J Electroceram (2011) 26:90–98
DOI 10.1007/s10832-011-9633-z

Electric properties of monophase polycrystalline sinters SiC, B_4C, TiC and their composites as non-inductive volume resistors

Ewa Klimiec · Ludosław Stobierski · Stanisław Nowak · Wiesław Zaraska · Szymon Kuczyński

Received: 18 December 2009 / Accepted: 24 January 2011 / Published online: 18 February 2011

Abstract Monophase polycrystalline SiC, B_4C, TiC and their SiC-TiC, SiC-B_4C composite sinters with a theoretical density of 97% are characterized by good mechanical and thermal durability as well as a wide range of electrical conductivity values. SiC, which has semiconductor conductivity and negative TCR, was combined with TiC, which has metallic conductivity and positive TCR. Produced in this way resistive elements, within a temperature range from 293 K to 348 K, exhibit a TCR close to zero, and an impedance independent of frequency within a range from 100 Hz to 1 MHz. The combination SiC with 40 wt% of B_4C has been produced resistive elements, which are resistive to oxidation. This combination has also completly resistive character, within a range of 100 Hz to 1 MHz. Most of the investigated materials are suitable for high temperature, noninductive volume resistors.

Keywords SiC · B_4C · TiC · SiC-TiC · SiC-B_4C · Electrical properties · Volume resistors · Non-inductivity

E. Klimiec (✉) · S. Nowak · W. Zaraska · S. Kuczyński
Institute of Electron Technology Cracow Division,
ul. Zabłocie 39,
30-701 Kraków, Poland
e-mail: eklimiec@ite.waw.pl

S. Kuczyński
e-mail: skuczyn@ite.waw.pl

L. Stobierski
University of Science and Technology,
al. Mickiewicza 30,
30-059 Kraków, Poland

1 Introduction

The development of new technologies allows the creation of materials, which are chemically and physically highly resistant. The monophase polycrystalline SiC, B_4C and TiC sinters and their SiC-TiC, SiC-B_4C composites which are described in this article, are examples of high durability materials [1–7]. They were investigate to use them as volume resistors.

Volume resistors manufactured, as monolith blocks, conduct electricity throughout their volume. These resistors are used in electrical circuits with a high constant power load, high voltage impulse load, and also in high frequency circuits [8]. For example, they are use in the power supply to X-ray machines roentgen, as artificial antennas in radio stations and radars, as anti-noise resistors, and as resistors for extinguishing electrical arcs. These resistors are characterized by high reliability.

Silicon carbide is a covalent bond compound. It crystallizes in cubic, hexagonal and rhombohedral crystal systems [3, 4, 9, 10]. Depending on the dopant used, it can be a p or n type semiconductor. At high temperatures ~1000°C, SiC is an intrinsic semiconductor [9, 10]. Nitrogen is a classic n type dopant [15]. A few donor levels were determined by Ikeda [13] and Tajim [14]: 93 meV from Raman spectrum investigations, 100 meV from luminescence spectrum observations [12] and 80–100 meV from Hall constant measurements and infrared absorption [17]. Boron is the most common p type dopant for SiC [11–19]. The activation energy of acceptor levels for SiC with boron doping varies from 300 meV to 400 meV [18]. It was determined by measurment of conductivity in function of temperature by Vodakov.

Boron carbide is a compound with covalent bonding. It crystallizes in a rhombohedral system. The basic cell,

$B_{12}C_3$, consists of 12 boron atoms, and 3 coal atoms. It is the best known phase in the system, conventionally referred to as B_4C. In the boron carbide rhombohedral structure there is an icosahedron (20 walls) boron B_{12} sub-cell. The icosahedrons are connected directly with each other, via a covalent bond, and indirectly with carbon chains. Investigation of the electron structure carried out by Emin [20, 21] shows that the B_{12} icosahedron has 13 molecular orbits related to its inner bonds. Every boron atom in the twenty-wall structure has only two electrons in the inner bonds and one electron in the covalent outer bond. The number of electrons supplied for the inner bonds amounts to 24, (2× 12) which is two electrons fewer than the 26 required. In the inter-icosahedron carbon chain some of the middle carbon atoms are replaced with a boron atom forming a ≡C-B-C≡ chain, which was confirmed by NMR (Nuclear Magnetic Resonance) and IRS (Infrared Spectroscopy). The central boron atom has one more electron than is required for a covalent bond, and it can be transferred as first to the unoccupied bonding orbital in the B_{12} icosahedron. That is why, boron carbide generally has a p type conductivity [1, 20, 21].

