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INVESTIGATION OF THE INFLUENCE OF THERMAL LOADING AND THE CONTENT OF MOLYBDENUM DISILICIDE ON THE ELECTRICAL RESISTANCE OF CERAMIC MATERIAL FOR PRODUCTION OF GLOW PLUGS

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The influence of the temperature of thermal shock and the content of $MoSi_2$ on the specific electrical resistance of a silicon-nitride ceramic with sintering additions has been investigated. The methods of mathematical experimental design and dispersion and regression analyses have been used for processing the results obtained for specific electrical resistance. It has been established that the greatest influence on the specific resistance is exerted by the content of molybdenum disilicide, regardless of the dispersity of the starting mixtures of powders.

Silicon nitride is a starting compound in the development of a wide class of modern structural ceramic materials that are promising in the creation of different devices that operate at high temperatures and in aggressive media [1].

The high fusion temperature of molybdenum disicilide ($MoSi_2$) in combination with its high electrical conductivity enables one to use it as a functional material for production of heating and conducting elements. Silicon nitride is a dielectric, and the addition of molybdenum disicilide makes it conducting, when the corresponding dispersity of the conducting phase is observed. A composite material combining the properties of these compounds and possessing electrical conductivity can find application as a structural and functional ceramic material for heating elements, one variant of which is the element of a glow plug in diesel engines for heating of fuel.

In this work, we have investigated the influence of the temperature of thermal shock (500, 600, and 700°C) and the weight content of $MoSi_2$ (20, 40, and 60 wt.%) on the specific electrical resistance ρ of a ceramic incorporating $MoSi_2 + Si_3N_4 + 5$ wt.% $Y_2O_3 + 1.5$ wt.% Al_2O_3. Mixtures of the above composition were prepared by two methods:

1. The starting $MoSi_2$ powder (A (Starck) grade, d_{10} = 0.733 μm, d_{50} = 2.907 μm, and d_{90} = 8.418 μm) was mixed and ground with an Si_3N_4-based charge in a planetary ball mill from ZrO_2 in an isopropyl alcohol medium with the use of ZrO_2 grinding balls of diameter 7 mm for 36 h, after which the dispersity of the mixture with 20 wt.% $MoSi_2$ was d_{10} = 0.193 μm, d_{50} = 0.851 μm, and d_{90} = 2.950 μm.

2. The same powder was preground under identical conditions; it was then dried in a rotary evaporator and was mixed with the Si_3N_4-based charge produced for 12 h in the above-mentioned mill in the isopropyl alcohol medium. After milling and mixing according to the above regime, the dispersity of the mixture with 20 wt.% $MoSi_2$ was d_{10} = 0.146 μm, d_{50} = 0.483 μm, and d_{90} = 1.303 μm.

Suspensions produced by these two methods were dried in the rotary evaporator, after which samples of diameter 10–13 mm and height 2–4 mm were compacted according to the scheme of uniaxial compaction with a load of 9–14 kN. Sintering was carried in a nitrogen medium at a pressure of 0.5 bar with a 1-h storage at a temperature of 1850°C. The rate of heating was selected on the basis of dilatometric measurements of the samples of composition $Si_3N_4 + 5$ wt.% $Y_2O_3 + 1.5$ wt.% Al_2O_3.

The electrical resistance was measured according to the scheme given in [2], whereas the specific electrical conductivity was calculated based on the indices of electrical resistance R_1 and R_2:

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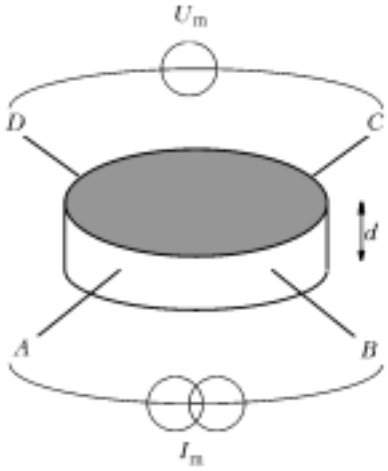

Fig. 1. Scheme of measurement of the specific electrical resistance of samples [2].

