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Densification, microstructure and properties of electroconductive Si_3N_4–TaN composites. Part II: Electrical and mechanical properties

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Abstract

Dense Si_3N_4–TaN composites with the TaN phase in the range of 5–50 vol.% were produced by a hot pressing technique in reducing (CO) and neutral (N_2) atmospheres. The experimental data of the electrical resistivity for conductive, TaN-reach areas and insulating Si_3N_4-based matrix are presented. A new numerical simulation was conducted to compute a threshold concentration of the conductive phase, X_c as a function of the radius of dielectric particles to the radius of conductive particles ratio, R_d/R_m, in a two and three-dimensional (bulk) structure. The electrical resistivity of CMC was predicted using the computed X_c parameter by applying the percolation theory and the general effective media (GEM) equation. Finally, the predicted values were compared with the obtained experimental data. Both values were in good agreement. It was proved that the resistivity of electroconductive ceramics is strongly affected by the amount and morphology of the filling phase and is slightly affected by the filling phase's formula. An evident influence of the grain size distribution of TaN powders and morphology of particles of the conductive phase on some electrical and mechanical properties was ascertained. A small quantity of BN powder was added to the starting composition for stabilisation of the porosity level in the manufactured composites which is essential for the production of reproducible electroconductive composites.

Keywords: Composites; Electrical conductivity; Electrical properties; Mechanical properties; Si_3N_4–TaN

1. Electrical properties

1.1. Resistivity of CMC at room temperature

The relationship of the electrical resistivity of CMCs based on coarse or fine filler powders (conductive phase), hot pressed in the CO atmosphere, is shown in Fig. 1. The electrical resistivity of the CMC decreases with the increase of the amount of dispersoid used and reaches lowest values for the composites with the fine filler powder applied.

The electrical resistivity is governed by the formation of chains of electroconductive particles and therefore is linked to the grain size distribution of the starting powders and distribution of the TaN powder in the composite. It was shown that for a different content of conductive pellets in the composite and different chemical activity of these particles, the coarsening of the microstructure is different. Four characteristic areas were distinguished in the tested composites (see Part I, Table 5). These four zones can also be seen in Fig. 1 presenting a real dependence of the electrical resistivity of the tested CMC on the concentration of the TaN powder. The resistivity variation presented by curve 1 in Fig. 1a is typical also for the CMC structure shown in Fig. 12a and Fig. 15a in Part I of this paper. A similar relationship was observed for Figs. 1b, 12b and 15b (Part I).

Composites made from a coarse powder are characterized by lower differences in the resistivity value of the bulk material and the conductive zone in the FGM material. In both cases, the variation in the resistivity parameter follows a "stepping" characteristic (Fig. 1a). The resistivity of the bulk material and the resistive area of FGM can differ by a factor of 10^2–10^6 at the same

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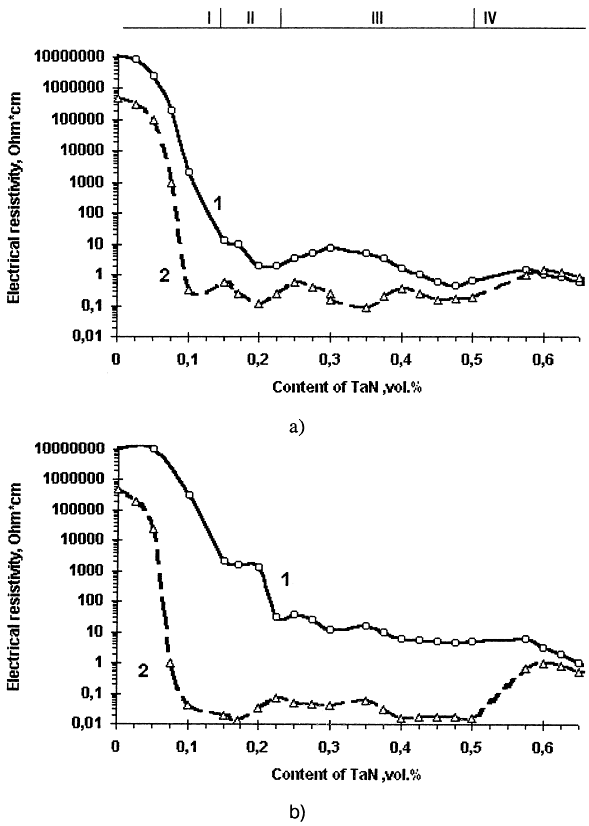

Fig. 1. Electrical resistivity of the Si_3N_4–TaN composite, hot pressed in a CO atmosphere as a function of TaN content: (a) CMC with a coarse TaN powder; (b) CMC with a fine TaN powder; 1, 3D samples, 2, conductive area of FGM.