Titanium carbide TiC crystallizes in a regular, flat centered system. Titanium atoms are densely packed and the carbon atoms are formed in octahedron gaps. A homogenous TiC phase occurs for carbon concentrations ranging from 22 at.% to 50 at.% [22]. Based on the physical properties of TiC it has been established, that the bonds between titanium and carbon are metallic in character. This can be described as carbon atoms trapped in a sea of electrons. According to the data in papers [23] TiC resistivity ranges from 10^{-7} Ωm to 10^{-6} Ωm. With a carbon concentration increase, TiC structure resistivity grows.

2 Material

The polycrystalline, monophase cuboid shaped sinters of SiC, B_4C, TiC and their composites SiC-TiC, SiC-B_4C, which are presented in this paper, were obtained by pressing powders with grains from 1 to 2 μm, under a pressure of 150 MPa, and then sinter at a temperature of 2000°C for 60 min. in an argon atmosphere. The samples were fired with a steady rate of 15°C/min. The sinter activators had 0.5 wt% of boron and 3 wt% of carbon. Boron was introduced before the Self Propagating High Temperature Synthesis process (SHS) in order to activate the diffusion mechanisms to sinter SiC grains. Before the sinter process, carbide grains were coated with carbon, in the form of resin dilutions. The layer of amorphous coal was 1.5–2 nm thick and it acted, as a deoxidant on the grain surface. Sinters made by this method are very dense, 97% of theoretical density, and they are mechanically and thermally durable; they have a wide range of electrical conductivity and they have been investigated for application as volume resistors. The samples described in this paper are a part of large series with common characteristics. Samples were a monolithic blocks of 5×10^{-2} m in length and a cross section ranging from 25×10^{-6} m^2 to 125×10^{-6} m^2.

3 Investigation of resistivity ρ, temperature coefficient of resistance TCR and electric conductivity activation energy ΔE of SiC, B_4C and TiC sinters

The investigation of resistivity, the temperature coefficient of resistance (TCR) and the activation energy ΔE of electric conductivity, was carried out within a range of 233 K to 433 K, which is typical in work on volume resistors. Measurements were performed by a computer controlled system composed of a Keithley 2002 multimeter, a measurement collector and a Heraeus Votsh firing chamber (with temperature stabilization of ±1°C).

The TCR, which indicates the rate and direction of resistance change under varying temperature, was determined by Eq. 1:

$$TCR_{(T)} = \frac{1}{R_{(T)}} \cdot \frac{dR}{dT} \cdot 10^6 [\text{ppm/K}] \tag{1}$$

In the calculations resistance $R_{(T)}$ was replaced with resistivity $\rho_{(T)}$ which is independent of sample dimensions.

The activation energy ΔE of electric conductance was calculated from the relation of electric conductance σ vs. temperature according to the Arrhenius relationship:

$$\sigma \sim \exp\left(-\frac{\Delta E}{2kT}\right) \tag{2}$$

(k – Boltzman constant)

3.1 SiC monophase polycrystalline sinter

The investigation of the electrical properties of the monophase polycrystalline SiC sinter were conducted on two sets of samples, one with copper electrodes and the other one with silver electrodes. The thermal treatment process for the copper electrodes was conducted in an argon atmosphere where they were fired from 20°C to 600°C, while the silver electrodes were fired in an air atmosphere at 20°C to 570°C. In both cases the firing rate was 20°C/min. The samples were held at peak temperatures for 15 min. The firing conditions were compliant with the requirements for the thermal treatment of electrodes.

