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The influence of zirconium oxide on Al_2O_3-TiC oxide-carbide ceramics

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Time-dependent change of electrical resistance for 56 vol. % Al_2O_3+36 vol. % TiC + 8 vol. % ZrO_2 sample, obtained by means of electrical consolidation has been investigated in the article. The mechanism of carbon concentration change while compacting has been investigated and it was determined that under the condition that the content is 36 vol. % TiC, that slightly exceeds percolation threshold, it is possible to obtain a dense sample having grain shape different from spherical. That allows us to reach coordination number 4 to provide the percolation process possibility.
Keywords: electrical resistance, oxide-carbide ceramics, percolation threshold, electrosintering.

У статті досліджено зміну електроопору від часу для зразка складу 56% об.Al_2O_3+36% об.TiC+8% об.ZrO_2, отриманого методом електроконсолідації. Досліджено механізм зміни концентрації вуглецю в процесі компактування та встановлено, що при вмісті 36 об.% TiC, що незначно перевищує поріг перколляції, можливе отримання щільного зразка з формою зерен відмінною від сферичної, що дозволяє досягти координаційного числа 4 для забезпечення можливості перколяційних процессів.
Ключові слова: електроопір, оксидо-карбідна кераміка, поріг перколяції, електроспікання.

В статье исследовано изменение электросопротивления от времени для образца состава 56% об.Al_2O_3+36% об.TiC+8% об.ZrO_2, полученного методом электроконсолидации. Исследован механизм изменения концентрации углерода в процессе компактирования и установлено, что при содержании 36 об.% TiC, что несколько превышает порог перколляции, возможно получение плотного образца с формой зерен отличной от сферической, что позволяет достичь координационного числа 4 для обеспечения возможности перколяционных процессов.
Ключевые слова: электросопротивление, оксидо-карбидная керамика, порог перколяции, электроспекание.

Al_2O_3-TiC oxide-carbide ceramics has found wide application as tool material in steel and alloy working. Cutting force, friction force, high temperature, which can reach 1200°C under high speeds, affect tool material during the process of cutting. It is natural, that under such conditions cutting material wears out intensively, that leads to frequent tool failures and disruptions.

Different physics-chemical processes, which take place in the cutting area, influence wear mechanism. The main wear mechanisms are: abrasive, adhesive, diffusive and electrical-chemical [2].

This or that wear mechanism prevails in each separate case, though it is obvious, that all the factors have definite effect.

To increase the instrument lifetime, first of all, it is necessary to improve the hardness and strength of cutting material, chemical inertness to the interaction with the material being worked [3, 4, 5].

From this point of view, zirconium oxide additives to Al_2O_3-TiC oxide-carbide ceramics are interesting. It is known that transformational transitions of zirconium oxide from tetragonal modification to monoclinic create microcrack structure, which substantially increasesfracture toughness of a composite [6].

The obtained material is interesting not only as instrumental but as a structural, particularly to be used as blades of a gas-turbine engine, for rocket nozzle inserts, for oil pumping O-rings etc. It is obvious that the investigation of not only mechanical but physical, particularly electrical, characteristics of the given composite is of great importance.

Electrical characteristics influence the workability of the material while applying electrical- physical methods of geometrically-complex product working. The mentioned methods allow decreasing structure imperfection being formed afterdiamond grinding, particularly diamond-spark grinding electric erosion machining.

The temperature in the cutting area is affected by the thermal conductivity of cutting material; in case of increased thermal conductivity the temperature decreases that in whole influences wear resistance of cutting

composite. The investigations of electrical resistance and thermal conductivity of similar composites are practically absent in the literature. The conducted investigations of Al_2O_3+TiC+ZrO_2 sample electrical resistance in the range of temperatures 290÷315 K revealed a number of interesting peculiarities of this material.

Methods of investigation

The sample has been produced by means of compacting a homogeneous mixture of 56 vol. % Al_2O_3+36 vol. % TiC+8 vol. % ZrO_2 powders at T=1550 °C, P=45 MPa and direct (alternating) current I = 5000A. Conducting phase is TiC, volume fraction of which is 0.36. The sample represented parallelepiped with the dimensions 16x16x4.8 mm.

The measuring of electrical resistance of the sample was conducted by means of a conventional four-probe method in ~10^{-5} torr in vacuum at constant temperature, which was supported by an analogue thermoregulator with the accuracy to ~0.1 K and was measured by platinum resistance thermometer. Temperature dependence was obtained in one-day cycle of measurements. Such cycle was repeated during 12 days.

Investigation results

It was determined that specific electrical resistance TiC_n is strongly dependent upon its imperfection on carbon, changing at 25°C from ρ=61 microOhm·cm for $TiC_{0.96}$ to ρ=147 microOhm·cm.

The sample specific resistance, as it was established, is by 2 orders higher than specific resistance of titanium monocarbide that can be the result of percolation nature of investigated samples conductivity.

Coordination number, that effects specific electrical resistance, can appear in the case when carbide grains of titanium monocarbide are bigger than the grains of other phases as well as the in the case when the grain shape of all the phases has the shape that is far from spherical.

The discussion of the results

As it turned out, the sample resistance depends upon the temperature linear, however the parameters of this dependence had been changed with the time passing and their values were stabilized only after 10 cycles. The time change of resistance for T=298 K is presented in Fig. 1. Maximal change of the resistance is 1.5%.