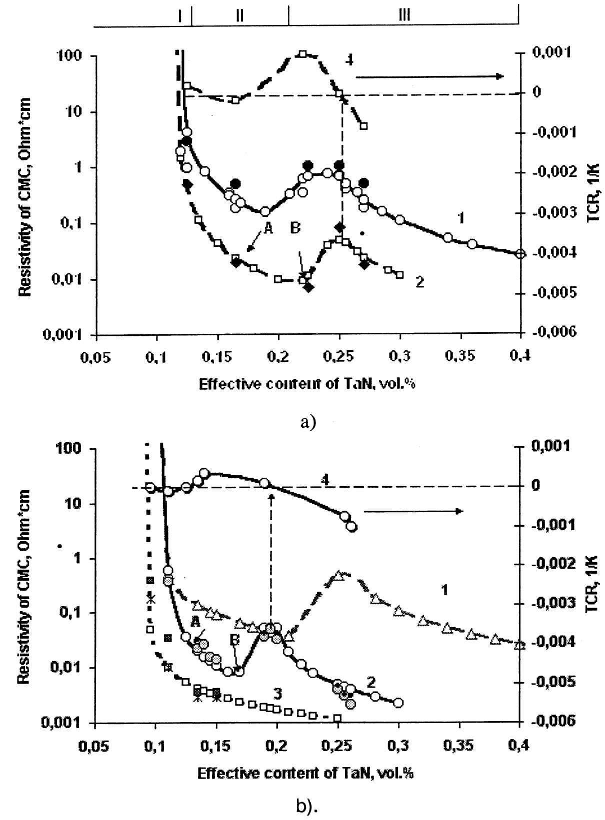

Fig. 2. Electrical resistivity of the Si_3N_4–TaN composite (as an area of FGM) hot pressed in (a) CO and (b) N_2 atmosphere as a function of TaN content. Curves 1 and 2, with roll milled/fined and 3, fine TaN powder; curve 4, temperature coefficient of resistivity for roll milled TaN.

filling phase concentration (Fig. 1b). This creates a lot of difficulties in designing a resistive composite with a defined resistance value. Obviously this non-monotonous resistance relationship has influence on the coarsening process of the conductive particles during the thermal treatment of composites. In the case of composites with fine TaN powder the resistivity of composites decreases in a smooth monotonous way with the dispersoid concentration (Fig. 2b, curve 3). A quite different behaviour of the electrical resistivity vs TaN content is characteristic for the composites with fine, roll milled powders (Fig. 2, curve 2). The fine TaN powder segregates during the heat treatment in a N_2 atmosphere and forms a new structural network of insulating pellets at the conductive phase content of about 17.0 vol.%. This causes an increase in the electrical resistivity of about 10 times. Sintering of composites with a coarse TaN powder under these same conditions promotes a further coarsening process and as a consequence, a much stronger growth in their resistivity. The electrical resistivity growth can also began at a much higher concentration of the dispersoid, above 22 vol.% (Fig. 2b, curve 1).

In the case of the composites sintered in a CO atmosphere this same process is observed, however the intensity of coarsening in the composite with a roll milled powder is stronger which leads to higher resistivity values (see Figs. 2a and 14 and 15 in Part I).

The probable reason for this phenomenon could be explained in the following way. Non-monotonous behaviour observed with curves of the electrical resistivity as a function of concentration of the conducting phase are not accidental and not a fault in the performed measurements. It is predicted that a similar behaviour will be characteristic not only for the investigated system Si_3N_4–TaN but also for other systems. The intensity of segregation will depend on the relative rate of the densification of the matrix phase and the inclusion phase at a designed temperature of the sintering process, variation in the technological parameters and in the pressure and atmosphere of sintering. The restriction in the dimensions of the resistive area (resistive zone in FGM) also promotes an amplification in the segregation process of the conducting phase and influences the integration of particles of this phase.

