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Journal of the European Ceramic Society 35 (2015) 2027–2032

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Spark plasma sintering behavior of AlON ceramics doped with different concentrations of Y_2O_3

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Received 9 November 2014; received in revised form 9 January 2015; accepted 12 January 2015
Available online 29 January 2015

Abstract

Aluminum oxynitride (AlON) ceramics were fabricated by spark plasma sintering (SPS) from Al_2O_3, AlN and different concentrations of Y_2O_3. Fully dense and single-phase AlON ceramics were obtained in a sample doped with 0.6 wt% Y_2O_3 sintered at 1600 °C. A proper amount of Y_2O_3 additive can reduce sintering activation energy and enhance sintering activity due to plasma activated effects. Excess Y_2O_3 would result in the formation of $Y_3Al_5O_{12}$ (YAG) as a second phase which decreased grain boundary mobility and prevented grain growth. Vickers hardness slightly increased from 15.9 to 18.1 GPa, whereas fracture toughness firstly increased and then decreased with increased Y_2O_3 concentration. This work demonstrates that the combination of doping Y_2O_3 and SPS method will produce fully dense AlON ceramics with improved performance at relatively low temperature (1600 °C). It is notable that Y_2O_3 concentration shall be about 0.6 wt%. SPS of AlON doped with Y_2O_3 is a rate controlled sintering.

Keywords: Spark plasma sintering (SPS); Aluminum oxynitride; Yttria; Sintering behavior

1. Introduction

Polycrystalline aluminum oxynitride (AlON, $Al_{(64+x)/3}O_{(32-x)}N_x$, $0 \le x \le 8$) is an ideal material for transparent armor owing to its high strength and high hardness, highly resistant to rain and sand damage, and excellent optical properties.[1,2] Unfortunately, AlON ceramic is a very difficult-to-sinter material because of its high phase formation temperature and low sintering activity or diffusion coefficient. Conventional synthesis of AlON ceramics usually needs to sinter the green body at very high temperature (>1850 °C) for a long period (>20 h).[3,4] The process is not cost-effective and hard to operate. In addition, high sintering temperature and long sintering time can easily lead to excessive grain growth and coarse microstructure, which in turn seriously affects the optical properties and mechanical strength of the materials.

To lower the sintering temperature and reduce the sintering time, so far the relatively effective sintering techniques are microwave sintering and spark plasma sintering (SPS). As for microwave sintering, the processing materials themselves must absorb microwave and heat within the sample. Cheng JP et al. reported the synthesis of single phase AlON ceramics with relative density of 82% by using microwave sintering at 1650 °C for 1 h,[5] while fully dense AlON ceramics were fabricated at 1800 °C for 1 h.[6]

Spark plasma sintering (SPS), also known as field assisted sintering technique (FAST), is a newly developed rapid-sintering technique for obtaining fully dense and fine-grained ceramics at low temperature with short dwell time.[7–9] The sintering driven force of SPS is the combined effects of force, heat, electrical field and plasma generated by a pulse current within the sample volume. It is different from the conventional sintering driven force that generated by external heating elements and transferred to the samples via radiation, conduction and convection. The heat generation of SPS is internal. Therefore, the SPS process is very rapid and cost saving. Most importantly, the SPS process can easily obtain marked improvements in properties

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http://dx.doi.org/10.1016/j.jeurceramsoc.2015.01.014
0955-2219/

of as-sintered materials and also be combined with doping of sintering additives.

Recently, Sahin et al.[10] reported a reactive SPS method to prepare dense AlON ceramics with a relative density of 98.5% from only Al_2O_3 and AlN powder mixtures as precursors. The AlON fabricated at 1650 °C for 30 min at 40 MPa showed nice hardness and fracture toughness. Wang et al.[11] reported using pressureless sintering to fabricate AlON ceramics with a relative density of 99% by using Y_2O_3 and La_2O_3 as sintering aids at 1950 °C for 2 h. It was found that the sintering additives can cause the formation of liquid phase during pressureless sintering at 1800 °C, which is beneficial for the densification and pore elimination of samples. Ashuach[12] also studied the influence of sintering additives on the microstructure and properties of AlON ceramics. It was found that the highest transmission was achieved in a sample doped with 0.3 wt% Mg (and optionally also 0.02 wt% La) and sintered at 2025 °C for 12 h. However, lack of information provides a systemic study of the effects of sintering additive concentration on the sintering behavior of AlON ceramics prepared by SPS method. The objective of the present work was to make a combination of doping sintering additive and SPS method to produce fully dense AlON ceramics with improved performance. Phase transformation, sintering activation energy, microstructure, microcomposition, Vickers hardness (H_v) and fracture toughness (K_{IC}) of fully dense AlON ceramics prepared by SPS were studied.