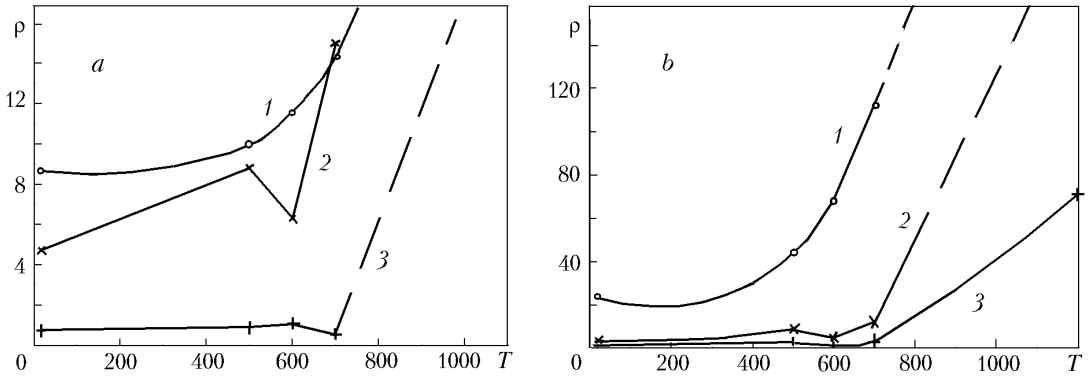

Fig. 2. Specific electrical resistance vs. thermal-shock temperature for d_{50} = 0.851 μm (a) and d_{50} = 0.483 μm (b): 1) 20; 2) 40 (a) and 50 (b); 3) 60 wt.% $MoSi_2$.

$$\rho = \frac{\pi d}{\ln 2}\left(\frac{R_1 + R_2}{2}\right) f\left(\frac{R_1}{R_2}\right),$$

where $f(R_1/R_2)$ is the correcting function whose value is equal to unity for $R_1 = R_2$, $R_1 = \dfrac{U_{CD}}{I_{AB}}$ and $R_2 = \dfrac{U_{DA}}{I_{BC}}$ (Fig. 1).

To process the results obtained for specific electrical resistance we used the methods of mathematical experimental design and of dispersion and regression analysis [3, 4]. The character of change in the specific electrical resistance of the samples with thermal-shock temperature is presented in Fig. 2.

For the experiment, we selected an orthogonal design of 2nd order whose matrix and the results of measurements of the specific electrical resistance are given in Table 1. We selected y as the optimization parameter and the temperature (x_1) and content of $MoSi_2$ (x_2) as the factors. The error of reproducibility of the results was 1.4 mΩ·cm (5% of the average value). In Table 1, x_1 and x_2 are the coded levels of the factors.

After processing the experimental results, we obtained the regression equation

$$y_1 = 3.87 + 12.27x_1 - 36.68x_2 - 16.53x_1x_2 + 4.32x_1^2 + 31.9x_2^2 . \quad (1)$$

However, this model turned out to be inadequate, since the ratio of the variance of the inadequacy S_{ad}^2 to the variance of the optimization parameter S_y^2 = 1.96, i.e., the Fisher number $F = S_{ad}^2/S_y^2$ turned out to be equal to $66.87 > 7$ for

TABLE 1. Matrix of the Orthogonal Two-Factor Design

No. of experiment	x_1	x_2	x_1x_2	x_1^2	x_2^2	$x_1^2x_2$	$x_1x_2^2$	y_e	y_c
1	+	+	+	+	+	+	+	4.05	4.09
2	+	—	—	+	+	—	+	112.00	112.01
3	—	+	—	+	+	+	—	1.18	1.23
4	—	—	+	+	+	—	—	43.00	43.29
5	+	0	0	+	0	0	0	9.13	9.05
6	—	0	0	+	0	0	0	7.40	7.33
7	0	+	0	0	+	0	0	0.69	0.63
8	0	—	0	0	+	0	0	71.00	70.91
9	0	0	0	0	0	0	0	3.72	3.87

the significance level α = 0.01 (F = 131.07/1.96 = 66.87). In this connection, it was decided to approximate the experimental results by an incomplete cubic model of the form

$$y = b_0 + b_1x_1 + b_2x_2 + b_{12}x_1x_2 + b_{11}x_1^2 + b_{22}x_2^2 + b_{112}x_1^2x_2 + b_{122}x_2^2 . \quad (2)$$