1.2. Temperature dependence of the electrical resistivity

The value of the thermal coefficient of resistance (TCR) depends strongly on the microstructure of the material (Fig. 2, curve 4). The value of the TCR for this material was calculated from the well-known formula (1):

$$\Theta = \frac{1}{\rho_{20}} \cdot \frac{\rho_T - \rho_{20}}{T} \tag{1}$$

where:

Θ, thermal coefficient of resistivity (TCR),
ρ_{20}, resistivity at room temperature,
ρ_T, resistivity at "T" temperature.

It is known that the TCR for ceramic composites can have a negative or zero value. It is shown in Fig. 2 that the TCR for resistive materials changes sign to positive and reaches its maximum value at the point B for some concentration of a dispersoid. A relatively high value of the TCR was calculated for the Si_3N_4–TaN composites sintered in a CO atmosphere, up to 2×10^{-3} K^{-1}. The cooling process of composites had also a strong influence on the value and sign of the TCR. The typical relationship of TCR vs cooling rate for hot-pressed Si_3N_4–TaN composites in a CO atmosphere is presented in Fig. 3. The rapid cooling process had a positive influence on the value of the TCR, which was characterized by a positive value of the TCR in the temperature range between 400 and 900°C. This is an interesting phenomenon from the point of view of future practical applications of these materials. The values of the TCR for composites made with fine powder TaN are lower than those measured for the materials made with coarse TaN powder. This phenomenon is less visible for composites sintered in a CO atmosphere than for those sintered in a nitrogen atmosphere. It is remarkable that the latter material contains significant quantities of residual pores and microcracks. Other characteristic properties of this material observed during performed tests were a complete lack of stability of measured values and sign of the TCR during the production cycle and also in the exploitation stage. It was observed that the TCR depends strongly on small changes in the manufacturing route and heating–cooling cycle applied during the production stage.

Another important observation was that the fully densified material was characterized by a zero value of the TCR. When the material contained a small quantity of closed pores then the growth in the TCR value was very slow; with a maximum at the critical concentration of pores, approximately 4.5%. A further growth in the total porosity resulted in lowering the TCR to the region of negative values. Therefore, trying to avoid such strong variation in the porosity of the developed material, the another type of conductive CMC was developed. A new type of the composite contained as well as Si_3N_4 and TaN powders a small quantity of the BN powder, usually between 0 and 10 vol.%.[1] The specific purpose of the BN, ceramic powder difficult to sinter, was the formation of a controlled volume of residual porosity in the composite and thus making the material less sensitive to the atmosphere of sintering. This type of composite was less sensitive to a variation in manufacturing parameters and designing of electrical parameters in advance was much easier (Fig. 4). The possibility of controlling the TCR value of the resistive composites has its practical application in manufacturing new functional products, i.e. heating elements. It is possible to manufacture a functional zone in the composite (see Fig. 2 in Part I) in this way so that the electrical heater will be self- stabilized under operation (Fig. 5). The self-stabilization phenomenon is usually very effective when the temperature on the surface of the heating element is in the range of 800–1100°C.

1.3. Relationship between the microstructure and electrical conductivity of CMC

To solve some problems related to the material engineering itself and non-destructive quality control it was necessary to make an analytical description of the electrical

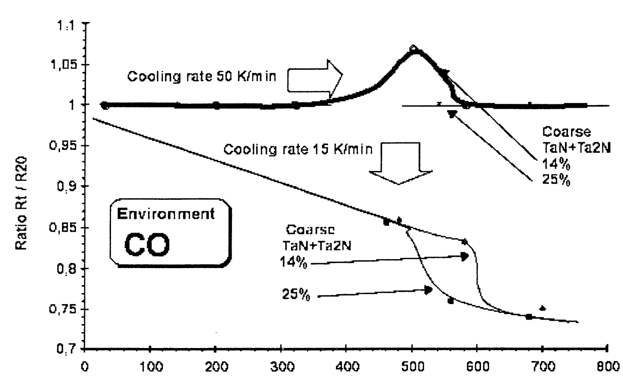

Fig. 3. TCR as a function of cooling rate for the resistive composite with coarse TaN powder (as a filling phase).