2. Experimental

Al_2O_3 (Sinopharm Chemical Reagent Co. Ltd., Shanghai, China, 99.99% purity) with an average particle size of 1 μm and AlN (Sinopharm Chemical Reagent Co. Ltd., Shanghai, China, 99.99% purity) with an average particle size of 0.5 μm were used as staring materials. Y_2O_3 (Jiangyin Jiahua Advanced Materials Resources Co. Ltd., China, 99.99% purity) with an average particle size of 30 nm were used as sintering additives.

64.3 mol% Al_2O_3, 35.7 mol% AlN powders and a certain amount (0, 0.3, 0.6, 1.2 wt%) of Y_2O_3 were mixed in ethanol using alumina balls for 12 h. The mixture was then dried at 80 °C for 24 h and passed through a 200-mesh sieve. The screened powder mixtures were poured into a graphite die with a diameter of 12 mm and then sintered by using a SPS apparatus (ED-PAS-111, Elenix Inc., Japan) in vacuum. The sintering temperature was measured by an optical pyrometer which was implanted in the SPS apparatus. The sintering temperature was increased to 600 °C in 1 min and to 1200 °C in 2 min. The temperature was further increased to 1300–1600 °C at 50 °C/min and maintained for 1-15 min. Pressure was maintained at 20 MPa up to 1200 °C, and then increased to 50 MPa in 1 min. Both sides of as-sintered specimens were mirror polished. The final thickness of the specimens was approximately 1 mm.

Density was measured by the Archimedes method in distilled water. Sintering shrinkage rate ($\Delta L/L_0$) was measured by a linear displacement gage installed in the SPS apparatus. Crystal phase was investigated by X-ray diffraction (XRD, Brucker D8 Advance) using Cu K_α radiation. The microstructure of the sintered bodies was observed by a field emission scanning electron microscope (FESEM, Nova Nano SEM450, FEI, USA) and elementary analysis was investigated by EDS attached on FESEM. Vickers hardness (H_v) and fracture toughness (K_{IC}) at room temperature were measured by a hardness tester (Struers, Duramin A300) at a load (P) of 9.8 N. Fracture toughness was derived from the average crack length. As for a ratio c/a >2.5, where c is the half-length of the crack and a is the half diagonal length of the indentation impression, K_{IC} was calculated using Eq. (1).[13]

$$K_{IC} = 0.075 \times \left(\frac{P}{c^{1.5}}\right) \quad (1)$$

3. Results and discussion

XRD patterns as a function of Y_2O_3 concentration for the samples sintered at 1600 °C for 15 min are shown in Fig. 1. It can be noticed that single spinel-phase AlON phase ($Al_{23}O_{27}N_5$, PDF # 80-2171) formed for all the samples and there were not unreacted Al_2O_3 and AlN phases remained in the samples. However, cubic yttrium aluminitum garnet phase ($Y_3Al_5O_{12}$, PDF # 72-1853) was detected in the samples containing 1.2 wt% Y_2O_3. In addition, very weak peaks of $Y_3Al_5O_{12}$ cube phase existed in the samples containing 0.6 wt% Y_2O_3. It illustrates that Y_2O_3 and Al_2O_3 react to form cubic yttrium aluminitum garnet (YAG) phase in the sample for spark plasma sintering at 1600 °C. There were not obvious diffraction peaks of YAG phase observed in the sample containing 0.3 wt% Y_2O_3. The reason is that Y_2O_3 concentration is too low to be detected or below the solubility limit.

In order to better tailor the proper microstructure of ceramics, it is important to understand what are the mechanisms that controlling grain growth and densification. One of the ways to find the method is to evaluate the sintering activation energy. According to the kinetic equation of rate controlled sintering

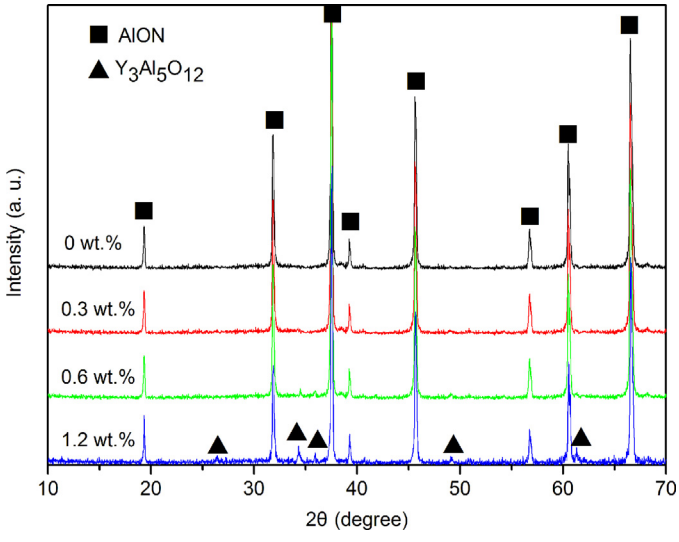

Fig. 1. XRD patterns as a function of Y_2O_3 concentration for the samples sintered at 1600 °C.