Development of AIN ceramic composites for multilayer ceramic devices

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Abstract
Mechanical and electrical properties of AIN ceramics are dependent of phase composition and sintering temperature. TiO₂ and TiH₂ additives were chosen as the structure and properties modifiers and HFC – as conductive phase. AIN ceramics was considered as dielectric and conductive layers of functionally graded materials. Our investigations showed that AIN-1.5-2%TiO₂ ceramic composites is a prominent dielectric with required properties and in combination with 11-17% HFC it serves as effective ceramic heater. Broadband dielectric spectroscopy was used for the nondestructive testing of microstructure: dispersion frequency gives information about the effective thickness of a conductive channel; the slope of α(ω) dependence gives distinction between “lattice” and “carrier” responses corresponding to “intrinsic”, which is irreducible, and “extrinsic” processes due to some impurities or injected carriers.

Keywords: aluminum nitride, hot pressing, dielectric response, ceramic substrates, functionally graded materials.

1. Introduction
Microminiaturization of electro technical devices leads to the development of the functionally graded materials (multilayer ceramic devices) - monolithic ceramic bodies with conductive and dielectric layers made by appropriate tapes and sintered together in one step [1]. They can serve as Multi-Chip Modules (MCM-C) (especially HTCC) or composite heating systems (Gradient, Ukraine [2], Fig. 1. KYOCERA Corporation, Japan [3]). Al₂O₃ [4 – 7] and Si₃N₄ [8, 9] are the most commonly produced materials for high temperature dielectric matrix, as well as AIN [10, 11, 12, 13], which has higher thermal conductivity (320 W/m·K vs. 40 W/m·K for Al₂O₃ and 125 W/m·K for β-Si₃N₄).

To improve mechanical and electrical properties of AIN dielectric substrates large cations may be applied [14] (Fig. 2). For example, titanium cations may be added in the form of TiO₂, TiH₂ etc. Titanium oxide increases relative density, reduces dielectric permittivity and losses [15]. Under dissociation of TiO₂, O²⁻ ions lead to the grain elongation and formation of plate-like morphology (i.e. the formation of polytypes in AIN). Thus they increase toughness of the material [16]. Titanium hydride also reveals a beneficial effect on mechanical and thermal properties of AIN: as TiH₂ dissociates at 600-800°C [17], H⁺ cations toughen the structure due to its refinement and formation of solid solution of hydrogen in aluminium nitride [18]. Ti⁺ ions may increase thermal conductivity of composites [19]. But the effect of such toughening additives on electrical properties of aluminium nitride ceramics was not observed or observed only fragmentary.

For active resistive layer formation different refractory compounds are chosen: TiN [20], MoSi₂ [21], TaN [22], Mo [23], Ni [5]. HFC [24] is a promising additive for high temperature operation. If dielectric matrix of the material is an active element it can produce thermal energy up to 10-30% more. Properties of resistive layer under the influence of various technological factors can vary both in a positive and...
in a negative way. Commercially viable thermoelectric heaters should possess a set of optimal parameters of resistive layer, such as: the sign and value of the resistance temperature coefficient, resistance reproducibility, maximal surface temperature at minimal surface density of the heat load.

Concentration dependence of electrical conductivity was approximated using effective medium equation (McLachlan’s equation) [25]:

\[ \theta = \frac{\sigma_i^{1/2} - \sigma_m^{1/2}}{\sigma_i^{1/2} + \left(\frac{1}{\theta_{c_{\text{crit}}}} - 1\right)\sigma_m^{1/2}} + \left(\frac{1}{\theta_{c_{\text{crit}}}} - 1\right)\sigma_m^{1/2} \]

where \( \sigma_i \), \( \theta \), \( \sigma_c \), \( \theta_{c_{\text{crit}}} \) - conductivity and volume content of insulator and conductive phases respectively; \( \theta_{c_{\text{crit}}} \) - critical volume content of conductive phase at which charge carriers can freely move from contact to contact (percolation threshold); \( t \), \( s \) - parameters which characterize morphology of inclusion particles, the “shape” factor [26]. A set of \( s \) and \( t \) values was given in [25].

3. Results and discussion

3.1 Dielectric composites

The highest density was achieved in AlN samples at 1800°C (99.9%). Addition of titanium oxide increased the temperature of maximal densification on 50°C.

Fig. 3 shows that the presence of TiO\(_2\) lowers the density of AlN-TiO\(_2\) composites at sintering temperatures below 1800°C. At the same time, at sintering temperatures of 1850-1900°C relative density of AlN-0.5-2 vol.% TiO\(_2\) composites was equal to that of pure AlN (99.9 %) and decreased with increasing the additive percentage in composites with more than 3 vol.% of TiO\(_2\) (< 99.7 %) (Fig. 3.a).