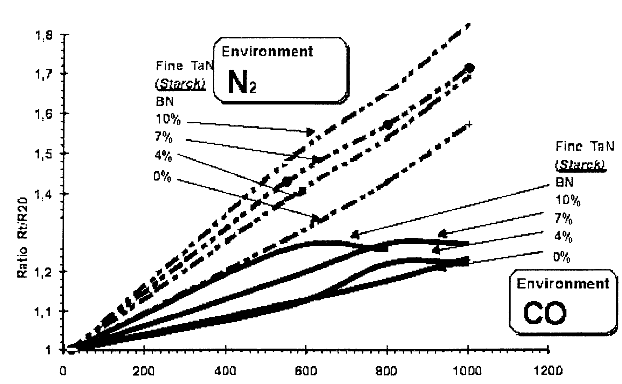

Fig. 4. TCR as a function of the surface temperature and amount of the BN additive in hot pressed CMC (in a CO and N_2 atmosphere).

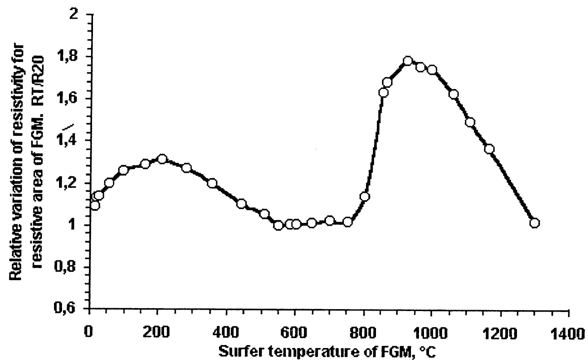

Fig. 5. Relationship between the resistivity of the CMC material and the surface temperature in the ceramic heater (Si_3N_4–TaN–BN-based).

resistivity as a function of the content of the filling phase. When the resistive composite is composed of the insulator as a matrix and the conductor as a filler then the overall electrical behaviour is controlled by the formation of the continuous network of conductive particles throughout the insulating matrix. It has been observed that in a resistive composite with metal like phase volume fraction, X_m, there exists a threshold volume fraction of the conductor, X_c, above which the electrical conduction through the composite takes place. This phenomenon can be described by two percolation equations.[2]

$$\rho_p = \rho_d^*\left(1 - \frac{X_m}{X_c}\right)^t; \quad \rho_p = \rho_u^*\left(1 - \frac{1 - X_m}{1 - X_c}\right)^{-t} \tag{2}$$

Where: ρ_d and ρ_b are the resistivity of insulator and resistivity of conductor respectively, t is an exponent. However, the percolation equations do not solve following practical problems:

- Segregation processes and microstructural anisotropy occur during the coarsening process (or not coarsening) of resistive non-isometric systems (as a result variations in X_c and t parameters are observed),
- Coarsening processes of conductive (or insulating) particles and the formation of conductive pellets (as a result variations in ρ_m, ρ_d, X_c and t parameters are observed).

In materials engineering it is necessary to know all these parameters enable a calculation of the specific value of X_m for a required value of ρ_p. Multi-thresholds in the coarsening process can be calculated also using the well known percolation models presented in Part I.[1,2] It has already been shown that with the increase in the conductor concentration, X_m (after formation of conducting clusters) a situation is created where the critical concentration X_c will no longer depend on the ratio R_d/R_m until there is a change in the size of insulator particles ensembles [Eq. (3)]:

$$X_c = z_m \frac{R_m}{R_d + R_m} \cdot \frac{R_d}{R_d + \left(\dfrac{1 - X_m^2}{X_m^2}\right) R_m} \tag{3}$$

where: z_m, coordination number of packed particles in a conductor.

The first part of this expression, a constant factor, describes the geometrical aspect of a mutual arrangement of particles in an insulating matrix and in a conductor. The second part describes a relationship between the effective concentration of the filling phase and the sizes of conductive and insulating pellets. The last part of the equation represents a relationship between the number of particles included in the percolation network of the cluster and the general number of conducting particles in the system and an array factor of the filling phase.

