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Surface oxidation to improve water-based gelcasting of silicon nitride

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During the process of water-based gelcasting of Si_3N_4, the gas discharged due to the reactions on the solid-liquid interface can lead to a great deal of big bubbles in the green bodies. To improve the process a type of method based on surface oxidation is developed. By means of the method a layer of SiO_2 and Si_2N_2O, which can prohibit the gas from being discharged effectively, is formed on the surface of Si_3N_4 powders. Oxidized powders can be dispersed better than those not oxidized, and after gas-pressure-sintering mechanical property of the gelcast samples made from the oxidized powder is much better than that of dry-pressed and then isostatic pressed samples.

1. Introduction

The forming process is a key to prepare ceramics materials, so it has gradually turned into one of the emphases investigated by ceramics scientist. During past years colloidal *in-situ* forming processes, such as gelcasting, slip casting and direct coagulation casting (DCC), have aroused considerable attention [1]. Gelcasting is a near-net-shape method combining physical chemistry for polymer, colloidal chemistry and ceramic technology [2, 3]. In recent years, it has been noticed, for its process is simple, the green bodies made through it have high homogeneity and high strength, and after sintered such bodies have good mechanical property [4, 5]. The main steps of gelcasting are as follows: First, monomer, crosslinker, medium (water or organism), initiator, catalyst, and ceramics powder are thoroughly mixed to form the homogeneous suspension with high solid volume loading and low viscosity. Second, the suspension is cast into non-pore molds. When heated, monomer and crosslinker polymerize, then form three-dimension network structure, thus the slurry are solidified *in situ*. After unmolded and dried the green body with bending strength of over 20 MPa is acquired, which possesses good mechanical properties after sintered. At present, water-based gelcasting can be used in preparing near-net-shaping green compacts with low polymer content, which have high strength and homogeneity as well. This method has been concerned greatly and utilized in the forming of many sorts of ceramic material system [6–8].

Silicon nitride (Si_3N_4), an important structural material, possesses superior mechanical properties at both room temperature and elevated temperature, but it is difficult to be used further because of its poor reliability and high cost. One way to improve its reliability and decrease its cost is to prepare homogeneous near-net-shape green bodies through colloidal forming process, such as gelcasting, slip casting and DCC [2, 5, 9]. However, it is a big puzzle how to remove bubbles away from the slurry during the gelcasting process of Si_3N_4. The bubbles come into being because of some gas-discharging reaction [10]. When exposed in the medium, free silicon in the unprocessed powders reacts with water as following:

$$Si + 4H_2O \rightleftharpoons H_4SiO_4 + 2H_2 \uparrow$$

After ball-milled for a long time, Si_3N_4 powder reacts with water as following:

$$Si_3N_4 + 4H_2O \rightleftharpoons 3SiO_2 + 4NH_3 \uparrow$$

In the meantime reaction between Si_3N_4 and initiator ($(NH_4)_2S_2O_8$) not only discharges gas, but also consumes the initiator partially so that the solidification of the slurry can be insufficient. The reaction takes place as following:

$$Si_3N_4 + 6S_2O_4^{2-} + 12OH^- \rightleftharpoons$$
$$3SiO_2 + 2N_2 \uparrow + 12SO_4^{2-} + 6H_2O$$

So there are many gases in the slurry, which lead to a great deal of large bubbles in the green compacts, decreasing mechanical properties of sintered bodies badly. To improve the gelcasting of Si_3N_4, our work has previously showed that a method of coating with sintering aid such as alumina and yttria is effective [11]. Such method can yield the following fruits: (1) the layer of sintering aid may separate Si_3N_4 from water to avoid the reaction between them, (2) it may change the colloidal behavior and improve its dispersibility in water, and (3) sintering aids may be well distributed in the green compact and be beneficial to densification. However, the process of coating indicated above is so complex that it can not be taken into practice widely. Therefore a method of oxidation to improve water-based gelcasting of Si_3N_4 was developed. This method is not only effective but also easy for utilization. It can restrain the detrimental reactions on the solid-liquid interface and improve the colloidal characteristics and rheology of the suspensions, solidification process, and homogeneity of green bodies greatly, because an effective coating layer of silica (SiO_2) could be formed on the surface of Si_3N_4 powder. Then high quality of green compact result in high mechanical properties of sintered bodies.