It can be assumed that maximum density of the low doped samples is explained by the formation of fusible eutectic \( \alpha\text{-Al}_2\text{O}_3\cdot\text{TiO}_2 + \text{Al}_2\text{O}_3 \) with a melting point of 1840±10 ºC which is confirmed by the results of Kume [15]. The presence of aluminium oxide is attributed to the interaction between aluminium nitride and water under milling.
Minimal d.c. conductivity for AlN samples without additives was observed at $T_{sn} = 1900^\circ$C (Fig. 3.b). TiO$_2$ addition lowers the temperature of minimal conductivity on 50 ºC despite of the additive percentage. Increase of TiO$_2$ amount from 0.5 to 4 vol.% increased conductivity of the composites from $7\cdot10^{-11}$ up to $1\cdot10^{-10}$ $\Omega\cdot$m due to TiN formation in AlN ceramics as a result of the reaction between TiO$_2$ and AlN at temperatures >1600ºC.

It can be noticed that despite of Kume’s results [12] (Fig. 4), addition of TiO$_2$ in amount of >1.5 vol.% increases dielectric loss tangent. Thus, it can be assumed that at first addition of titanium oxide improves $\tan \delta$ due to the low loss tangent of TiO$_2$ (< 10$^{-3}$) but then after in-situ formation of TiN complexes an opposite effect can be observed.

Dielectric permittivity of AlN composites with TiO$_2$ and TiH$_2$ addition decreases with the temperature (up to optimal sintering temperature) and increases at increasing of amount of the additive (Fig. 5).

The first one usually “turns off” at lower frequencies ($10^3$-$10^4$ Hz at 300 K). But in the case of the present studies this disabling was observed at higher frequency ($f_d = 2.5\cdot10^3$ Hz).

Ceramics and polycrystalline materials are usually multiphase systems. The difference of the concentration of the charge carriers of these phases causes polarization at the boundaries which is usually considered as Maxwell-Wagner’s (M-W). The model of it can be described by a conductive layer with constant value of electric conductivity $\sigma$. In this case the system is characterized by uniform electric field so all the charges are located only on the interfaces and space charge is neglected. According to Trukhan [28] who described such system to be uniform (heterogeneous) dielectric without leakage currents (but with losses), both flat conductive layers and conductive spherical particles surrounded by dielectric medium, $\varepsilon'$ ($\varepsilon'' = \varepsilon$) decreases monotonically with frequency and $\varepsilon''$ has its maximum at the dispersion region. Dispersion frequency can increase with increasing the dielectric contribution (geometrical enlargement or decrease of permittivity). It asymptotically approaches to Maxwell-Wagner’s dispersion frequency when concentration of charge carriers rises. As the variation of conductor parameters in heterogeneous systems almost always exists, dispersion is less sharp than it follows from the theory of Maxwell-Wagner.

If the heterogeneous system is assumed as flat conductive layers (with a width of $d$) surrounded by a dielectric medium with low charge concentration, then the effective thickness of conducting channel $d$ can be estimated on the basis of the equation for frequency dispersion [34]:

$$\omega_d = 2\pi f_d = \frac{12D}{d^2}$$

(2)

where $D$ is the diffusion coefficient for the electron in the medium considered, which can be calculated from Einstein’s equation:

$$D = \frac{\mu kT}{e}$$

(3)
If charge mobility $\mu$ in AlN is assumed to be equal to 14 cm$^2$/V·sec (at 290 K), it gives the value of $D = 0.35$ cm$^2$/sec.

Thus from (2) the value of $d = 16$ µm can be obtained. All the samples regardless of the amount and type of the additives had the same frequency of dispersion and subsequently an effective thickness of conductive channel. In the authors’ opinion, it is also a typical situation for the materials below the percolation threshold.

The mechanism of charge transfer in amorphous materials is primarily hopping. Subsequently a.c. conductivity is the sum of d.c. conductivity, $\omega$ – angular frequency, $\varepsilon$ – relative permittivity of the material, $\omega_0$ – the electric constant, $\varepsilon_0 = 8.85 \times 10^{-12}$ F/m, $tg\delta$ – loss tangent. This equation can be expressed as $\sigma(\omega)\omega^n$. In all the previous works [29, 30] where a number of $n$ values was given it was believed that $n \leq 1$.

