Effect of cooling rate after hot pressing on electrical conductivity of Si₃N₄-cermics with TiO₂ and TiH₂ additives

Iryna Cherniakova¹²*, Svitlana Zdolnik¹, Vitaly Petrovsky¹²
¹Frantsevich Institute for Problems of Materials Science of NASU, 3 Krzhyzhanivsky Str., 03680 Kyiv, Ukraine
²National Technical University of Ukraine “Kyiv Polytechnic Institute”, 37 Peremoga av., 03056 Kyiv, Ukraine

Received 15 October 2009; received in revised form 12 April 2010; received in revised form 8 June 2010; accepted 16 June 2010

Abstract
It has been established that cooling rate after hot pressing has influence on microstructure, electrical conductivity and charge storage in Si₃N₄ ceramics with TiO₂ and TiH₂ additives, which can be used as substrates for the large capacity microassemblies by Flip-Chip technology. It was shown that the critical cooling rate is 30°C/min for the Si₃N₄-TiO₂ and 50°C/min for the Si₃N₄-TiH₂ ceramics. Electrical conductivity is structurally sensitive property, strongly connected with evolution of Si₃N₄ microstructure. The best properties are typical for Si₃N₄ ceramics characterized by mono-trap state level with the activation energy of about 0.8 eV, obtained at the characteristic cooling rates.

Keywords: sialon, titanium oxide, titanium hydride, hot pressing, cooling rate, d.c. conductivity

1. Introduction
Designing of silicon nitride properties is still actual, but not enough investigated. It is known that properties of Si₃N₄ amorphous layers, synthesized in nonequilibrium conditions, are sensitive to different technology factors [1]. Thus, heating and cooling modes play the important role in formation of grain structure and composition of an insulating material. Heating mode determines chemism and kinetics of interaction between different components [2], but cooling rate after hot pressing governs the crystallization and amorphization processes.

Ideal activating additive for good consolidation of sialons during hot pressing should turn into a liquid phase at sintering temperatures [3]. It is reported [4] that addition of small amount of titanium compounds to precursor mixture for production of sialons reduces sintering temperature and increases temperature interval of existence of melt in grain boundary region. During interaction of titanium with β-Si₃N₄ solid solutions can be formed [5]. Titanium compounds can be added to precursor mixture in the form of TiO₂ or TiH₂. Application of TiO₂ prevents the abnormal grain growth during sintering of Si₃N₄ [6–8]. On the other hand, to improve fracture strength of silicon nitride ceramics compounds with high-melting point and high diffusion coefficient, for example TiH₂, can be used [9]. Hydrogen also activates material consolidation. In addition, on the end of isothermal soaking during hot pressing the liquid phase can be depleted by aluminum and titanium ions. Thus, it is possible to obtain electroneutrality violation of crystalized grain-boundary phase, which is compensated by localization of hydrogen with formation of many weakly bounded defects.

There is still not enough information about: i) which technology factors has effect on sialon so that it comes to amplification or impairment of defect generation, ii) which type of trap levels arises in hot pressing sialon and iii) how traps participate in processes of an electromigration and polarization of ceramic composites. It is also important to develop additional appropriate methods for non-destructive quality control of Si₃N₄ ceramics.

*Paper presented at 8th Students’ Meeting, SM-2009, Processing and Application of Ceramics, Novi Sad, Serbia, 2009
* Corresponding author: tel: +380 44 42 415, e-mail: Sowelnu@i.ua

63
The objectives of this work are to investigate microstructure evolution and electrical conductivity of Si₃N₄ ceramics with TiO₂ and TiH₂ additives obtained by different cooling rate after hot pressing and to ascertain the interaction: technology - structure - properties.

II. Experimental

Silicon-nitride ceramics with TiO₂ (sample Si₃N₄-TiO₂) and TiH₂ (sample Si₃N₄-TiH₂) additives were prepared from β-Si₃N₄ powder, 92 vol% (Baku plant of powder metallurgy, Azerbaijan, with chemical composition given in Table 1) by hot pressing at 1700°C. A grain boundary phase was formed from: i) chemically pure α-Al₂O₃ powder, 5 vol% (Nikolaev aluminous plant, Ukraine), ii) titanium oxide, 3 vol% (Zaporozhye Titanium-Magnesium plant, Ukraine) or titanium hydride, 3 vol% (Donetsk chemical plant, Ukraine). Powder mixtures were prepared in planetary-type mill for 15 minutes in acetone with aluminum oxide balls. Pressing temperature was controlled by heat-radiation pyrometer OPIR-17 on wall of a graphite matrix through a hole in the screen with accuracy ±10°C. Isothermal soaking has been made throughout 30 minutes under pressure of 20 MPa in air. Different cooling rate (Vc) of samples after hot pressing were used: 10, 20, 30, 40, 50, 60, 90 °C/min. The obtained samples had size of 10 mm × 10 mm × 5 mm.

