PROPERTIES OF PRESSURELESS SINTERED SILICON NITRIDE

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Abstract

Silicon nitride find its application in quality of high-temperature ceramics and can be considered as one of the most promising dielectrics. Different properties and microstructure of pressureless sintered silicon nitride have been described a lot. The effect of various oxide additives and sintering regimes has also been often shown and discussed. However, there is not so much information about the influence of complex triple additives on properties of silicon nitride. In our work, we described the manufacture of high-dense Al_2O_3-MgO-Y_2O_3, Al_2O_3-MgO-La_2O_3 and Al_2O_3-La_2O_3-Y_2O_3 doped presureless sintered silicon nitride with high microhardness. The effect of different oxide compositions of yttrium, magnesium and lanthanum with Al_2O_3 on such important properties as shrinkage, microhardness and both green body density and density of sintered ceramics have been characterized.

Keywords: Materials science, ceramics, properties, oxide additives, powders

1. INTRODUCTION

Obviously, morphology of initial powders is one of the key factors affecting both microstructure and mechanical properties of pressureless sintered silicon nitride. Also, phase transformation of silicon nitride and formation of β-silicon nitride is characterized by a higher fracture toughness due to the ability to stop the propagation of cracks by elongated grains. Thus, it is obvious that investigation of mechanical properties and microstructure depending on the type of additives is very important at the moment. Rare earth oxides are usually used as additives. But the high cost is the main disadvantage of these oxides. Influence of such oxides as La_2O_3 has recently been of great interest. In particular, the separate and combined effect of Y_2O_3, La_2O_3, MgO and Al_2O_3 on microhardness, oxidation resistance, microstructure and phase composition of silicon nitride have partially been analyzed [1]. In particular, Guedes-Silva et al. showed that Gd_2O_3 leads to an intensification of the phase transformation and formation of elongated β grains of silicon nitride, an increase in crack resistance, while La_2O_3 led to an increase in microhardness [1]. Tatarko et al. showed decreasing of fracture toughness of silicon nitride with an increasing of the ionic radius of rare-earth element [3]. At the same time decreasing of the ionic radius of rare-earth element leads to increasing of the aspect ratio of Si_3N_4 composites [3]. Choi et al. reported hot pressed Y, Yb, Dy, Er, Sm, Ce, Lu, La, Pr, and Gd doped silicon nitride [4]. So, in described paper authors showed increasing of flexural strength and oxidation resistance with decrease in cation radius. Hong et al. reported that the rare-earth oxides affect such key properties and regularaties as the densification process and the shrinkage temperature [5]. Kitayama et al. described hot pressed fully dense Si_3N_4 with such rare−earth oxides as La, Nd, Gd, and Yb [6]. These authors showed the linear dependence of the phase transformation kinetics from the ionic radius of rare earth element atoms. Satet et al. investigated influence of various rare-earth and related elements (R = Lu, Sc, Yb, Y, Sm, La) on mechanical properties and grain growth anisotropy of β-silicon nitride ceramics [7]. They showed increasing of grain anisotropy with increasing of ionic radius because of non-linear growth kinetics.

In our work morphology of the starting powders of such oxide additives as La_2O_3,Y_2O_3, Al_2O_3, and MgO are demonstrated and characterized. Hirosaki et al. described the effect of rare earth oxides on densification of silicon nitride produced by pressureless sintering at 1600-1700°C and silicon nitride manufactured by gas pressure sintering at 10 MPa and 1800-2000 °C. Such single−component oxides as CeO_2, Nd_2O_3, La_2O_3, Sm_2O_3, and Y_2O_3 were used as an additive. It was shown that in this case the sintering temperature required to reach approximate theoretical density became higher as the melting temperature of the oxide increased. It was also clearly shown that the higher densification was achieved below 2000°C because of a lower liquid formation temperature when a mixed of such oxide additive as Y_2O_3-Ln_2O_3 (Ln=Ce, Nd, La, Sm) was used [2].

Short-term pressureless sintering is a relatively inexpensive and promising method for silicon nitride manufacture.

The main aim of the present study is to investigate features of the effect of different triple Al_2O_3, MgO, Y_2O_3 and La_2O_3 compositions on the linear shrinkage, microhardness and density of both green-compacts and pressureless sintered silicon nitride.