For this purpose we supplemented the matrix of Table 1 with the x_1^2 and $x_1x_2^2$ columns and then calculated the corrected values of the coefficients b_1^1, b_2^1, b_{112}, and b_{122}.

The coefficients b_1^1 and b_2^1 were found from the formula

$$b_i^1 = \rho_{4i} - \rho_{5ijj} , \quad (3)$$

where $\rho_4 = 0.5(iY)$ and $\rho_5 = 0.5(iijY)$. It turned out that b_1^1 = 36.8–35.94 = 0.86 and b_2^1 = –35.14.

The coefficients b_{112} and b_{122} were determined as

$$b_{ijj} = \rho_{6ijj} - \rho_{4j} . \quad (4)$$

Here $\rho_6 = \frac{3}{4}(iij)$, i.e., for $x_1^2x_2\rho_6\frac{3}{4}(-149.77)$ = –112.33, and $x_1x_2^2 = \frac{3}{4}\cdot 71.87$ = 53.9. We obtained b_{112} = –2.29 and b_{122} = 17.1. In final form, the regression equation has the form

$$y_1 = 3.87 + 0.86x_1 - 35.14x_2 - 16.53x_1x_2 + 4.32x_1^2 + 31.9x_2^2 - 2.29x_1^2x_2 + 17.1x_1x_2^2 . \quad (5)$$

This equation adequately describes the factor space, since F = $\frac{0.1338}{1.96} < 1$ for all confidence levels α and an experimental error of 0.162 mΩ·cm (less than 1% of the average value).

An analysis of (5) shows that the largest influence on the specific electrical resistance is exerted by the content of $MoSi_2$ (x_2). The influence of the thermal-shock temperature is an order of magnitude lower. The specific electrical resistance will be minimum (y_1 = 0.63 mΩ·cm) for x_1 = 0 and x_2 = +1, i.e., for a temperature of 600°C and an $MoSi_2$ content of 60 wt.%, and maximum (y_1 = 112 mΩ·cm) for x_1 = +1 and x_2 = –1, i.e., for a temperature of 700°C and an $MoSi_2$ content of 20 wt. %. Thus, we have determined the conditions for obtaining the minimum value of the specific electrical resistance of the ceramic of this composition. A more accurate analysis of (5) for x_2 = +1 shows that the dependence of the optimization parameter on the thermal-shock temperature (x_1) can be represented in parabolic form

$$y_1 = 0.63 + 1.43x_1 + 2.03x_1^2 \quad (5a)$$

TABLE 2. Matrix of the Orthogonal Design

No. of experiment	x_1	x_2	x_1x_2	x_1^2	x_2^2	y_e	y_c
1	+	+	+	+	+	0.73	1.77
2	+	—	—	+	+	14.38	15.15
3	—	+	—	+	+	0.94	0.69
4	—	—	+	+	+	9.97	9.43
5	+	0	0	+	0	14.80	13.00
6	—	0	0	+	0	8.80	9.60
7	0	+	0	0	+	1.07	0.29
8	0	—	0	0	+	11.56	11.35
9	0	0	0	0	0	9.36	10.36

with the point of inflection $x_{1e} = -\dfrac{1.43}{2 \cdot 2.03} = -0.35$ (565°C), at which $y_1 = \rho_1 = 0.38$ mΩ·cm (92% of the average value) differs only slightly from $y_1 = 0.63$.