Moreover, surface status of Si_3N_4 particles is relatively complex [12–14] because of the diversity of their preparation method. Different Si_3N_4 powders have different surface characteristics, therefore their dispersion in media is quite different. Sometimes even little change in producing conditions can make the Si_3N_4 powders with the same trademark behave much differently in media. To obtain the same rheology of slurry with these different powders, the technical parameters have to be adjusted, which will be disadvantageous to industrialized forming process of Si_3N_4 ceramics. If a layer of oxide was coated on Si_3N_4 particles, it would make different Si_3N_4 powders exhibit the same colloidal characteristics in media and advantageous to maintain stable colloidal forming process. In addition, the colloidal characteristics of oxide have been relatively thoroughly studied, and oxide can disperse well in water with the aid of some dispersants. The dispersing ability of oxide coating redounds to dispersion of Si_3N_4 particles [15, 16].

2. Experimental procedure

The Si_3N_4 powder from Beijing Founder High Technology Ceramics Corporation was used in this study with an average size $d50$ of 0.6 μm (Fig. 1). Its other characteristics could be seen through the former report [17]. The deionized water with conductivity of 1.02 $\mu S\cdot cm^{-1}$ was used. The monomer is acrylamide (AM), the crosslinker is methylenebisacrylamide (MBAM), the initiator is $(NH_4)_2S_2O_8$, and the catalyst is N,N,N′,N′-tetraethylmethylenediamine (TEMED).

Photoelectron spectra were obtained using an ESCALAB220i-XL electron spectrometer with base pressure of 1×10^{-9} mbar and an EP300 electron spectrometer with base pressure of 1×10^{-8} mbar. The apparent viscosity of Si_3N_4 suspensions was measured by rotating viscosimeter (model NSX-11, Chengdu Instrument Plant, China). The ion concentration of the suspension was measured by IONPACDX-100 ion chromatography instrument. The ion conductivity of suspensions was measured by ion conductivity meter (model DDS-II A_T, Shanghai Leici Instrument Plant, China). The bending strength of samples was measured through three points bending method. The micrograph of gelcast green bodies was observed through a CSM950 SEM from OPTON Corporation of Germany.

3. Results and discussion

3.1. The influence of surface oxidation on the composition and surface status of Si_3N_4 powder

Under the conditions of high temperature and high oxygen pressure, the following reactions take place:

$$Si_3N_4 + 3O_2 \rightleftharpoons 3SiO_2 + 2N_2$$

After SiO_2 appears the reaction on the interface between SiO_2 layer and Si_3N_4 powder is controlled by diffusion of oxygen across the SiO_2 layer. In the meantime, the following reactions take place:

$$Si_3N_4 + SiO_2 \rightleftharpoons 2Si_2N_2O$$
$$2Si_2N_2O + 3O_2 \rightleftharpoons 4SiO_2 + 2N_2$$

Si_3N_4 powders were oxidized in the molybdenum silicide furnace, keeping the temperature for 2 hours at 600°C, 800°C, 850°C and 900°C respectively. The weight of oxidized powders was compared with raw powders, and the results were shown in Fig. 2. The thermal gravity analysis (TGA) curves of keeping Si_3N_4 at 600°C, 800°C, 850°C, and 900°C respectively were shown in Fig. 3.

It can be observed through Fig. 2 that the oxygen content from 600°C to 850°C increases slowly, but it rises sharply when the oxidizing temperature reaches 900°C. Furthermore Fig. 3 indicates that the gain of oxidation speed at 900°C is relatively high. It is because that the transformation from α-quartz ($\rho = 2{,}533$ g/cm^3) to α-tridymite ($\rho = 2.228$ g/cm^3) at 870°C takes place in the SiO_2 layer. Due to the change of density, SiO_2 film layer cracks, and the oxygen infiltrates through the

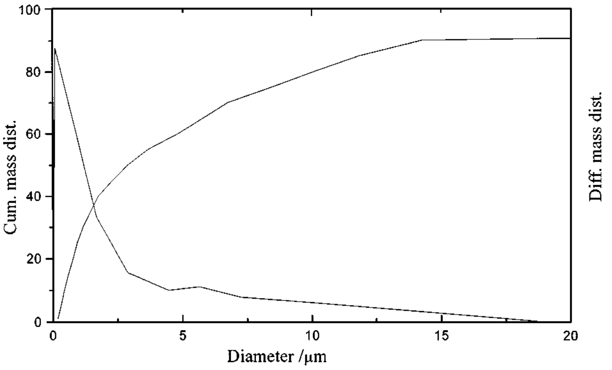


Figure 1 Particle size of cumulative and differential mass distribution of Si_3N_4.

