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The effect of Al_2O_3-MgO additives on the microstructure of spark plasma sintered silicon nitride

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ABSTRACT

It was shown that spark plasma sintered silicon nitride with a high content of Al_2O_3 and MgO consists of α and β silicon nitride, the main phase being α silicon nitride. The increase in the sintering temperature did not lead to significant changes in the phase composition as occurs in silicon nitride added with Al_2O_3-Y_2O_3. It was found that increasing in SPS temperature above 1650 °C leads to an insignificant increase in the density. A complex shaped equiaxed grain microstructure was shown in both cases. However, doping with aluminum and yttrium oxides allows obtaining an elongated grain microstructure. The Hall-Petch effect was observed for the microhardness of the investigated SPSed silicon nitride. The microhardness of the described ceramics was rather high and more than 1900 HV compared to the pressureless sintered at 1800 °C silicon nitride with the microhardness equal to 1511 HV.

1. Introduction

Nowadays, silicon nitride has been studied extensively and widely used for high temperature applications due to its superior thermo-mechanical and tribological properties, namely, high-temperature strength, good oxidation resistance and low thermal expansion coefficient [1]. The control of mechanical properties as well as the microstructure of silicon nitride has been investigated extensively over the past few decades. It can be realized by using of various additives and different manufacturing methods. Mechanical properties of silicon nitride are determined by their microstructure meaning both grains and grain-boundary glass phase.

Magnesium oxide and aluminum oxide are the most promising sintering additives because of its relatively low cost. The influence of magnesium oxide on the microstructure and mechanical properties of silicon nitride a few have been reported [2,3], but, have not been as comprehensively studied as such compositions as MgO-Y_2O_3, Al_2O_3-Y_2O_3 [4–7]. Previous studies concerned with mostly on performing the fruitful complex of high strength and thermal stability of silicon nitride [8–15]. However, a few studies have been explored the correlation between the microstructure, phase composition and density with a temperature of spark plasma sintering of the aluminum oxide and magnesium oxide doped silicon nitride [16,17]. Relatively low sintering temperatures proposed in our study can be also justified by the fact that magnesium oxide reduces the melting point of the silicate glass on the surface of silicon nitride powder according to some Refs. [4,18].

It has been recognized that the reaction bounded silicon nitride (RBSN) has a constant strength in a wide range of temperatures despite on its relatively low mechanical properties compared with the hot isostatic pressed (HIPed) silicon nitride. However, HIPed silicon nitride had ultimate strength but the mechanical properties dramatically decrease with a slight increasing in temperature due to degradation of the glass phase. Thus, the absence of a glass phase is preferred and necessary in terms of potential high temperature applications.

The Spark Plasma Sintering (SPS) is one of the most promising alternatives to HIP and GP (gas pressure sintering) for sintering silicon nitride due to its low sintering time. Also the spark plasma sintering is characterized by such advantages as a relatively high sintering speed and comparatively low sintering temperature. Also it is possible to slow down the intensive grain growth of ceramics by SPS in contrast to traditional sintering methods. Nishimura et al. described dense silicon nitride manufactured by spark plasma sintering at 1550 °C during 5.5 min under 49 MPa minimized the grain growth during sintering and allowed the fabrication of dense silicon nitride [19].

Spark plasma sintered silicon nitride were selected as representative of ceramics have a large number of various commercial applications and frequently used in basic research of structure–property relationships. The choice for study only these two selected sintering temperatures was based on the interest in the effect of the investigated additives on the completeness of the α→β phase transformation of the silicon nitride.

The evaluation of the microstructure of spark plasma sintered

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silicon nitride with an increased content of such cheap additives as alumina and magnesium oxide remains unclear and has attracted much interest. The aim of the current study is to clarify the effect of the self-made magnesium oxide and high content of aluminum oxide on the microstructure of the silicon nitride ceramics. Finally, the features of the microstructure and properties i.e. microhardness, density, morphology and average grain size of both produced ceramics, are presented and discussed.

It is important to note that described ceramics would be attractive for various high-temperature applications due to its fine equiaxed microstructure [7,20]. Another point in this study was a better understanding of the role of sintering additives in the densification and microstructural development of silicon nitride ceramics and the consequences for final properties [19].

2. Material and methods

Fine α -silicon nitride powder (92 wt%) was mixed with 2 wt% self-made MgO and 6 wt% Al_2O_3(A16 SG, 600 nm) using vibratory disc mill Retsch RS-200. Other details were reported previously [21–28]. A new innovative technology has been used to produce a nanoscale high-purity powder of magnesium oxide. In particular, proposed magnesium oxide powder was synthesized from the magnesium nitrate hexahydrate $Mg(NO_3)_2{\cdot}6H_2O$ leached in the nitric acid from the natural raw material of serpentinite after several cycles of magnetic separation. [25].