The electrical resistivity of the conductive phase, ρ_m^*, the value of the critical volume fraction, X_c, the critical exponent, t, and also the coefficient of depolarization of the ellipsoidal inclusions were calculated from the experimental data. The depolarization factor of dispersoids was calculated using "X_c" and "t" values and depending on these calculations a relationship between the ellipsoids size in the direction of current flow (H) to the ellipsoids size perpendicular to the direction of current flow (D) was determined. It is obvious that if $H/D = 1$ then dispersoids are characterized by the isometrical form, when $H/D > 1$ the particles are of a "cylindrical" form and when $H/D < 1$ the particles are characterized by a "plate" shape. Results of these calculations are presented in Table 1.

It was also proved that the multiphase composites made with coarse TaN powder are characterized by a high value of the resistivity, ρ_m, which was 15 to 60 times higher than values measured for a pure TaN powder. Using the fine TaN powder, no influence of the manufacturing route (milling according to route A, B or C) or the atmosphere of sintering was found. The critical volume fraction of the conductive phase in the composite was lowered to about 3 vol.% and the index "t" decreased to a value of 1.1–1 3 (at room temperature). Each group of samples was characterized by a specific tendency in the distribution of measured values on the approximation curve.

1.4. Summary

On the basis of the results presented in this chapter it can be concluded:

- In real resistive composites the threshold concentration X_m (as provided by Ref. 3) is a periodic function of the sizes of individual structural fragments in the

Table 1
Characteristic data calculated from approximation curves for Si_3N_4–TaN composites

	3D samples	Area of functional graded material				
	CO environment			N_2 environment		
	Coarse TaN + Ta_2N					Pure TaN
Properties	As delivered		Fine	As delivered	Activated by milling	Fine
Resistivity of conductor, ρ_m, Ohm•.cm	0.00493–0.01576	0.00138–0.00217	0.000197	0.000493–0.00788	0.000197	0.000197
Threshold of percolation, X_{cm}	0.11–0.165–0.227	0.116–0.2–0.225	0.091–0.116	0.092–0.11–0.225	0.11	0.088
Characteristic index'' t''	2.4–2.7–1.9	1.65–1.8–2.9	1.85–1.9	1.2–1.8–1.8	1.31	1.1
H/D value for conductor pellets	0.68–0.91–1.09	0.92–1.13–1.19	0.73–0.92	0.69–0.91–1.03	0.694	0.511
H/D value for insulator pellets	1.47–1.1–1.15	1.38–1.0–1.36	1.0–1.1	1.19–1.0-1.0	1.0	1.96

system (R_d/R_m — size of the insulator pellets compared to the size of conductor pellets). The threshold concentration does not depend on the size of the resistive composite (size of the resistive zone in the functionally graded composite) but it is defined by the degree of shredding of the inclusion phase and the chemical activity of the system during the sintering process.

- The critical exponent "t" is also a periodic function of the R_d/R_m ratio and depends on the number of particles belonging to the conducting cluster and on the size of conducting pellets (R_m) and insulator pellets (R_d). The change in the "t" parameter occurs later than the change in the X_c parameter (movement along the axis R_d/R_m from right to left). Besides this, the critical exponent "t" is a function of the size of conductor pellets, and the size of the resistive composite or of the resistive zone in the functionally graded composite. It was also observed in the optical images that there is some kind of "competition" between the value of the critical exponent "t" and the value of the fractal "t_F" (calculated from microstructural images) of conducting pellets. When the critical exponent $t = t_F$ then a two dimensional percolation network of clusters is formed in the composite, and the cluster dimension coincided with the fractal dimension of linear sizes of conducting inclusions. If in the resistive composite the 3D percolation network of clusters was formed, then $t = t_F + 1$ (the cluster dimension coincides with the fractal of the area of conducting inclusions).
- The size of the conductor percolation network of clusters ρ_m^* is also a periodic function of the composite structure and is dependent on the size of conductive pellets, and the size of ceramic items or the resistive zone in the functionally graded material. However, changes in the value of the ρ_m^* parameter require further study. At this stage of the investigation it is possible to state that for resistive composites made with superfine but not active powders the value of their resistivity could be close to the resistivity of the filling phase. On the other hand if the structure of conductive pellets is built from 2 particles then the value $\rho_m^* = M \cdot \rho_m$, where $M = 2$. If such a fragment consists of 4 particles then $M = 1.67$. With a greater number of particles the value M will be described by the equation $M = (\sqrt{5} + 1)/2$. If the conductive pellets are a "lace-like" shape and form closed capsules of the conducting particles around the insulator pellets then they are perforated by the insulator inclusions into its internal part. As a result the resistance of such particles will depend on the size of the outside capsule of the conducting unit and on a perforation degree of the internal part. The size of the outside capsule will depend on the size of the resistive items or the resistive zone in FGC, and the perforation degree will be determined by the activity of the sintering components in the multiphase system. In the performed experiment the value $\grave{I} = 6$–32 was observed for the resistive zones in FGC and $\grave{I} = 26$–130 for the volumetric (bulk) materials.
- The presented results allow us not only to determine a required composition of raw materials and to design processing parameters for the production of resistive components but also to control the formation of a "real structure" in the product. Predictions are based on a correlation between X_c and t parameters and the coefficient of dispersoids depolarization. It is also possible using this correlation to calculate the aspect ratio for agglomerates of the filling phase (from the slope of log R_p–log ($X_m - X_c$), where R_p is the resistance in the direction of each 3D axis). Such calculations for the H/D ratio are shown in Fig. 6. This relationship can be used also for improving the mechanical properties of CMC materials by reinforcing them with needle-like particles.

