O_3-GNP composite with electrical conductivity of 5700 S m^{-1} [11]. In addition to improvements in mechanical and electronic behavior, the addition of GNPs has also been shown to suppress oxide formation in TaC-GNP by up to 60% [41].

The vast majority of GNP reinforced ceramic matrix composites have been synthesized using the spark plasma sintering (SPS) technique. SPS has been shown to fully densify a variety of ceramic systems effectively including Al_2O_3 [43–51] often with improvements in mechanical and functional behavior. Alumina consolidated by SPS has been shown to have superior hardness [43], fracture toughness [43,49], plasticity [44,48] and optical translucency [47] compared to conventionally processed alumina. Spark plasma sintering possesses distinct processing advantages over conventional techniques due to the use of a

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direct current to serve as the heating source. The direct current heating enables heating rates as high as 1000 °C/min [52] thereby allowing much lower temperatures and sintering times to be used [52,53]. Lower temperatures and sintering times enable retention of very fine grain sizes while achieving full densification. The attainment of fully densified alumina with nanometric grain sizes is the primary factor responsible for enhanced mechanical and optical properties when utilizing SPS [43,45,47].

Despite the numerous studies on GNP reinforced ceramics in recent years, inspection of the literature indicates that the effects of this nano-reinforcement on the sintering behavior of the ceramic matrix have not been previously investigated. Recent work by Inam et al. [19] provides the only processing study on GNP reinforced ceramics to date; however, the focus of that study was on the effects of sintering parameters on the structural stability of the GNP themselves, not on their effects on sintering behavior. Previous studies have shown grain growth suppression, however comparisons are made only across small variations in GNP content. Thus, there is a lack of previous work, and therefore a need, to systematically vary the sintering parameters to understand and quantify how GNPs interact with the matrix under varying sintering temperatures, dwell times, applied pressures, and GNP contents. Knowledge of how GNPs influence sintering behavior is important to effectively process and manufacture reproducible, high quality GNP reinforced ceramic nanocomposites that consistently exhibit the superior behavior described above. Therefore, in this study the effects of GNPs on the SPS processing of Al_2O_3 are investigated by systematically varying sintering temperature (1100–1500 °C), dwell time (3–10 min), pressure (45–90 MPa), and GNP content (5–15 vol%). High volume fractions of GNPs are utilized to accentuate the effects of GNPs on the microstructural evolution, grain growth kinetics, and microhardness of the Al_2O_3-GNP nanocomposites. The results of this study provide a fundamental understanding of the effects of GNP on sintering behavior, thereby providing a foundation for future optimization of the processing of these promising nanocomposite systems.

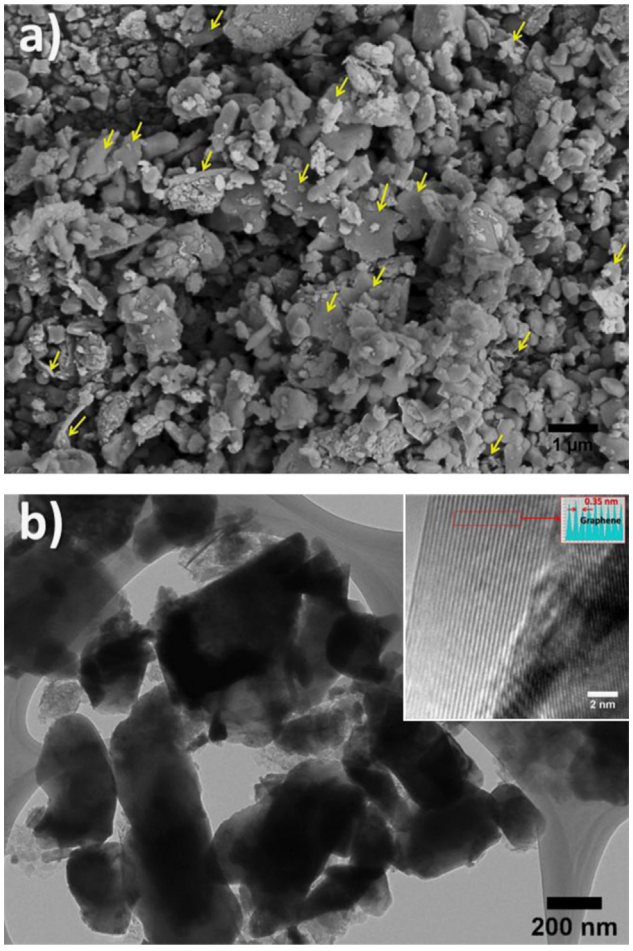

Fig. 1. Alumina-GNP powder, (a) scanning electron microscopy micrograph of Alumina-15GNP powder, yellow arrows denote GNPs, and (b) transmission electron microscopy micrograph of Alumina-15GNP powder, inset: HRTEM image showing GNP consisting of ~30 graphene layers. (For interpretation of the references to color in this figure legend, the reader is referred to the web version of this article.)

2. Experimental procedure

2.1. Materials

The starting alumina-graphene nanoplatelet powders (Al_2O_3-GNP) are obtained from Applied Carbon Nanotechnology (Pohang City, Republic of Korea). The composite powders have GNP contents of 5 vol% (A-5G), 10 vol% (A-10G), and 15 vol% (A-15G). The pure alumina powder used in the composite powder is procured from Sumitomo Chemical (AES-11 grade, Tokyo, Japan). The powder specifications indicate that the alumina powder consists of 99.8% pure α alumina with a density of 3.93 g/cm^3 and has an average particle and grain size of 450 nm and 300 nm, respectively, which have been confirmed via scanning and transmission electron microscopy. The average particle size is similar in value to the average grain size value because many particles are single grains. The use of finer powders is avoided in this study because the thermodynamics and kinetics of nano-ceramic sintering are not fully understood and most studies on GNP reinforced alumna utilize submicron powders. The GNPs are synthesized at Applied Carbon Nanotechnology and have an average thickness of 6–8 nm and a lateral dimension of ~5 µm. The GNPs are mixed with the alumina powder by Applied Carbon Nanotechnology using a combination of high energy ball milling and wet chemistry methods. Agglomerated GNPs are first processed by high energy ball milling using zirconia balls in an alcohol solvent for one hour. The high shear forces present during ball milling alleviate heavy agglomeration that cannot be alleviated by ultrasonication alone. The ball milled GNPs are then ultrasonicated in alcohol and the alumina powder is gradually introduced into the GNP suspension until the desired composition was attained. The alumina-GNP mixture is then dried in an oven for one hour.

2.2. Spark plasma sintering

The Al_2O_3-GNP composite powders are consolidated by spark plasma sintering using a DR. SINTER SPS-825 S (Fuji Electronic Industrial Co., Kawasaki, Japan). Composite powders