The relationship between temperature and resistivity ρ, TCR and conductivity σ for monophase polycrystalline SiC

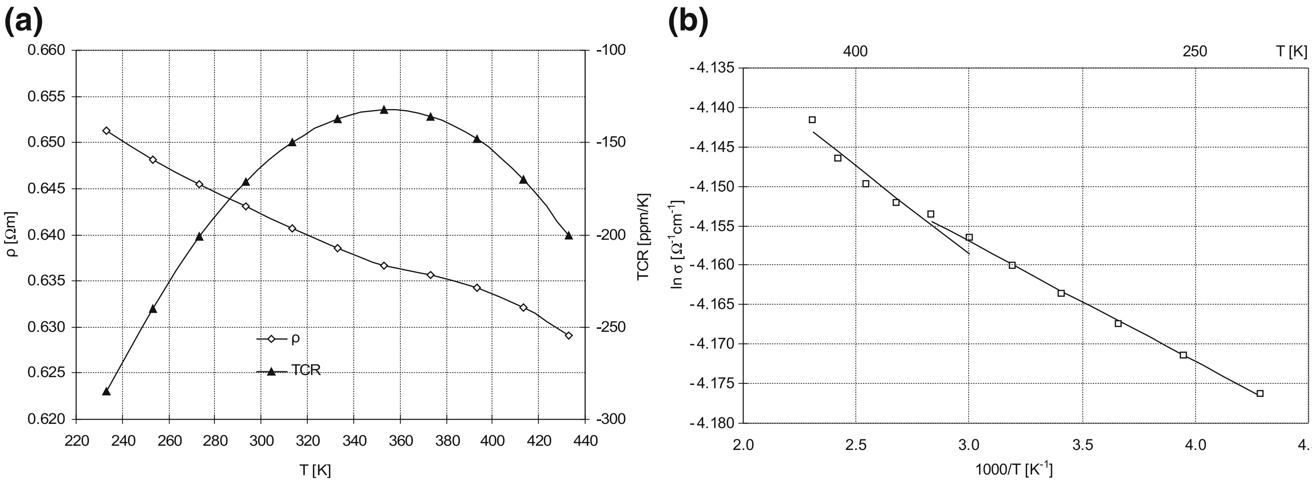

Fig. 1 (**a**) Resistivity ρ and TCR vs. temperature, (**b**) conductivity vs. converse temperature for polycrystalline SiC fired in an argon

fired in an argon atmosphere is presented in Fig. 1(a) and (b). For lnσ error propagation is $7{\cdot}10^{-3}[1/\Omega cm]$. The ρ=f (T) plot indicates that with increasing temperature there is only an insignificant decrease in the value of resistivity from 0.65 Ωm to 0.62 Ωm. The TCR has a negative value and it ranges from −280 ppm/K to −120 ppm/K. The calculated activation energy was very small: 3 and 4 meV. The results obtained indicate a large doping concentration in the samples.

The relationship between temperature and resistivity ρ, TCR and conductivity σ for polycrystalline SiC fired in air atmosphere is presented in Fig. 2(a) and (b). For lnσ error propagation is $9{\cdot}10^{-3}[1/\Omega cm]$. A comparison of the curve in Fig. 1(a) with the curve 1 in fig. 2(a) indicates that the resistivity of samples after firing in an air is three orders of magnitude higher than that of samples fired in an argon atmosphere. The TCR is negative and has a high absolute value from −4,000 ppm/K to −17,000 ppm/K. Electric conductivity is thermally activated. Sample firing process in air at 570°C was repeated twice. Each time the old electrodes were removed and new electrodes were applied to avoid mistakes connected with ageing of the electrodes. Each consecutive thermal cycle of the sample, caused resistivity and the absolute TCR value increase (curve 2 and 3 in Fig. 2(a)). At temperature of 433 K, the resistivity value is similar for all samples fired in air. The calculated activation energy values are included in Table 1. For lower temperatures, the activation energy is in range from 65 to 102 meV and is close to the literature values for nitrogen donor levels [11, 13, 14]. For higher temperatures, the energy is range from 67 meV to 398 meV and is close to the literature values for boron acceptor levels [13–18]. As described before, boron (0.5%) is one of the SiC sintering modifiers. It can be assumed, that for high temperatures, increase of activation energy is caused by the conduction mechanism change, from donor to acceptor.