2. Mechanical properties

The mechanical properties of Si_3N_4–TaN composites were measured at room temperature and analyzed together with their microstructure.

2.1. Mechanical properties as a function of the TaN content

The fracture toughness of the CMC material increases with the increase in the TaN content to a maximum of about 30–35%. This behaviour is independent of the particle size; similar values of the fracture toughness were obtained for composites with coarse or roll-milled TaN powders (Fig. 7, curves 3C and 3F). On the contrary the microhardness decreases with the increase in the TaN content. The CMC material with the coarse TaN powder has reached a maximum hardness at a TaN content between 30 and 35% (curve 2C). During the hardness measurement elongated and large agglomerates were avoided so that the indentations were made in the zone with homogenous TaN content. The room temperature flexural strength of the CMC material is greatly influenced by the type of TaN powder used (Fig. 7, curves 1C and 1F). A maximum value of the bending strength parameter was revealed for composites with their microstructure typical of the structural zone 3 which corresponds to a maximum aspect ratio of conductive pellets. Therefore it can be concluded that the whiskers reinforcement of the CMC material with a filling phase content of 30 vol.% is really beneficial for this parameter. Additionally, the mechanical properties of the optimized Si_3N_4–TaN composite with 13.5 vol.% TaN + Ta_2N coarse powder, hot-pressed in a CO atmosphere, are presented in Table 2. Measured values are at a similar level as the mechanical properties obtained[4,5] for non-optimized, hot-pressed silicon nitride ceramics.[4]

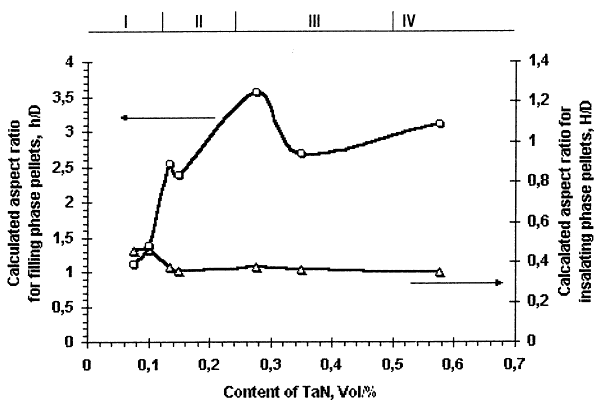

Fig. 6. Calculated aspect ratio for conductive pellets in CMC with roll milled (fined) TaN powder.

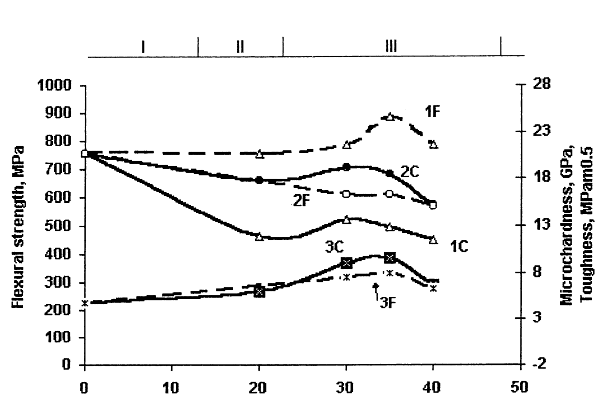

Fig. 7. Mechanical properties of the Si_3N_4–TaN composite, hot pressed in a CO atmosphere, as a function of TaN content. Curve 1, flexural strength; 2, microhardness; 3, fracture toughness; F, CMC with roll milled/fined TaN; C, CMC with coarse TaN powder.