XRD data were obtained by X-ray apparatus DRON-3. The amount of phases was determined by the intensities ratio of certain analytical dashes of each phase (equation 1).

\[ \frac{I_{\beta K L}}{I_{\alpha h K L}} = K_{\alpha \beta} \frac{V_{\beta}}{1-V_{\alpha}} \]  
(1)

Interaction factor \( K_{\alpha \beta} \) was determined experimentally by comparison of X-ray patterns of well-known premixes. Relative volume of one of the phases was determined in accordance to equation 2.

\[ V_{\beta} = 1 - V_{\alpha} \]  
(2)

Images of materials’ microstructure were obtained by microscope Neofot and the picture scanner Epikvant. The quantitative analysis of images was made with the analyzer SIAMS-620.

Electrical conductivity (direct current), at different temperatures up to 600°C, was measured by an electrometer with an input resistance of 10¹² Ω at a running voltage of 100 V. Samples were heated-cooled in the exterior furnace with the temperature rate of 4±1°C/min in a measuring chamber, providing fixed contact with a force of 10 kPa [10].

III. Results and discussion

3.1 Phase composition and microstructure

Characteristics and mechanical properties of the sintered Si₃N₄-TiO₂ and Si₃N₄-TiH₂ samples are given in Table 2. Porosity of all sintered samples is between 4%

### Table 1. Chemical composition and particularly impurities of starting powder β-Si₃N₄

<table>
<thead>
<tr>
<th>Si&lt;sub&gt;gen&lt;/sub&gt;</th>
<th>N</th>
<th>Si&lt;sub&gt;uncomb&lt;/sub&gt;</th>
<th>Fe</th>
<th>Al</th>
<th>Ca</th>
<th>O</th>
<th>Mg</th>
<th>Ti</th>
<th>C&lt;sub&gt;gen&lt;/sub&gt;</th>
<th>C&lt;sub&gt;uncomb&lt;/sub&gt;</th>
<th>Mn</th>
<th>Ni</th>
</tr>
</thead>
<tbody>
<tr>
<td>58.8</td>
<td>36.2</td>
<td>0.15</td>
<td>0.42</td>
<td>0.40</td>
<td>-</td>
<td>1.56</td>
<td>-</td>
<td>-</td>
<td>1.4</td>
<td>&lt;0.1</td>
<td>&lt;0.1</td>
<td>&lt;0.1</td>
</tr>
</tbody>
</table>

### Table 2. Characteristics of the sintered samples

<table>
<thead>
<tr>
<th>Additive</th>
<th>Cooling rate [°C/min]</th>
<th>Porosity [%]</th>
<th>( K_{IV} ) [MN/m&lt;sup&gt;1/2&lt;/sup&gt;]</th>
<th>( H_p ) (P = 5 N) [GPa]</th>
</tr>
</thead>
<tbody>
<tr>
<td>TiO₂</td>
<td>10</td>
<td>5.2</td>
<td>5.6</td>
<td>14.0</td>
</tr>
<tr>
<td></td>
<td>20</td>
<td>5.7</td>
<td>6.5</td>
<td>16.1</td>
</tr>
<tr>
<td></td>
<td>30</td>
<td>6.0</td>
<td>6.4</td>
<td>14.5</td>
</tr>
<tr>
<td></td>
<td>40</td>
<td>5.2</td>
<td>5.8</td>
<td>16.9</td>
</tr>
<tr>
<td></td>
<td>50</td>
<td>5.2</td>
<td>6.9</td>
<td>15.8</td>
</tr>
<tr>
<td></td>
<td>60</td>
<td>4.4</td>
<td>6.5</td>
<td>16.7</td>
</tr>
<tr>
<td></td>
<td>90</td>
<td>5.0</td>
<td>5.4</td>
<td>14.0</td>
</tr>
<tr>
<td>TiH₂</td>
<td>10</td>
<td>4.6</td>
<td>5.4</td>
<td>14.3</td>
</tr>
<tr>
<td></td>
<td>20</td>
<td>5.0</td>
<td>6.7</td>
<td>14.7</td>
</tr>
<tr>
<td></td>
<td>30</td>
<td>4.7</td>
<td>6.8</td>
<td>14.3</td>
</tr>
<tr>
<td></td>
<td>40</td>
<td>4.0</td>
<td>6.3</td>
<td>13.9</td>
</tr>
<tr>
<td></td>
<td>50</td>
<td>4.3</td>
<td>6.0</td>
<td>13.5</td>
</tr>
<tr>
<td></td>
<td>60</td>
<td>4.0</td>
<td>6.1</td>
<td>13.0</td>
</tr>
<tr>
<td></td>
<td>90</td>
<td>4.3</td>
<td>5.4</td>
<td>14.0</td>
</tr>
</tbody>
</table>
and 6 vol% and the corresponding density between 3.0 and 3.1 g/cm³. It can also be seen that the influence of cooling rate on mechanical properties is negligible.