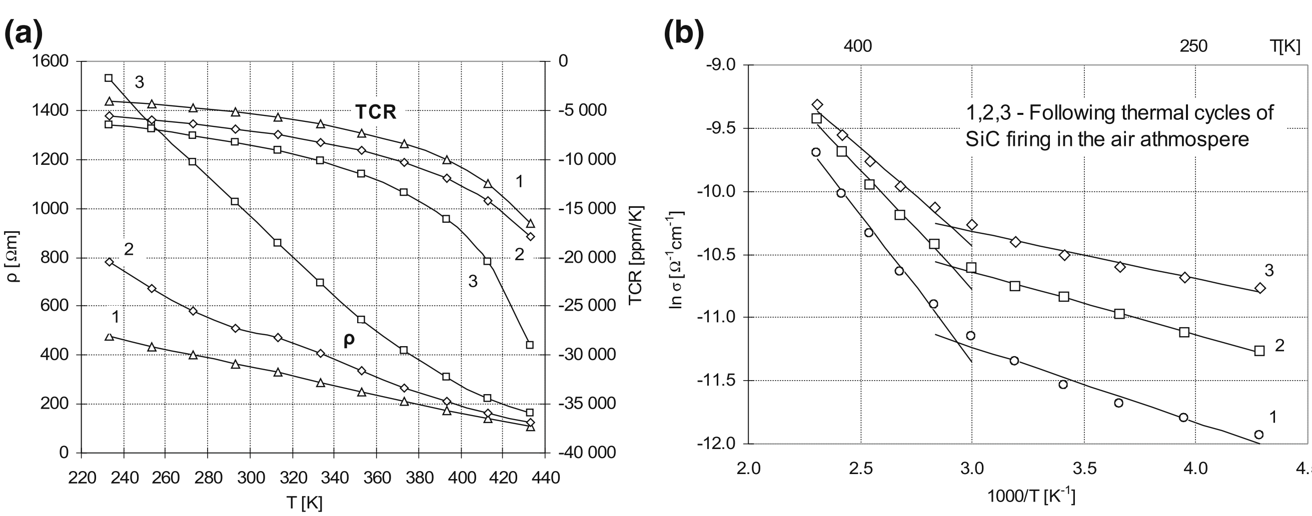

Fig. 2 (**a**) Resistivity ρ and TCR vs. temperature, (**b**) Conductivity vs. converse temperature for polycrystalline SiC fired in an air

Table 1 Activation energy ΔE of electric conduction for polycrystalline SiC fired in air

Samples fired in the air	Temperature [K]	
	233–333 ΔE (meV)	333–433
1×	65	267
2×	85	327
3×	102	398

The data presented in Figs. 1(a) and 2(a) indicate that the resistivity of polycrystalline SiC is dependent on the electrode firing temperature, and whether in argon or air. In our case it ranged from 0.64 Ωm to 1.0×10^{3} Ωm, measured in ambient temperature. It may be assumed that the resistivity increase is caused by material oxidation. The oxidation is not visible on the material surface so samples were compared using X-ray diffraction. The diffractograms are identical, it means that changes in electric conduction, caused by firing in air, do not affect to the structure of the sinter and they are not visible on the diffractograms. It is supposed that the sample oxidation occurs at grain boundaries. It is known from the literature, that the slow oxidation of SiC in the form of fiber occurs for temperatures above 500°C, and for solid material above 600°C [19].

Additional procedures were performed to determine the SiC oxidation temperature of monophase polycrystalline sinter and to confirm previous results. Samples were fired in an air atmosphere at temperatures of 300°C, 400°C, 500°C, and 570°C for 1 hour. After cooling to ambient temperature sinter resistance was measured. The electrodes were made as a eutectic layer of Ga-In (10%). Up to a temperature of 500°C the resistance of the sinters did not change. After firing at 570°C the resistance of the sinters increased by three orders of magnitude, which is consistent with previous results.