Thus, increase in the $MoSi_2$ content to 60 wt.% enables us to sharply decrease the specific electrical resistance from 112 to 0.63 mΩ·cm.

In the next series of experiments, we investigated the influence of the same factors (a thermal-shock temperature of 500, 600, and 700°C and a content of $MoSi_2$ of 20, 40, 50, and 60 wt.%) on the specific electrical resistance of the ceramic $MoSi_2 + Si_3N_4 + 5$ wt.% $Y_2O_3 + 1.5$ wt.% Al_2O_3 with an average dispersity of the starting mixture of 0.483 μm.

The experiment was carried out according to the same design as the previous one. The results of measurements of the specific electrical resistance are given in Table 2. The experimental error was $S_2 = 0.6$ mΩ·cm (7.5% of the average value). After processing the experimental results, we obtained an adequate model of the form

$$y_2 = 10.36 + 1.7x_1 - 5.53x_2 - 1.16x_1x_2 + 0.94x_1^2 - 4.54x_2^2 . \quad (6)$$

Here the largest influence on ρ is exerted by the $MoSi_2$ content x_2: the higher the content, the lower is the specific electrical resistance y_2. We will have the minimum value $y_2 = 0.56$ mΩ·cm and the maximum value $y_2 = 15.15$ mΩ·cm under the same conditions as those in the previous experiment.

Thus, the minimum value of the specific electrical resistance $\rho_1 = 0.63$ mΩ·cm for samples with a dispersity of the starting mixture of 0.851 μm and $\rho_2 = 0.56$ mΩ·cm for those with a dispersity of the starting mixture of 0.483 μm are attained at a thermal-shock temperature of 600°C ($x_1 = 0$) and a content of molybdenum disilicide of 60 wt.%.

Under these conditions, there is no difference, in practice, in the value of the specific electrical resistance for samples with dissimilar dispersities of the starting charge. Under other conditions (T = 500 and 600°C and $MoSi_2$ of 20, 40, and 50 wt.%), this difference is significant ($y_1 = 7.4$ and 71 and $y_2 = 14.38$ and 14.80 mΩ·cm).

Upon the substitution of $x_2 = +1$ (60 wt.% $MoSi_2$) into Eq. (6), we obtain a parabolic dependence of the form

$$y_2 = 0.29 + 0.54x_1 + 0.94x_1^2 \quad (6a)$$

with the point of inflection $x_{1e} = -0.29$ (571°C) at which the calculated value of the specific electrical resistance is equal to 0.21 mΩ·cm.

If we take into account the error of reproducibility of the experiments $S_2 = 0.6$ mΩ·cm, this result does not differ, in practice, from the conditions of experiment 7 in which we have $x_1 = 0$ (T = 600°C) and $x_2 = +1$ (60 wt.% $MoSi_2$).

Also, it is noteworthy that the difference in the value of the specific electrical resistance between these two compositions of the ceramic will be significant for other levels of thermal-shock temperature and $MoSi_2$ content. For

TABLE 3. Matrix of the 2 × 3 Design (d_{50} = 0.483 μm)

No. of experiment	x_1	x_2	x_1x_2	x_2^2	$y_1 = \rho_1$	$y_2 = \rho_2$
1	—	—	+	+	10	43
2	—	0	0	0	11.6	71
3	—	+	—	+	14.4	112
4	+	—	—	+	8.8	7.4
5	+	0	0	0	9.4	3.7
6	+	+	+	+	14.8	9.1

example, when $x_1 = +1$ and $x_2 = -1$ (T = 700°C and 20 wt.% $MoSi_2$) we have $\Delta\rho = 112 - 15.15 = 96.9$ mΩ·cm, and the Student number t, after calculation according to the formula from [4], will be written as

$$t = \frac{y_{c1} - y_{c2}}{S}\sqrt{\frac{n_1 n_2}{n_1 + n_2}}\,, \tag{7}$$

where n_1 and n_2 are the numbers of measurements (observations) for y_1 and y_2. In our case we have $n_1 = n_2 = 9$; therefore, t is equal to $\frac{96.9}{0.6}\sqrt{\frac{9\cdot 9}{18}} = 342.6$, which is much higher than the tabulated value. From Eqs. (5) and (6) it is seen that in the range $MoSi_2$ 20–60 wt.%, the content exerts a much larger influence on the specific electrical resistance than the thermal-shock temperature. However if we restrict ourselves to a content of $MoSi_2$ of 20 and 40 wt.% for the same levels of thermal-shock temperature (500, 600, and 700°C), the role of the factors changes.