XRD results (presented in Fig. 1 only by positions of the characteristic peaks) confirmed that beside the basic β-Si₃N₄ phase two additional phases, X₁ and Si₂ОN₂, were found in all sintered samples. These two secondary phases were formed during cooling of the liquid phase (obtained at the sintering temperature) around the solid β-Si₃N₄ grains. It can also be seen that the cooling rate after hot pressing has influence on phase composition, i.e. the state of these secondary phases (Fig. 1).

As can be seen from the Fig. 2, addition of titanium to silicon nitride ceramics in the form of TiH₂ (in comparison with TiO₂) considerably increases the oxygen content in system. Probably, this situation can be caused by titanium hydride dissociation at 600–800°C with the subsequent formation of hydroxyl complexes which hydrate silicon nitride [11].

Also, formation of titanium nitride complexes is possible.

3.2 Electrical d.c. conductivity

Electrical d.c. conductivity (σ) of the sintered samples was measured in heating-cooling mode and some of the results (for the samples with cooling rate of 30 and 90°C/min) are presented in Figs. 3 and 4. Non-linear temperature dependence of d.c. conductivity can be observed and it is connected with release of weekly bounded carriers localised at attachment levels*. Only

*Attachment level is a level at which probability of electron ejection in conduction band is higher than probability of its recombination with the hole in valence band, and occurrence depth can be compared with kT (<0,4–0,5 eV). Electron is in delocalized state, and its wave function has continuous spectrum.
decreasing dependence $\sigma(T)$ was analyzed as analysis of increasing dependence was obstructed by releasing of redundant carriers on capture levels. Temperature dependence of electrical conductivity follows the Arrhenius law with different activation energies, $E_a$ (which describes the depth of carrier localization level) for various cooling rates of a composite after hot pressing. It is possible to distinguish two areas on temperature dependence with different $E_a$: i) area $E_1$ in low-temperature region 100–350°C and ii) area $E_2$ in high-temperature region 350–600°C. Accordingly, activation energy for carriers in materials with different additives (TiO$_2$ and TiH$_2$) was calculated and presented in Figs. 5 and 6 in correlation with cooling rate after hot pressing (HP). Few characteristic zones of correlation can be seen.

If the electric field is applied along direction of HP (Fig. 5), it is possible to distinguish two characteristic regions separated by the critical cooling rate at which crystallization of structural components starts. They are 30°C/min and 50°C/min for the Si$_3$N$_4$-TiO$_2$ and Si$_3$N$_4$-TiH$_2$ ceramics, respectively. If cooling rate exceeds critical one, for the material with TiH$_2$ additive, occurrence depth in both (low and high) temperature regions is equal to 0.9±0.05 eV and does not depend on technological cooling rate (Fig. 5a).

For the Si$_3$N$_4$-TiO$_2$ ceramics, different occurrence depths for low and high-temperature region are observed, 0.9±0.05 eV and 1.2±0.05 eV, respectively (Fig. 5b). On the other hand, the samples cooled by rate which is lower than the critical one (Fig. 5) behave differently.

There is one stable level for the material with TiH$_2$ additive, which is not dependent on technological cooling rate (1.2±0.05 eV), and a spectrum of trap levels with activation energies 0.8±0.05 eV and 0.4 eV (the minimum at $V_c$ = 30°C/min). For the Si$_3$N$_4$-TiO$_2$ ceramics (Fig. 5b) activation energy in low-temperature region decreases a little (from 1.3 to 0.8 eV), but in high-temperature region increases considerably (from 0.6 to 1.2 eV).

If the electric field is applied perpendicularly to direction of HP, activation energy of carriers for the material with TiH$_2$ additive (Fig. 6a) depends parabolically on technological cooling rate. For cooling rates between 30–60°C/min two levels of carriers occurrence, at 1.2±0.05 eV and 0.9±0.05 eV, exist. At higher cooling rate energy level of 0.8±0.05 eV was calculated for

---

**Figure 3.** Temperature dependences of conductivity of samples with TiO$_2$ additives during heating (1) and cooling (2) with the rates $V_c$ = 30 (a) and 90°C/min (b)

**Figure 4.** Temperature dependences of conductivity of samples with TiH$_2$ additives during heating (1) and cooling (2) with the rates $V_c$ = 30 (a) and 90°C/min (b)
low-temperature region and remarkable reduction of activation energy (from 1.2 to 0.4 eV) for high-temperature region. In the Si₃N₄ ceramics with TiO₂ additives (Fig. 6b) structural components appear. There is a spectrum of energy levels with occurrence depth from 0.8 to 0.9 eV (“a tail of trap states”) in the forbidden zone of such structural components. Only by cooling rate close to the critical one ($V_c = 50°C/min$) occurs a stable energy level of deep occurrence with $E_a = 1.2$ eV.