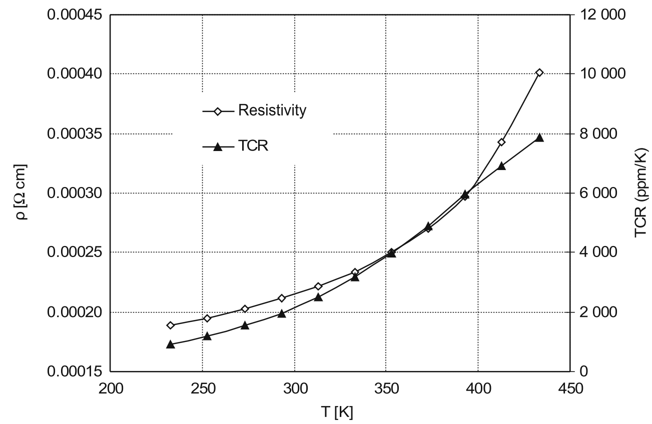

Fig. 4 Resistivity ρ and TCR vs. temperature for polycrystalline TiC sinter

3.2 B_4C monophase polycrystalline sinter

An investigation of the electrical properties of polycrystalline B_4C sinter was performed on the samples with silver electrodes made by the same process as for SiC. The electrodes were screen printed, and then the samples were fired at temperatures ranging from 20°C to 570°C in air atmosphere, and the samples were held at peak temperature for 15 min. Sample firing was repeated with new electrodes being made each time.

The relationship between temperature and the resistivity ρ, TCR and conductivity σ for monophase polycrystalline B_4C is shown in Fig. 3(a) and (b). For lnσ error propagation is $9{\cdot}10^{-3}[1/\Omega cm]$. The ρ=f(T) curve indicates that an increase in temperature results in a decrease in the

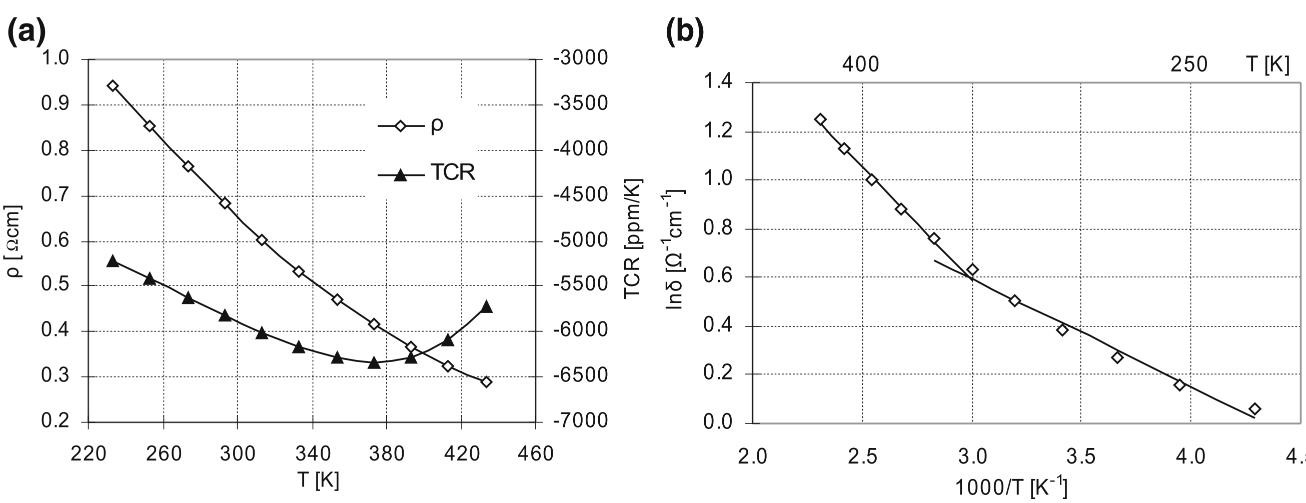

Fig. 3 (**a**) Resistivity ρ and TCR vs. temperature, (**b**) conductivity vs. converse temperature for polycrystalline B_4C after multiple firing in an air at 570°C

Table 2 Resistivity ρ, TCR and activation energy ΔE for SiC, B_4C and TiC sinters within a temperature range of 233 K to 433 K