The sintering temperature was controlled by a pyrometer. Disc samples of 40 mm diameter were SPSed (Sumitomo Coal Mining Co. Ltd.) at 1550 °C and 1650 °C under 50 MPa during 10 min.

The samples were cut with a band saw from a sintered billet. The structural observations have been carried out with secondary electrons (SE) on the polished surfaces using a Quanta 600 FEG scanning electron microscope.

The density of the specimens was determined by helium pycnometry (Micromeritics Accu Pyc 1340). Crystalline phases were determined by X-ray diffraction (XRD, Rigaku Ultima IV).

Microhardness tests were carried out on samples using an automatic microhardness analysis system DM-8 at 30-N loads, a total of ten indentation points were made on the polished surface for each sample.

3. Results

Fig. 1 shows the microstructures of produced ceramics sintered at different temperatures. Their microhardness, densities, and average grain size are summarized in Table 1. The silicon nitride ceramics produced by SPS at 1550 °C is marked in Table 1 as SPS155, ceramics SPSed at 1650 °C is denoted as SPS165 and ceramics pressureless sintered at 1880 °C is referred as SN18 [26], respectively. Both ceramics demonstrate almost the same type of microstructure. SEM micrographs revealed the fine microstructure of the SPS155 with different amount of

Table 1
Properties of produced silicon nitride ceramics.

Type	Method	Grain shape/average size	HV	g/cm^3	β- phase content, %	Ref.
SPS155	SPS	equiaxed 440–600 nm + elongated 1.0 μm	1957	3.13	11	This work
SPS165	SPS	equiaxed 540–860 nm + elongated 1.0 μm	1985	3.14	15	This work
SN18	Sintering	equiaxed 1.3 μm + elongated 2.6 μm	1511	3.03	100	[26]

the complex form relatively large equiaxed grains with an average size of 440–600 nm and with a very small amount of elongated 1 μm grains. The microstructure of the SPS165 ceramics also consists of the nearly hexagonal large grains with the size ranged from 540 nm to 860 nm in addition to small amount of elongated grains with an average size of 1 μm. The lack of the surface porosity was observed for both investigated ceramics. The equiaxed α-Si_3N_4 grains connected randomly with each other and formed fine-grained microstructure that could be benefit for the various high-temperature applications of silicon nitride ceramics [26,28].

The density of the obtained materials was nearly the same and equal to 3.13 g/cm^3 and 3.14 g/cm^3 for SPS155 and SPS165, respectively.

Only α and β silicon nitride were observed, however the major phase was α-Si_3N_4.

4. Discussion

Clarke and Thomas showed the features of the structure of MgO doped hot pressed silicon nitride and indicate that the second phase does not exist as a continuous wetting layer at the grain boundaries at room temperature, but is generally localized at some of the β-grain junctions and, occasionally, as a very thin layer between 2 grains [29].

The features of the structure of pressureless sintered silicon nitride with the same amount and type of additives have been discussed in more detail in our previous study. The microstructure of this silicon nitride is duplex and quite different compared to the described material and mostly consists of the equiaxed α-grains, while the secondary elongated β-grains can also be distinguished. The advantages and disadvantages of this material have been described elsewhere [26]. Different type of microstructure indicates a difference in the mechanisms of microstructure evolution for both corresponding sintering methods. The microstructure of the silicon nitride with various amounts of magnesium oxide has been also described in detail in our previous works [25]. We showed that the optimum content of magnesium oxide in the initial charge is equal to 2 wt% in terms of the linear shrinkage,

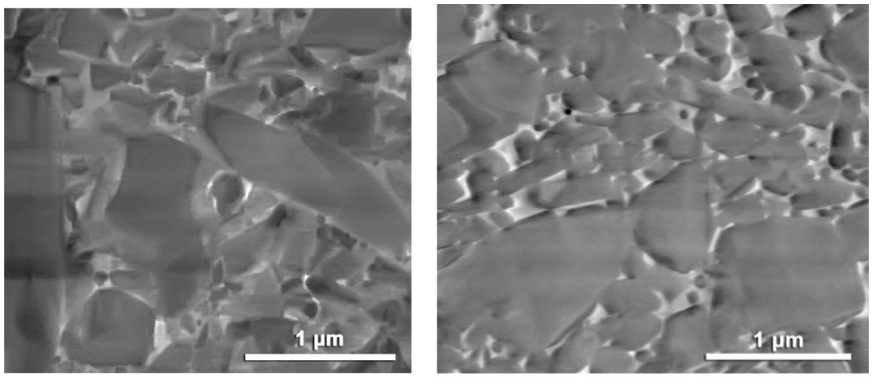

Fig. 1. Microstructure of the produced ceramics SPSed at a) 1550 °C b) 1650 °C.