2. FIGURES, EQUATIONS, TABLES

The ground and homogenized powder mixture was cold isostatically pressed at 180 MPa (EPSI CIP 400B-9140 press) during 30 s. Conventional sintering of samples was carried out in a high temperature furnace (Nabertherm VHT8/22-GR) in nitrogen atmosphere at 1780 ºC for 60 min. All reported compositions are listed in **Table 1**.

The microstructure of initial powders was characterized by scanning electron microscopy (SEM). Structural characterization was performed using Quanta 600 FEG (FEI company, Hillsboro, OR) scanning electron microscope. The density of the test samples was measured by the Archimedes method. The microhardness was measured by an automated Shimadzu DUH-211/DUH-211S.

There are three main criteria affecting properties and microstructure of ceramics. These criteria are: morphology, type and microstructure of initial powder, sintering conditions and type and content oxide additives. They play an important role in both equiaxial pressing and liquid phase sintering. It is expected that globular morphology of powder is more preferable. Morphology of initial powders is shown in **Figure 1**. Aluminum oxide grade Granolox (**Figure 1b**) demonstrated the most preferable morphology in comparison with the calcined aluminum oxide. Agglomerates of powder are shown in **Figure 1b**. Lanthanum oxide and magnesium oxide are distinguished by small particles of powder, as can be seen in **Figure 1c** and **Figure 1e**, respectively. **Table 1** shows described compositions.

Table 1 Described powder compositions

№	Si3N4 (wt%)	Al_2O_3 (wt%)	MgO (wt%)	Y_2O_3 (wt%)	La_2O_3 (wt%)
1	90	4.3	-	5.7	-
2	90	5.0	2.0	-	3.0
3	92	6.0	2.0	-	-
4	90	5.0	2.0	3.0	-
5	-	4.0	-	3.5	2.5

There is a large number of papers devoted to manufacturing of silicon nitride with such typical additives as Al_2O_3-Y_2O_3 and Al_2O_3-MgO. In our work, we considered such triple additive systems as Al_2O_3-MgO-Y_2O_3, Al_2O_3-MgO-La_2O_3 and Al_2O_3-La_2O_3-Y_2O_3, respectively. On the one hand, the ternary systems have low-melting eutectics allowing lowering the sintering temperature. On the other hand, there are not so many works describing the complex effect of lanthanum oxide with other more popular oxide additives on properties and microstructure. The density of green bodies, microhardness and the shrinkage of the produced ceramics are shown in **Table 2**. The maximum shrinkage equal to 19 % and 18 % was measured for Al_2O_3-MgO-Y_2O_3 and Al_2O_3-La_2O_3-Y_2O_3 doped silicon nitride, respectively. Maximum density was demonstrated for Al_2O_3-MgO-Y_2O_3. The growth of linear shrinkage of manufactured silicon nitride linearly depends on the density of the sintered body, however, there is no linear correlation with the green body density. Al_2O_3-La_2O_3-Y_2O_3 doped silicon nitride showed maximum microhardness equal to 1798 HV (see **Table 2**). Detailed information on the properties of pressureless sintered silicon nitride can be found in our earlier articles [8-15].