Temperature range of 233 [K] to 433 [K]				
Sinter	Resistivity ρ [Ωm]	TCR [ppm/K]	Activation energy of electric conductivity ΔE (meV)	Comments
SiC	Argon 0.6	-10^2	3 to 4	Electric conductivity is activated thermally. Resistance value depends on the atmosphere and temperature in which electrodes are fired (air 570°C, argon 600°C).
	Air 10^2 to 10^3	-10^2 to -10^4	65 to 398	In air atmosphere the sinters keep their electrical parameters to 500°C.
B_4C	Air	-10^3	80 to 160	Electric conductivity is activated thermally.
	10^{-3}			Firing in air to 570°C does not affect to the resistivity.
TiC	10^{-6}	10^3		Electric conductin has a metallic character.
				In temperatures over 300°C the sinter oxidizes on the surface.

resistance of the samples, suggesting that B_4C electric conductivity is thermally activated. The temperature coefficient of resistance is negative and ranges from −5,200 ppm/K to −6,400 ppm/K, and the resistivity of the sinters is about 10^{-3} Ωm within the investigated temperature range. Multiple firing of samples in air within a temperature range of 20°C to 570°C did not affect their electrical parameters. A DTA (Differential Thermal Analysis) performed by the authors showed that, slow oxidation of polycrystalline boron carbide starts at 815°C. Calculated activation energy was 80 meV for temperature range from 233 K to 350 K and 160 meV for temperature range from 350 K to 433 K. For higher temperatures the activation energy value is consistent with that given by Emin [20, 21].

B_4C polycrystalline sinter structure was determined using X-ray diffraction. It can be indexed in the rhombohedral R3m space group. The lattice constants are: a=5.601 Å and c=12.074 Å. Graphite was also found in the samples. The graphite had a hexagonal structure and lattice constants: a=2.463 Å, c=6.722 Å. As discussed in the introduction, carbon was introduced as a sinter activator (3%).

3.3 TiC monophase polycrystalline sinter

The electrical properties investigation of TiC polycrystalline sinter were performed on samples with electrodes, made of silver wire mounted with a clamp. This method was used because of the low resistivity of the samples. The relationship between resistivity ρ, the TCR, and the temperature for TiC samples is presented in Fig. 4. The ρ=f(T) curve shows that temperature increase cause resistance increase of the samples. This indicates the metallic characteristics of TiC conductivity. The temperature coefficient of resistance is positive, and in the

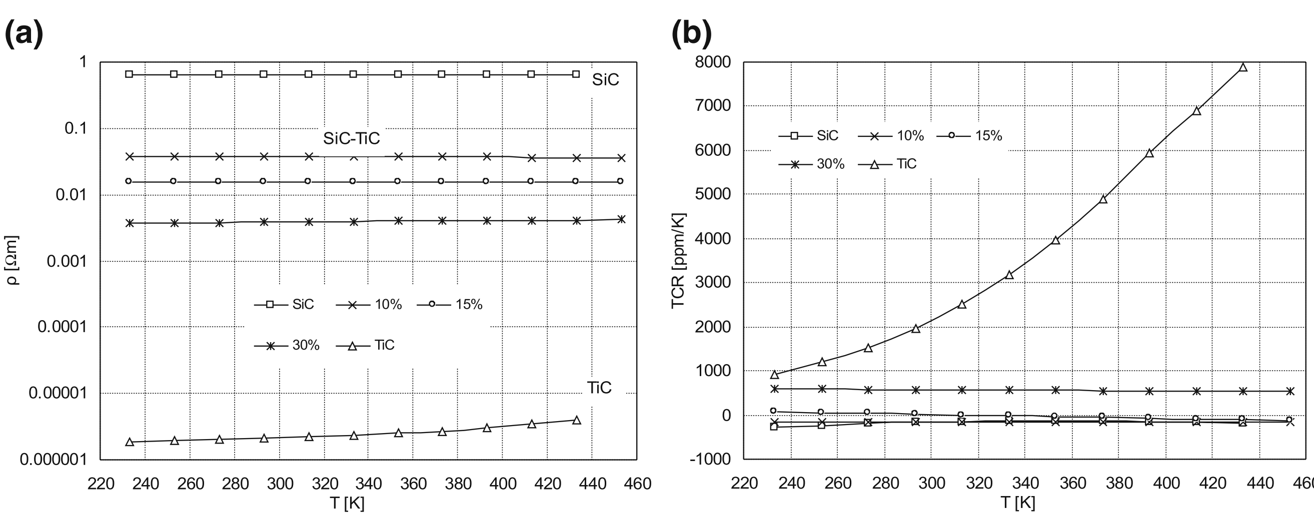

Fig. 5 (**a**) Resistivity and (**b**) TCR vs. temperature and TiC content for SiC-TiC sinters