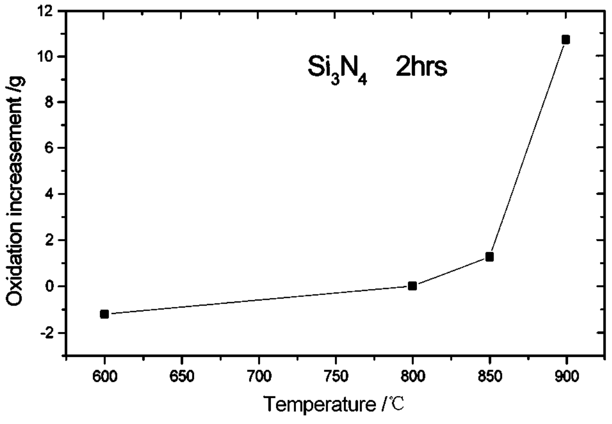


Figure 2 Oxidation increasement of Si_3N_4 powder oxidized in the molybdenum silicide furnace for 2 hrs.

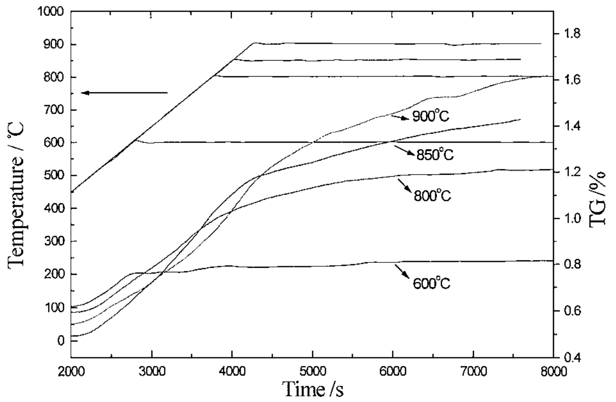
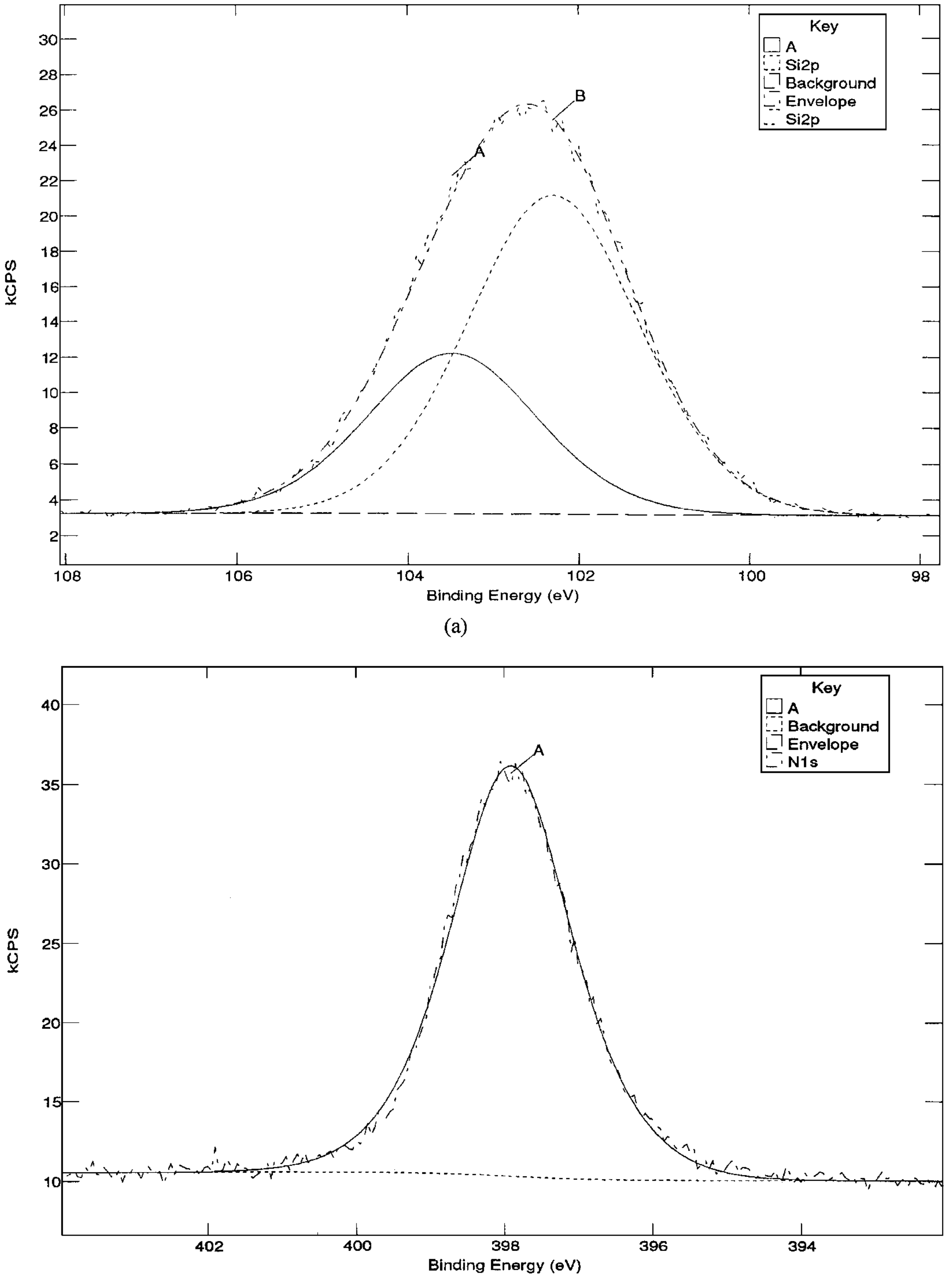