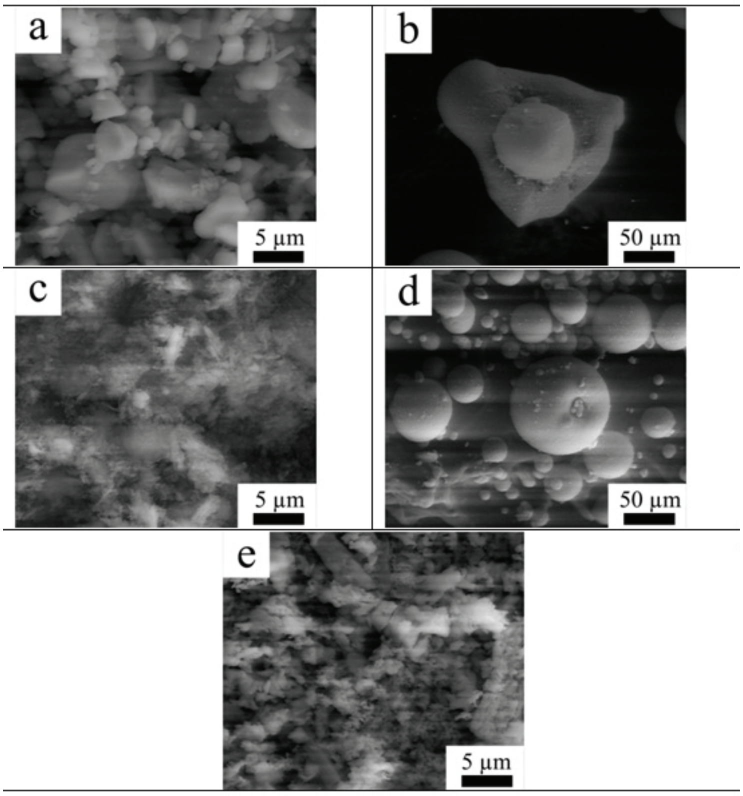

Figure 1 Microstructure of initial powders a) Al_2O_3 calcined b) Al_2O_3 Granolox c) MgO d) Y_2O_3 e) La_2O_3

Table 2 Density, microhardness and shrinkage of the obtained materials

№	$\rho_{green\ body}$, g/cm^3	$\rho_{sintered}$, g/cm^3	Shrinkage, %	HV
1	2.23	96	15	1506
2	1.81	96	17	1784
3	1.93	93	16	1710
4	1.98	97	19	1665
5	1.94	94	18	1798

For comparison, we briefly review the results of other authors. The density of the green body is an important indicator in ceramics processing. In particular, Almeida et al. described manufacturing of low temperature pressureless sintered silicon nitride with high content of Al_2O_3-SiO_2-Y_2O_3. Green body density varied from 1.74 g/cm^3 to 1.94 g/cm^3 in comparison with our materials1.81-2.23 g/cm^3 [16]. Huang et al. described AlN-La_2O_3-Y_2O_3 doped high-strength pressureless sintered silicon nitride ceramics [17]. However, Ling et. al described MgO-Y_2O_3 doped high-strength pressureless sintered silicon nitride ceramics [18]. Terwilliger et al. described the fundamental processes of the liquid-phase sintering of pressureless sintered silicon nitride with magnesium oxide. In particular, he showed pore growth due to decomposition leading to a decrease in the driving force for sintering and leads to the cessation of shrinkage [19]. Also Yang et al. established efficiency of MgO-CeO_2 additive for pressureless sintered silicon nitride compared to a single MgO or CeO_2. The optimal ratio of reported oxides was equal. Linear shrinkage of the considered ceramics was approximately 16-18 % [20]. Yonezawa et al. reported about slip casted and pressureless sintered silicon nitride ceramics with whiskers. A high density, good mechanical and thermal shock resistance properties, characterizes this ceramics. However, the shrinkage of such materials was not uniform [21].

3. CONCLUSION

Such important properties as linear shrinkage, green body density and density of sintered materials have been described. This study is devoted to show the influence of various oxides as lanthanum, yttrium, magnesium and aluminum on the linear shrinkage, microhardness, green body and sintered density of silicon nitride obtained by pressureless sintering. Suitable powder morphology of such reported oxide additives as Al_2O_3, MgO, La_2O_3 and Y_2O_3 have been shown. Pressureless sintered silicon nitride with Al_2O_3-MgO-Y_2O_3, Al_2O_3-MgO-La_2O_3 and Al_2O_3-La_2O_3-Y_2O_3 with high density and microhardness have been obtained, discussed and analyzed. It has been shown that ceramics with triple Al_2O_3-MgO-Y_2O_3, Al_2O_3-MgO-La_2O_3 and Al_2O_3-La_2O_3-Y_2O_3 additives have higher microhardness compared to ceramics with traditional double Al_2O_3-Y_2O_3 and Al_2O_3-MgO additives equal to 1506 HV and 1710 HV, respectively. Also, considered ternary additives led to a higher linear shrinkage 17-19 % of reported silicon nitride in contrast with the 15-16 % linear shrinkage of Si_3N_4 with traditional binary additives. Similarly, density of manufactured silicon nitride with ternary additives was even higher compared to reported Al_2O_3-Y_2O_3 and Al_2O_3-MgO silicon nitride density. The growth of linear shrinkage was coexisted by increasing the density of the sintered body. However, the density of the sintered material did not depend linearly on the density of the green body.

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