To check this conclusion for a composition with a dispersity of the mixture of 0.483 μm we carried out an experiment according to a 2 × 3 design, where 2 is two levels of the $MoSi_2$ content (wt.%) and 3 is three levels of temperature (500, 600, and 700°C). The matrix of the design and the results of the experiments are presented in Table 3. The error of reproducibility of the experiments was 0.6 mΩ·cm.

After processing the results (see Table 3), we obtained an adequate model of the form

$$y_2 = \rho_2 = 10.5 + 2.6x_1 - 0.5x_2 + 1.5x_1^2\,. \tag{8}$$

Here the larger influence is exerted by x_1 (thermal-shock temperature) but the specific electrical resistance is much higher than that for a content of 60 wt.% $MoSi_2$. Consequently, as the content of $MoSi_2$ increases from 40 to 60 wt.%, qualitative changes contributing to a sharp increase in the electrical conductivity occur in the structure of the ceramic.

For a composition with a dispersity of 0.851 μm, the experiment carried out under the same conditions as that for a composition with a dispersity of 0.483 μm, i.e., $x_1 = \pm 1$ and 0 (500, 600, and 700°C) and $x_2 = \pm 1$ (20 and 40 wt.% $MoSi_2$) yielded the following adequate model (even for S_1 = 0.5 mΩ·cm):

$$y_1 = \rho_1 = 37.4 + 17.7x_1 - 34.3x_2 - 16.8x_1x_2 + 5.5x_1^2\,. \tag{9}$$

In this case the larger influence is exerted by the content of $MoSi_2$ (x_2). The optimum conditions are attained in experiment 5, i.e., at a thermal-shock temperature (x_1) of 600°C and an $MoSi_2$ content (x_2) of 40 wt.%, since in this case we obtain the minimum value of the specific electrical resistance $y_1 = \rho_1$ = 3.7 mΩ·cm. However, here a substantial influence of the thermal-shock temperature is also noteworthy.

It is of interest to reveal the difference in the specific electrical resistance $\Delta\rho = \Delta y$ at room temperature (T = 20°C) and a thermal-shock temperature of 600°C for different contents of $MoSi_2$ (20, 40, 50, and 60 wt.%). For this purpose we carried out an experiment according to a 2 × 3 design; the results of the experiment for the two methods in question are given in Table 4 whose analysis shows that a significant difference is observed for a content of 20 wt.% $MoSi_2$ (48 mΩ·cm for the first composition and 3 mΩ·cm for the second composition). This difference is insig-

TABLE 4. Matrix of the 2 × 3 Design (d_{50} = 0.851 μm)

No. of experiment	x_1	x_2	x_1x_2	x_2^2	$y_1 = \rho_1$	$y_2 = \rho_2$
1	—	—	+	+	20.3	8.6
2	—	0	0	0	5.4	4.8
3	—	+	—	+	0.9	0.8
4	+	—	—	+	71.0	11.6
5	+	0	0	0	6.3	9.4
6	+	+	+	+	0.7	1.1

nificant for a composition with a dispersity of 0.851 μm (with a reproducibility error of 0.9 mΩ·cm) for contents of 40 and 60 wt.% $MoSi_2$ and for the second composition only for 50 wt.% $MoSi_2$. Processing of the results given in Table 4 enabled us to obtain adequate mathematical models:

for the first method, we have

$$y_1 = \rho_1 = 5.9 + 0.7x_1 - 12.7x_1x_2 + 17.4x_2^2 - 22.4x_1^2x_2 + 12x_1x_2^2 , \quad (10)$$