Figure 3 TGA curves of oxidizing Si_3N_4 at different temperature.

crack, which lead to more active reactions. At 900°C the sharp oxidation reaction results in the large increase of SiO_2 content in the Si_3N_4 powder. In fact the real increase of SiO_2 is more than what we have measured, because the weight loss during the experiment, which can be attributed to the combustion of the organism and carbon in the Si_3N_4 powder [18], is not considered. As is well known, too much glass phase deriving from too much SiO_2 will degrade mechanical properties of Si_3N_4 at elevated temperature remarkably. Obviously, it is necessary that the Si_3N_4 powder should be oxidized below 900°C.

Fig. 4 was provided by X-ray photoelectron spectrometer (XPS) with the oxidation powder at 850°C. In



(a)

(b)

Figure 4 (a) Si (2p) and (b) N (1s) peak of the Si_3N_4 oxidized at 850°C.

Fig. 4a, Si (2p) peak divides into two, one in 102.30 eV representing Si_2N_2O and the other in 103.49 eV representing SiO_2. In Fig. 4b, N (1s) peak at 397.91 eV represents Si_2N_2O [18–20]. It can be concluded that powder surface consists of Si_2N_2O and SiO_2 mainly, and surface modification based on oxidation can yield a layer of coating.

3.2. Influence of surface oxidation on slurry colloidal characteristics and green body structure

In the gelcasting process of Si_3N_4 some cations in the slurry, namely antiions, are very disadvantageous to rheologys of slurries [21]. Impurity ions of Si_3N_4 powder can be removed by washing and ions exchange resin, but these methods cost too much time and money. It has been found in our study that oxidizing at high temperature could easily and effectively reduce ion concentration in the slurry. Original Si_3N_4 powder and several kinds of oxidized Si_3N_4 powders were dispersed into deionized water respectively and corresponding homogenous suspensions were acquired. After a few days, they were centrifuged and the ion conductivity of the watery solution on top of the suspensions was measured. Fig. 5 shows the curves of the ion conductivity versus time. With the rise of the oxidizing temperature, the ion conductivity of the watery solutions decreased greatly, which pointed out that the ion concentration in the slurry decreased remarkably. The decrease may be attributed to the isolation of the SiO_2 layer and the change of the ions' formation on the surface of Si_3N_4. Table I presents the variation of K^+ and NH_4^+ concentration versus time. It can be seen from the table that the concentration of both K^+ and NH_4^+ decreased after the powder has been oxidized. The higher the oxidizing temperature, the more greatly the ion concentration decreased. The decreasing of K^+ concentration may root in the volatilization of K salts and the formation of insoluble solid solution. The concentration of NH_4^+ decreased obviously because of the decomposition of ammonium salts and the isolating function of the oxide layer on Si_3N_4 particles. In addition, Fig. 5 indicates that ion conductivity of the oxidized powder varies relatively smoothly, while that of the raw powder varies rather sharply. Summarily, it could be concluded that a homogeneous coating was formed on the surface of the oxidized powder retraining the deleterious reaction on the surface of the Si_3N_4 powder effectively, and that after oxidizing the improvements of rheologys of Si_3N_4 slurries should be partly attributed to the decrease of impurity ions.