Temperature dependence of a stabilized resistance can be described by the ratio

$$R(T)=R_0+B*T, \qquad (1)$$

Where $R_0=(4.98\pm0.02)\cdot10^{-2}$ Ohm and $B=(3.5\pm0.1)\cdot10^{-5}$ Ohm/K. The parameter $R_0=R(0)$ makes sense of a residual resistance. Temperature

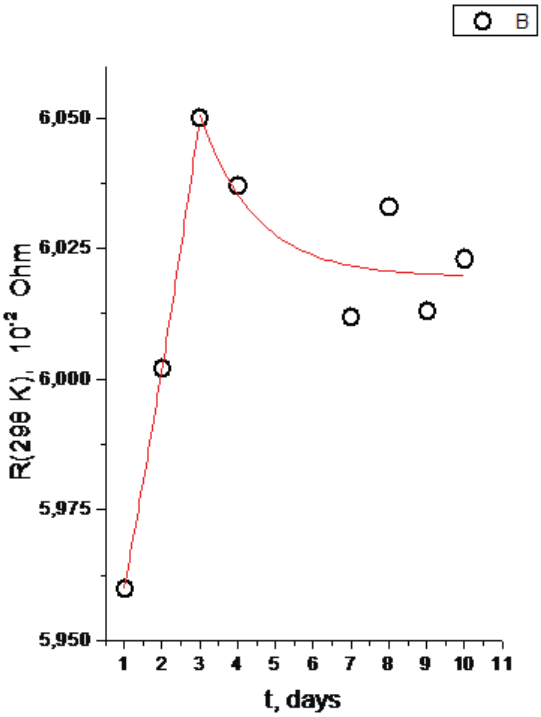

Fig. 1 Time-dependent change of electrical resistance for 56 vol. % Al_2O_3+36 vol. % TiC+8 vol. % ZrO_2 sample for T=298 K

coefficient of resistance (TCR) at 298 K is $\frac{1}{R}\frac{dR}{dT}\approx 5.8\cdot10^{-4}K^{-1}$, that approximately 3 times less than ZrC has and approximately 4 times less than HfC has [7]. The ratio R(298 K)/R_0≈1.2 that features "dirty" conductor.

Resistivity TiCn depends heavily upon its carbon faultiness, changing at 25°C from ρ=61 microOhm*cm for $TiC_{0.96}$ to ρ=147 microOhm*cm for $TiC_{0.62}$ [8] and can be described by the ratio

$$\rho(25°C, n)=(302–252*n)\ \text{mcOhm*cm} \qquad (2)$$

As we know virtually nothing about relative position of conducting areas, it is impossible to calculate the sample resistance knowing TiC resistance and its inclusion volume fraction. However, based on the results of the work [9], we can determine the frames within which there is a value of the sample conductivity on the basis of the results of the work:

$$0\le\sigma^*\le\sigma_2\frac{2v_2}{3-v_2} \qquad (3)$$

Here σ* is effective conductance of the system, σ2 and v_2 – productivity and TiC inclusion volume fraction respectively.

We get ρ(25°C, 0.79)=103 microOhm*cm, v_2=0.36 from (2) for n=0.79 then

$$380\ \text{mcOhm*cm} \le \rho^* < \infty, \quad (4)$$

Where ρ* - the sample measured resistance.

We have ρ*(298 K)=2.9·104mcOhm*cm from (2) and the sample geometry, that is the sample measured resistance is within frames (4), however these frames are rather broad because all the other sample components (phases) are insulators.

According to [10] the difference between impedance of the material, i.e. its resistance to the direct current (ρgeneral) and the resistance of the material grain volume (ρvolume) is interpreted as the grain boundary resistance, ρboundary. However, as opposed to the volume, the conductivity of grain boundary depends on crystallite size and the resistivity of intercrystalline boundaries is higher than grain volume resistivity, as the quantity of intercrystalline boundaries per the unit of the sample length, which the current must overcome, changes depending on grain size.

Impurity segregation [11] is considered as one of the reasons of increased specific resistivity of intercrystalline boundaries.

The fact, that measured sample resistivity (specific resistance) is by a factor of hundred higher than TiC resistivity (specific resistance) can be caused by the percolation character of the sample conductivity, namely, by the proximity of conducting phase inclusion volume fraction to percolation threshold.

It is known [12], that percolation threshold for bound system with coordination number (the number of bounds) z=4 equals 1/3, that is quite close to conducting phase inclusion volume fraction (0.36) but less than it. Coordination number 4 can appear in the case if TiC particles are bigger than other phase particles or in a case if the shape of the particles of all phases is far from spherical.

Let's mention that there is a connection between parameters R_0 and B (1) which can be expressed by B=(21.0±0.5)–(3.5±0.1)*R_0 ratio. As (1) testifies to "metallic" conductivity of the system, the residual resistance R_0 is determined by the faults of conducting component (TiC). Thus, the dependence B(R_0) points to the dependence of TCR sample on titanium carbide defects. In this connection we can assume that the concentration of carbon in TiC changes while compacting at high temperatures, but in the sequel this concentration will tend to some equilibrium value including the influence of the experiment conditions – vacuum and weak temperature cycling.

Conclusions

Thus, the conducted investigations allow assuming that the content of TiC has a substantial effect on percolation threshold of Al_2O_3-TiC-ZrO_2 composite as well as on its carbon imperfection which can change, increasing electrical resistance approximately by factor of 2.5. The ratio of 56 vol. % Al_2O_3+36 vol. % TiC+ 8 vol. % ZrO_2 phases is optimal not only from the point of view of mechanical features but also from the point of view of workability by electrosparking method.

Electrical resistance can be substantially decreased by grain size reduction and the creation of nonspherical polyhedral grain size. The coefficient of thermal expansion depends to a large extent on TiC defect rate.

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