Rheological properties of Si$_3$N$_4$ and Si$_3$N$_4$ with sintering additive CaO-Al$_2$O$_3$ powders

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Abstract
In this paper were considered the rheological characteristics of Si$_3$N$_4$ powders and the mixture of Si$_3$N$_4$ powders with sintering additive based on CaO-Al$_2$O$_3$. The dependence of optimal density on the applied stress during pressing was established. The powders compressibility coefficients were studied. It was shown that upon addition of a sintering additive CaO-Al$_2$O$_3$ the compressibility coefficient decreases and the compressibility modulus increases.

1. Introduction
Modern ceramic materials are in great demand because they have a wide variety of types and properties. In particular, structural ceramic materials based on silicon nitride Si$_3$N$_4$ are in demand, due to their physical and mechanical characteristics. Since ceramics are obtained from the initial ceramic powders, which are pressed previously in green body, the properties of ceramics directly depend on the accompanying processes of the powder particles deformation, the density of the green body and rheological properties.

The dilatometry and the sintering kinetic analyses of ceramics are very demanding on the quality of a green body, which should have a similar or identical density. The study of powders rheology, in turn, allows establishing the relationship between the applied pressure and the density of powder samples [1]. The rheology properties of the powder allow setting the relationship between applied stress $\sigma$ and deformation of powder particles $\varepsilon$.

2. Experimental part
In this study, the powders based on silicon nitride Si$_3$N$_4$ (Figure 1A) and Si$_3$N$_4$ with 10 wt.% CaO-Al$_2$O$_3$ (sintering additive) mixture (Figure 2) were studied.

The Si$_3$N$_4$ powder was crystallized properly with fibrous particles structure, the average size was from 1.5-2 $\mu$m in a length and up to 200 $\mu$m in a width. Sintering additive CaO-Al$_2$O$_3$ was obtained by solid-phase synthesis and previously used in study [2-3]. The sintering additive particles had sizes from 100 up to 300 nm and represented as agglomerates with dimensions up to 3 $\mu$m (Figure 1B).

The samples prepared as follows: 0.15 g for each sample was pressed by INSTRON, which registered measures of applied pressure and powder deformation. Max pressing pressure was 200 MPa for each test, and the total quantity of tests amounted to 3 for both samples. The total height of the samples was...
4.45 ± 0.2 for pure Si₃N₄ and 4.25 ± 0.2 for the mixture Si₃N₄ with 10 wt.% CaO-Al₂O₃. At least 3 measurements were carried out for each sample, then the values were averaged (the average value of the standard deviation of deformation in the entire interval of the experiment was σ₁ = 0.26% and σ₂ = 1.28% for Si₃N₄ powder and Si₃N₄ with 10 wt.% CaO-Al₂O₃, respectively).

![Figure 1](image1.png)  
**Figure 1.** SEM microstructure of powders: A – Si₃N₄ «PlasmoTerm», B – sintering additive CaO-Al₂O₃

![Figure 2](image2.png)  
**Figure 2.** SEM microstructure of a mixture Si₃N₄ with 10 wt.% CaO-Al₂O₃ powders

### 3. Discussion of results

As a result of the measurements, stress-strain curves were constructed for pure silicon nitride and the mixture of silicon nitride with a sintering additive (Figure 3). The stress-strain curves represent a transition from linear to exponential increase, however, to study the compressibility modulus (G), compressibility coefficient ($k_{strain}$) and final strain ($\varepsilon^*$), it is the linear section that corresponds to the first stage of deformation (Figure 4). At the first stage, an initial increase in stresses occurs and is accompanied by compaction of the structure due to the sliding of particles and filling of voids with smaller powder particles [4-5]. Further stages correspond to the exponential growth of deformation and density due to sliding, deformation, and growth of particle contacts.

Considering the fact that Si₃N₄ and CaO-Al₂O₃ powders have a completely different structure, this implies a difference in the values of deformation for pure Si₃N₄ and the mixture of Si₃N₄ with 10 wt. % CaO-Al₂O₃ powders. It is noticeable the Si₃N₄ powder had the highest strain value, and, consequently, the compression coefficient (Figure 3).
The dependence of the relative density of the powders on the stress was established. It was found that samples from a mixture of $\text{Si}_3\text{N}_4$ with 10 wt. % $\text{CaO}\cdot\text{Al}_2\text{O}_3$ had the highest density at the same stress value (Fig. 5). This dependence allows us to determine the optimal stress range, which is 60-120 MPa for the mixture and 100-200 MPa for pure $\text{Si}_3\text{N}_4$ to obtain a similar green body density (45%).
From the linear sections of the curves, the modulus of compressibility ($G$), compressibility coefficient ($k_{\text{strain}}$), and final strain values of the linear sections ($\varepsilon^*$) were determined (Tab. 1).

**Table 1.** The rheological characteristics of Si$_3$N$_4$ and Si$_3$N$_4$ + 10 wt.% CaO-Al$_2$O$_3$ powders

| Powders                  | $G$, MPa | $\varepsilon^*$, % | $k_{\text{strain}}$, 10$^3$ Pa$^{-1}$ |
|--------------------------|----------|--------------------|--------------------------------------|
| Si$_3$N$_4$              | 4.81     | 17.56              | 7.7                                  |
| Si$_3$N$_4$ + 10 wt.% CaO-Al$_2$O$_3$ | 8.78     | 15.12              | 5.4                                  |

The sintering additive CaO-Al$_2$O$_3$ (10 wt.%) into Si$_3$N$_4$ powder leads to an increase in the elastic modulus and a decrease in the compressibility coefficient. It is associated with the structural features of the powders. Si$_3$N$_4$ powder particles have a fibrous structure and have a certain elasticity, which affects their compressibility. When granules of CaO-Al$_2$O$_3$ powder are added, voids are filled with spherical particles due to this fact the samples have the highest relative density.

4. Conclusions

- The rheological characteristics of the compressibility modulus ($G$), compressibility coefficient ($k_{\text{strain}}$), and final deformation ($\varepsilon^*$) were studied for Si3N4 powders and a mixture of Si$_3$N$_4$ + 10 wt. % CaO-Al$_2$O$_3$. It was found the sintering additive CaO-Al$_2$O$_3$ in an amount of 10 wt.% lead to decreases of the compressibility coefficient from 7.7 · 10$^{-3}$ to 5.4 · 10$^{-3}$ Pa$^{-1}$ and the compressibility modulus increases from 4.81 to 8.78 MPa.

- The dependence of the powders relative density on the applied stress was established. The optimal stress range is 60-120 MPa for a mixture of Si$_3$N$_4$ + 10 wt.% CaO-Al$_2$O$_3$ and 100-200 MPa for pure Si$_3$N$_4$ to obtain the dense green body (40-45%).

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References

[1] Stolin A M, Bazhin P M, Pugachev D V 2009 *Russian Journal of Non-Ferrous Metals* 50 290
[2] Lysenkov A S et al. 2018 *Journal of Physics: IOP Conf. Ser.* 1134 012036
[3] Kargin Y F et al. 2010 *Inorganic Materials* 46 799
[4] Kempen D, Piccolroaz A, Bigoni D 2019 *International Journal of Mechanical Sciences* 156 146
[5] D D Titov et al. 2019 *IOP Conf. Ser.: Mater. Sci. Eng.* 525 012077