Although in contrast to electrons, ions move much smaller, nearest-neighbor distances, neither the magnitude of a.c. conductivity, its activation energy nor its frequency dependence can be taken as guides to the nature of the dominant carrier process due to some impurities or injected carriers, may prove to be useful tools in the assessment of dielectric materials [29].

The frequency dependence of a.c. conductivity can be considered within Jonscher’s universal power law. The slope of it in logarithmic coordinates results an exponent which values can be found in the range $0.5 < n < 0.9$ are to be associated with the “lattice” response. The distinction between “lattice” and “carrier” responses corresponding to “intrinsic”, that is irreducible, and “extrinsic” processes due to some impurities or injected carriers, may prove to be useful tools in the assessment of dielectric materials [29].

Four plots with different slopes can be distinguished on the frequency dependence of active part of admittance: at low- ($10^3$–$10^5$ Hz, $10^9$ Hz) and radio-frequencies ($10^9$ Hz, $3 \times 10^9$–$10^10$ Hz). The second and the third plots have the same slope regardless of the type or amount of the additive and sintering temperature: $\approx 1.1$ (for the second) and 0.8 (with TiO$_2$) - 0.9 (other additives) (for the third one) which reveal dielectric response of AlN grain.

In radio-frequency range the value of $n$ of AlN-TiO$_2$ composites increases from 0.5 to 0.8-0.9 at increase of TiO$_2$ concentration regardless of sintering temperature. In AlN-TiH$_4$ composites increase of TiH$_4$ amount increases $n$ from 0.5 to 0.9-1. At higher sintering temperatures (1850–1950 °C) $n = 0.4$-0.5 irrespective of titanium hydrate concentration.

The present studies have demonstrated that $n$ could be higher than unity in contrast to the most common opinion that it is always less than 1. Thus obtained results require further more deeply theoretical understanding.

Dielectric loss factor did not change with the temperature below 150°C and increased with it above (Fig. 6) which indicates conduction losses. Deviation from optimal sintering temperature increases $\varepsilon''$ that is associated with the formation of structure defects.

3.2 Active resistive composites

All AlN-TiO$_2$-HfC composites had high density, 97.5–99.5%.

As it can be seen from the percolation curve (Fig. 7), resistivity of the composites decreases with increasing concentration of conductive additive HfC. At the lowest HfC content (11%) the resistivity is equal to 0.15 Ω·cm. Such low value shows that all the studied concentrations are beyond the percolation threshold.

Metallographic analysis of composites showed (Fig. 7) that conductive clusters are formed in a shape of longitudinally elongated structure under the influence of magnetic field.

Modeling of percolation curve gives the values of percolation threshold $\theta_{\text{crit}} = 9.9\%$ and coefficient $t = 1.35$. Besides, SIAMS analysis showed that the ratio of conductive phase was $\approx 7.9\%$ (for 2TO-11HC samples).

According to [25] $t$ characterizes the shape of inclusion particles and it is associated with “demagnetization or depolarization” coefficients $L_1$ and $L_\|$, of conductive and insulator phase via equation:

$$t = \frac{1}{1 - L_\| - L_1}$$

Assuming $L_\| = L_1$ one can obtain $L_1 = 0.13$ which according to [25] indicate the formation of disk-shaped particles. Comparing these results with Fig. 7 authors believe that 3D morphology of conductive particles is elongated in the third direction. The fact that actual ratio of conductive phase is lower than expected confirms authors’ assumption.

Temperature dependence of electric resistivity is linear (Fig. 8). Steady positive temperature coefficient of resistance (Fig. 8) for all the studied concentrations of HfC in a wide temperature range makes AlN-HfC ceramic heaters the contenders to the
analogues used today [3]. Besides, ceramic gradient materials provide higher thermal shock and crack resistance because of similarity of thermal expansion coefficient of the components (5.6 \times 10^{-5} and 4.6 \times 10^{-5} K^{-1} for HfC and AlN respectively).

Dependence of the surface temperature on the applied power density (Fig. 9) showed that all the composites beyond percolation threshold have the same characteristics despite of the conductive phase content.

4. Conclusions

AlN-TiO₂-HfC composites. But further increase of the additive content has the opposite effect. Deviation from the optimal sintering temperature leads to the formation of structure defects and increases dielectric loss.

Broadband dielectric spectroscopy was used for the nondestructive testing of microstructure: dispersion frequency gives information about the effective thickness of a conductive channel; the slope of \( \sigma(\omega) \) dependence gives distinction between “lattice” and “carrier” responses corresponding to “intrinsically,” which is irreducible, and “extrinsically” processes due to some impurities or injected carriers.

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