2.2. Relationship between electrical and mechanical properties of CMC

In the present work, no effort was made to optimize the mechanical parameters of the manufactured composites. The main goal was to optimize the electrical properties of the produced FGC and to develop the material with a maximum resistance to thermal shock. A correlation was made between the characteristic parameters in the percolation equation obtained from the experimental data and the mechanical parameters of the resistive composites. Characteristic parameters of the percolation system such as the exponent "t", the critical concentration "X_c", the resistance of conducting clusters $\rho_m^* = M\rho_m$ and the degree of depolarization of conductive dispersoids were calculated. Results of this analysis are summarized in Fig. 8. A very weak correlation was found between the H/D parameter for conductive pellets and mechanical characteristics of the CMC material made with roll milled (fined) and coarsening TaN addition. However, the relationship between other parameters such as the anisotropy of insulating pellets and the resistivity of percolation clusters was quite strong. Each mechanical parameter was plotted as a function of these two electrical parameters. Having empirical or analytical equations for such relationships, it is possible to predict in advance the mechanical properties of the resistive composite. The presented

Table 2
The porosity and mechanical properties of the composite Si_3N_4–TaN (13.5 vol.%), hot-pressed in a CO atmosphere

Parameter	Unit	Value
Porosity	%	0.5
Flexural strength	MPa	460
Toughness	MPa $m^{1/2}$	6.4
Young's modulus	GPa	310
Microhardness	GPa	19
Thermal linear coefficient, α	10^{-6} 1/°C	3.4

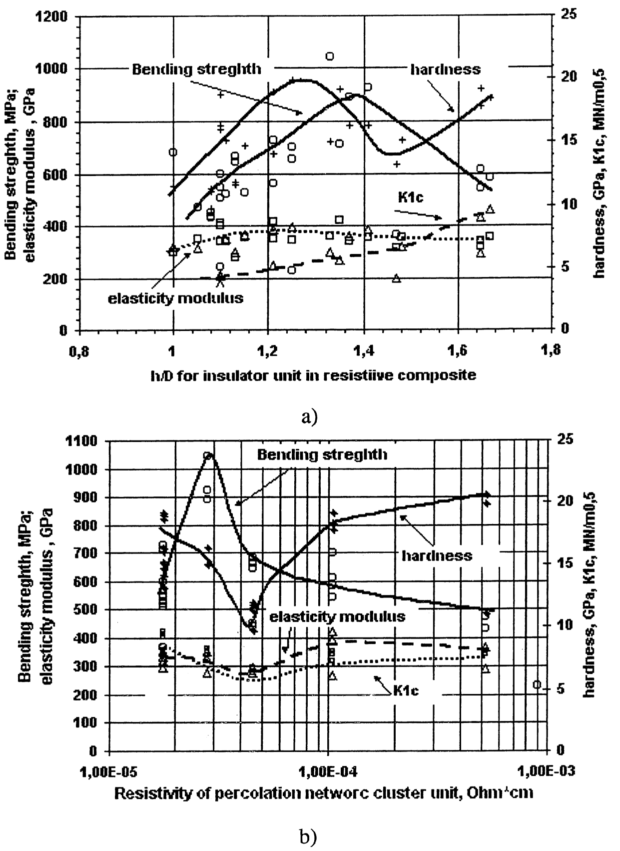

Fig. 8. Relationship between mechanical properties of the resistive composite and (a) aspect ratio of dispersoids and (b) resistivity of the percolation clusters.

interrelations therefore allow us to predict the mechanical properties of such CMC materials in the future. Another possible application of these relationships is applying them for the non-destructive monitoring of the quality of ceramic objects.