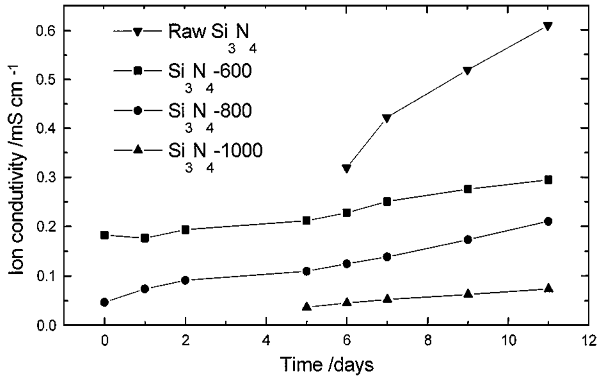


Figure 5 Curves of the ion conductivity for silicon nitride suspensions versus time.

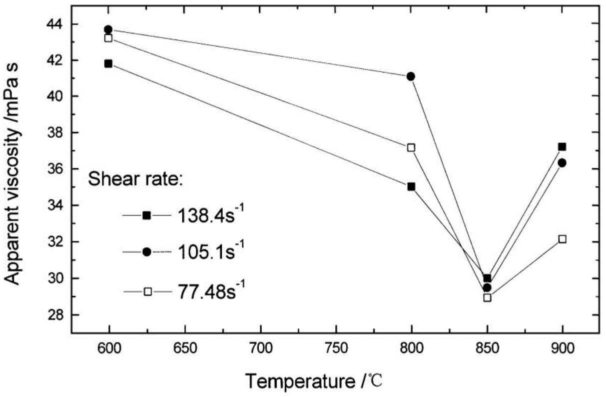


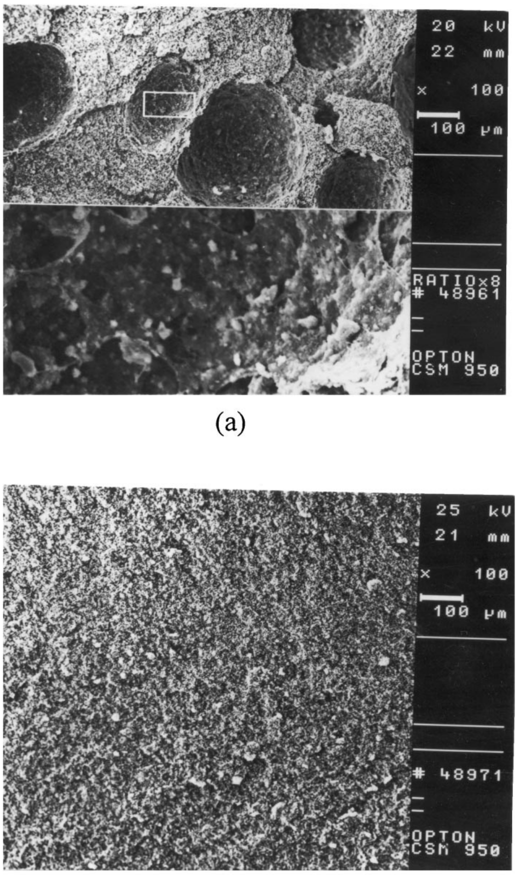
Figure 6 Viscosity of suspensions for oxidized Si_3N_4 powders at different temperature.

Fig. 6 shows the viscosity at different shear rates of the slurries of the Si_3N_4 powders oxidized at different temperature and with the same solid volume loading of 42% (the solid density is considered as 3.18 g/cm^3). It indicates that below 850°C the suspension viscosity decreased along with the increase of oxidizing temperature and above 850°C the suspension viscosity increased again because of the sharp increase of SiO_2 and the resulted increase of solid volume loading. To obtain slurries with low viscosity, 850°C was determined as oxidizing temperature.