Silicon nitride Si₃N₄ is the compensated semiconductor, which contains both donor (at the expense of oxygen) and acceptor (at the expense of aluminum) levels in a forbidden zone. Only by cooling rate close to the critical one ($V_c = 50°C/min$) occurs a stable energy level of deep occurrence with $E_a = 1.2$ eV.

So by technological cooling rate which is higher than the critical one, the maximum contribution to electrical conductivity is made by the structural components with type at temperatures lower than 500°C and n-type above 900°C. In the work [14] occurrence depth of trap levels is theoretically calculated for various types of defects (Table 3). It is shown that the values, calculated and obtained by us, correlate well with each other. It tells about structural sensitivity of electrical conductivity. We can assert that the technological mode, and namely the cooling rate of samples, influences morphology of structure and films formation on boundaries of crystalline grains of multicomponent materials, first of all on a crystallization degree of a grain boundary phases.

![Image 1](https://via.placeholder.com/150.png)

**Figure 5. Activation energy distribution of low- $E_1$ (•) and high-temperature regions $E_2$ (▲) of electrical conductivity of Si₃N₄ ceramics with the TiH₂ (a) and TiO₂ additives (b) (electric field is parallel to direction of HP)**

![Image 2](https://via.placeholder.com/150.png)

**Figure 6. Activation energy distribution of low- $E_1$ (•) and high-temperature regions $E_2$ (▲) of electrical conductivity of Si₃N₄ ceramics with the TiH₂ (a) and TiO₂ additives (b) (electric field is perpendicular to direction of HP)**

<table>
<thead>
<tr>
<th>Level</th>
<th>Type of defect</th>
<th>Type of trap</th>
<th>Occurrence depth of level, [eV]</th>
<th>Comments</th>
</tr>
</thead>
<tbody>
<tr>
<td>A</td>
<td>Two coordinated nitrogen atom in amorphous Si₃N₄</td>
<td>For electrons</td>
<td>0.8</td>
<td>For holes a defect is a trap only in oxygen-enriched silicon oxynitride</td>
</tr>
<tr>
<td>B</td>
<td>Silicon-silicon bond by formation of nitric vacancy in amorphous Si₃N₄</td>
<td>For electrons</td>
<td>1.6</td>
<td></td>
</tr>
<tr>
<td>B'</td>
<td>For holes</td>
<td>1.0</td>
<td></td>
<td></td>
</tr>
<tr>
<td>C</td>
<td>Two coordinated silicon atom (sililen centre) in amorphous SiO₂</td>
<td>For holes</td>
<td>1.5</td>
<td>Electron is not trapped with this defect</td>
</tr>
</tbody>
</table>

occurrence depth of about 0.8 eV, supposedly two co-ordinated nitrogen atoms in Si₃N₄. Defect in the form of two coordinated atom of silicon in amorphous SiO₂ leads to formation of traps for holes with activation energy of about 1.2 eV. After transformation of silicon oxide to amorphous silicon as a result of dissociation, the occurrence depth of defective levels decreases from 1.2 to 0.8 eV. The same occurs, if the crystal grains Si₃N₄ with two coordinated atoms of nitrogen dominate in substance. The increase of occurrence depth of traps from 0.4 to 1.2 eV tells about defect origin in dehydrogenated films of amorphous silicon nitride, oxidation of these films and formation of defects in amorphous SiO₂ [15].

IV. Conclusions

Control of cooling rate after hot pressing of Si₃N₄ ceramics with TiO₂ and TiH₂ additives has influence on: crystallization and amorphicity, composition and state of grain boundary phase, and anisotropy of microstructure. It is shown that the critical cooling rate is 30°C/min and 50°C/min for the Si₃N₄-TiO₂ and Si₃N₄-TiH₂ ceramics, respectively. It is also shown that cooling rate after hot pressing has influence on electrical conductivity and charge storage in Si₃N₄ ceramics. Electrical conductivity is structurally sensitive property, strongly connected to evolution of Si₃N₄ microstructure. The best properties are typical for Si₃N₄ ceramics characterized by monotrap level with occurrence depth of 0.8 ± 0.05 eV, obtained at the characteristic cooling rates.

References