3. Final conclusions

- The chemical composition of the ceramic powders, powder size distribution, atmosphere of sintering and interaction between matrix, conductive phase and products of pyrolysis of the organic binder have a significant influence on the mineralogical composition of composites in the system Si_3N_4–TaN.
- The composite made from the silicon nitride powder with the additive of coarse, non-stoichiometric ($TaN + Ta_2N$) tantalum nitride powder, with alumina as a sintering additive and hot-pressed in the CO atmospheres was characterized by an increased quantity of the conductive phase (in comparison to a pure TaN powder based composite) and preferred from the electrical properties point of view and microstructure (network of elongated chains).
- The composites in the Si_3N_4–TaN system, hot-pressed in the CO atmospheres consisted of the following mineralogical phases: Si_3N_4, TaN and SiC and a number of minor phases such as O′-Sialon, Si_2ON_2, $TaSi_2$, Ta_5Si_3, $TaC_{0.5}Si$ and $Ta_5Si_3N_7$.
- The percolation theory was used to describe the physical properties of the manufactured composites, such as electrical resistivity, thermal conductivity and others. Experimentally it was confirmed that in the real resistive composites the threshold concentration is a periodical function of the ratio between the sizes of the individual structural fragments of the system R_d/R_m. The critical exponent "t" is also a periodic function of the R_d/R_m ratio, and depends on the number of particles belonging to the conductive clusters and the size of the conducting particles (R_m) and insulator ensemble (R_d). A change in the threshold value "t" occurs later than the change in the X_c value itself (movement along the axis R_d/R_m from right to left). The critical exponent "t" is a function of the particle size of the conductor, the size of the resistive composite or the resistive zone in the functionally graded material. The resistance value calculated for the percolation network of conductive clusters ρ_m^* is also a periodic function of the composite microstructure and depends on the size of the percolation clusters and size of the resistive zone in the functionally graded material.
- The conductive particles forming the conductive network have a strong influence on the electrical resistivity/conductivity of the ceramic composites. A complicated "chain" type system of the conductive agglomerates is preferred for the electrical charge transfer and is characterized by a 5 to 60 times higher value of the specific conductivity than those measured for the composite with a "ring" type microstructure. The latter contains a lot of clusters which is characteristic of the composites made with a high purity fine TaN powder.
- The optimized composites were characterized by a positive thermal coefficient of resistivity in the temperature range of 400–1100°C.
- The stabilization of the porosity level in the manufactured composites is essential for the production of reproducible electroconductive composites and this was achieved by the addition of a small quantity of BN powder (4–10 vol.%) to the starting composition of the ceramic composite.The interrelations between other parameters of the percolation equations (anisotropy of insulator fragments expressed by a H/D ratio and resistivity of the percolation network of clusters) and mechanical properties are observed to be quite strong. The

specific character of the established interrelations allows us to establish the possibility of designing the mechanical parameters of the produced materials in advance. Another possible application for these interrelations is non-destructive quality control of the ceramic objects.

- The developed novel electroconductive material with a small quantity of BN is superior to the traditional Si_3N_4–TaN composite due to a higher resistivity to oxidation, better matching of the thermal expansion coefficient of the used nitrides and the possibility of designing the electrical properties of the material in advance. The developed electronductive composite could find application as a base material for the production of electrically heated systems such as infrared radiators, domestic appliances (hot water heaters, electric cookers), and for technical installations (small furnaces for melting noble metals, sintering of ceramics, bioceramics, etc.).

References

1. Petrovsky, V. Ya. and Skorochod, V. V., Physical principles and technological aspects of the production of gradient composites based on an oxygen-free ceramics. *Powder Metallurgy and Metal Ceramics*, 1999, **38**(3–4), 115–125.
2. Boitsov, O. F. and Petrovsky, V. Ya., Effect of the fractal of percolation cluster on the conductivity of resistive composites. In *Polish Ceramic Bulletin (Modern Test Method and Technology of Ceramic Materials)*, Warsaw, 1998; 213–219 (in Russian).
3. Kim, W. J., Taya, M., Yamada, K. and Kamiy, N., Percolation study on electrical resistivity of SiC/Si_3N_4 composites with segregate distribution. *J. Applied Physics*, **83** (1998) 5, 2593–2598
4. McLachan, R. N., Blaszkiewicz, M. and Newnham, R., Electrical resistivity of composites. *J. Am. Ceram. Soc.*, 1990, **73**(8), 2187–2203.
5. Gogotsi, Yu.G., Review; particulate silicon nitride-based composites. *J. Mat. Sci.*, 1994, **29**, 2541–2556.