As has been stated before, some gas-discharging reactions between Si_3N_4 particle and medium happen when the raw Si_3N_4 powder touches medium. In the gas-gathering experiment [22], the harm reactions were detected in the slurry of the unprocessed Si_3N_4 powder. And no reaction was detected between oxidized Si_3N_4 powder and the basic media, which indicated that surface oxidizing could effectively restrain the deleterious gas-discharging reactions in the slurry system. Fig. 7 shows scanning electron microscope (SEM) micrographs of the green body gelcast from (a) the original powder and (b) the oxidized powder. It could be seen through Fig. 7 that the former had notable bubbles,

TABLE I Variation of K^+ and NH_4^+ concentration versus time

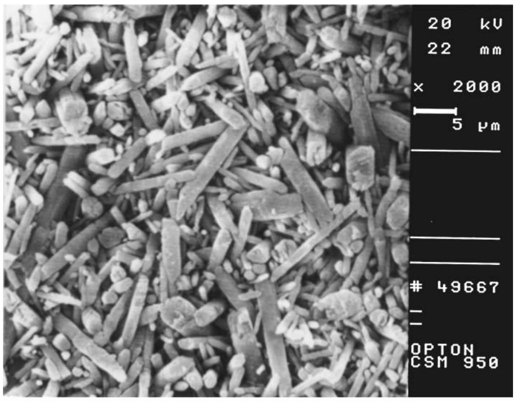
	Original Si_3N_4 powder (0 day)	Original Si_3N_4 powder (7 days)	Si_3N_4 powder oxidized at 600°C (11 days)	Si_3N_4 powder oxidized at 800°C (11 days)
K^+ (ppm)	3.47	3.43	1.13	0.59
NH_4^+ (ppm)	24.8	92.73	10.57	1.21



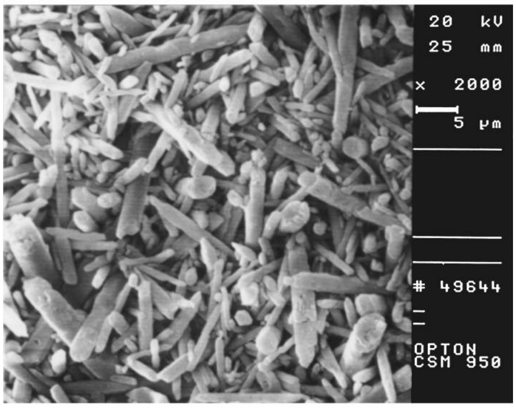
(a)

(b)

Figure 7 Micrograph of gelcast green bodies from (a) the raw Si_3N_4 powder and (b) the oxidized powder.



(a)Oxidation + gelcasting + GPS



(b)Dry press+isostatic press + GPS

Figure 8 Micrograph of different samples: (a) Oxidation + gelcasting + GPS (b), Dry press + isostatic press + GPS.

while the latter was homogeneous and no bubbles. Thus the strength of the green bodies after surface modification was greatly improved. It is about twice as much as that without surface modification and reaches about 20 MPa.

3.3. Influence of surface oxidation on sintering

Because oxygen content in Si_3N_4 powder increased after oxidizing, the liquid phase in the process of sintering also increased. As a result, mechanical property and microstructure of samples could be influenced. The mechanical properties of the gelcast samples with oxidized powder and the dry-pressed and then isostatic-pressed samples is shown in Table II, and their microstructure is shown in Fig. 8.

It is shown in Table II that mechanical property of gelcast samples is much better than that of dry-pressed and then isostatic pressed samples, but in Fig. 8 no obvious difference of microstructure can be observed. This indicates that the increase of liquid phase during sintering did not lead to excessive growth of grains. The difference in this mechanical property may be due to the defects caused by inhomogeneity in the dry-pressed and then isostatic pressed samples and their different grain boundary phases.

TABLE II Comparison of mechanical property of different samples

	gas pressure sintering	
	bending strength at room temperature $\sigma_{f,RT}$(MPa)	Weibull modulus m
Gelcasting of oxidized powder	785.16	11.78
dry press and isostatic press	582.7	6.04

4. Conclusions

1. After oxidizing in the air, a layer of SiO_2 and Si_2N_2O was formed on the surface of Si_3N_4 particles and their oxygen content increased obviously, which increased the liquid phase in sintering. But the mechanical properties of the gelcast samples with oxidized powder are still much better than that of dry-pressed and then isostatic pressed samples.

2. After oxidizing, the impurity ions in Si_3N_4 suspensions decreased. The higher the oxidizing temperature, the more obvious the effect was.

3. After surface oxidation, viscosity of the Si_3N_4 slurry was sharply decreased and the lowest viscosity can be obtained when the Si_3N_4 powder was oxidized at 850°C for 2 hours.

4. After surface oxidation, the oxide layer on particle surface could restrain the reaction between free silicon in Si_3N_4 powder and basic solution, and as a

result, the homogeneous gelcast green bodies without macroscopic pores were obtained.

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