and for the second method, we obtain

$$y_2 = \rho_2 = 7.1 + 1.3x - 4.6x_2 - 0.7x_1x_2 - 1.6x_2^2 . \quad (11)$$

From these equations it is clear that the minimum values y_1 = 0.9 mΩ·cm and y_2 = 0.8 mΩ·cm are obtained at 20 and 600°C in samples with a content of 60 wt.% $MoSi_2$, and the difference in specific electrical resistances is fairly large for a content of 20, 40, and 50 wt.% $MoSi_2$.

Thus, at high testing temperatures, the electrical resistance will be low if the mixture contains 60 wt.% $MoSi_2$.

From the data presented in the figures and in the tables, it is clear that the value of the specific electrical resistance in samples produced from a mixture of powders with an average dispersity of d_{50} = 0.483 μm is much lower than that in samples with a dispersity of 0.851 μm. A tendency toward increasing specific electrical resistance is observed with growth in the thermal-shock temperature.

According to the regression equations (5) and (6) obtained, the largest influence on the value of the specific electrical resistance is exerted by the content of molybdenum disicilide: the higher the content, the lower is the value of the specific electrical resistance. This fact is also confirmed by the given plots of the specific electrical resistance as a function of the thermal-shock temperature (see Fig. 2). The curves corresponding to 60 wt.% $MoSi_2$ lie lower than the remaining curves.

At temperatures of 20 and 600°C and 60 wt.% $MoSi_2$, we detect the minimum values of the specific electrical resistance ρ = 0.9 and 0.63 mΩ·cm for a composition with a dispersity of 0.851 μm and ρ = 0.8 and 0.56 mΩ·cm for a composition with a dispersity of the mixture of 0.483 μm respectively (experimental error S_2 = 0.6 mΩ·cm or 7.5% of the average value).

Under other conditions (T = 500 and 600°C and 20 and 40 wt.% $MoSi_2$), the difference in the value of the specific electrical resistance is significant: ρ = 7.4 and 71 mΩ·cm and ρ = 14.38 and 14.80 mΩ·cm respectively for samples produced from mixtures of powders with dissimilar degrees of dispersity.

In the temperature interval 500–700°C, according to the regression model (8), of considerable importance is the thermal-shock temperature, whereas the electrical resistance is subjected to bifurcations. This is due to the qualitative changes in the ceramic structure that contribute to a sharp increase in the specific electrical resistance of the material and to the phenomenon of "pesting" of molybdenum disicilide — its selective low-temperature oxidation, whose mechanism has been described in a number of works [5–9].

Increase in the percentage of molybdenum disicilide ensures a larger number of conducting contacts in the silicon-nitride-based matrix. It is clear that samples with a lower content of molybdenum disicilide, i.e., with 20, 40, and 50 wt.%, are more sensitive to the phenomenon of oxidation of molybdenum disicilide because of the smaller number of contacts in its conducting chain than that in samples containing 60 wt.% $MoSi_2$. At 500–700°C, we have

a discontinuity at individual sites of the conducting "chain" owing to the formation of a loose layer of filamentary MoO_3 crystals and SiO_2 cluster formations [6], which leads to a sharp decrease in the electrical conductivity and accordingly to an increase in the electrical resistance.

NOTATION

b_0, b_1, b_2, b_{12}, b_{11}, b_{22}, b_{112}, and b_{122}, coefficients of the regression equation; d, height of the sample measured; d_{10}, d_{50}, and d_{90}, size of the powder fractions; F, Fisher number; R_1 and R_2, measured values of the electrical resistance, mΩ; S, variance; t, Student number; T, temperature, ^oC; U and I, values of the voltage and the current, mV and mA; $Y_{i,j}$, index of the ith and jth properties; ρ, specific electrical resistance, mΩ·cm. Subscripts: e, experiment; c, calculation; ad, adequacy; m, measured.

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