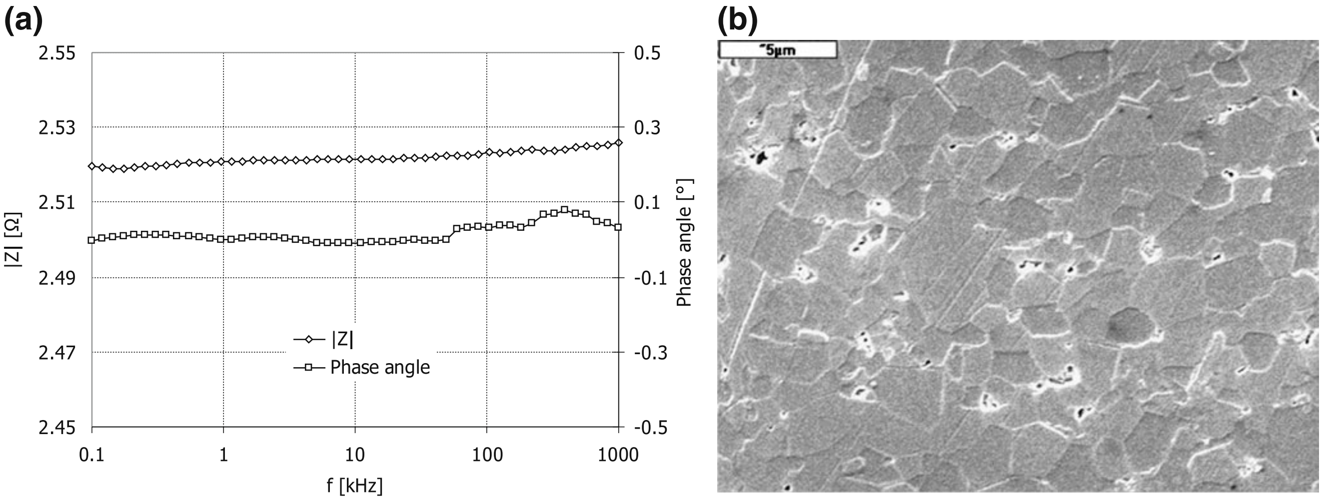

Fig. 6 (**a**) Impedance vs. frequency for B_4C sinter fired in an air at 570°C, (**b**) microstructure (polished cross-section)

investigated temperature range is from 1,000 ppm/K to 8,000 ppm/K. The resistivity of the sinters is 10^{-6} Ωm. Samples firing up to 300°C, does not affect to their electric properties. Samples firing over 300°C results in surface oxidation, which is visible to the naked eye.

X-ray diffraction analysis of the investigated TiC sinter, showed the homogeneity of the TiC phase.

3.4 Comparison of the electrical properties of monophase polycrystalline SiC, B_4C and TiC sinters

The values of resistivity ρ, TCR and activation energy ΔE for the investigated polycrystalline SiC, B_4C and TiC sinters in a temperature range from 233 K to 433 K are compared in Table 2.

4 SiC-TiC, SiC-B_4C composite sinters – electrical and physical properties modification

4.1 Compensating for the negative TCR value of SiC in composite SiC-TiC sinters

Investigations carried out by the authors were focused on the possibility of compensating for the negative TCR value of SiC, by combining this material with TiC, which has positive TCR. The investigations were performed on composite SiC-TiC sinters, with a TiC content ranging from 10% to 30%. Figure 5(a) and (b) present the values of resistivity, TCR vs. temperature, and TiC content. It can be noticed, that an increase of TiC content results in a decrease of the TCR value. With 15% of TiC in the composite SiC-

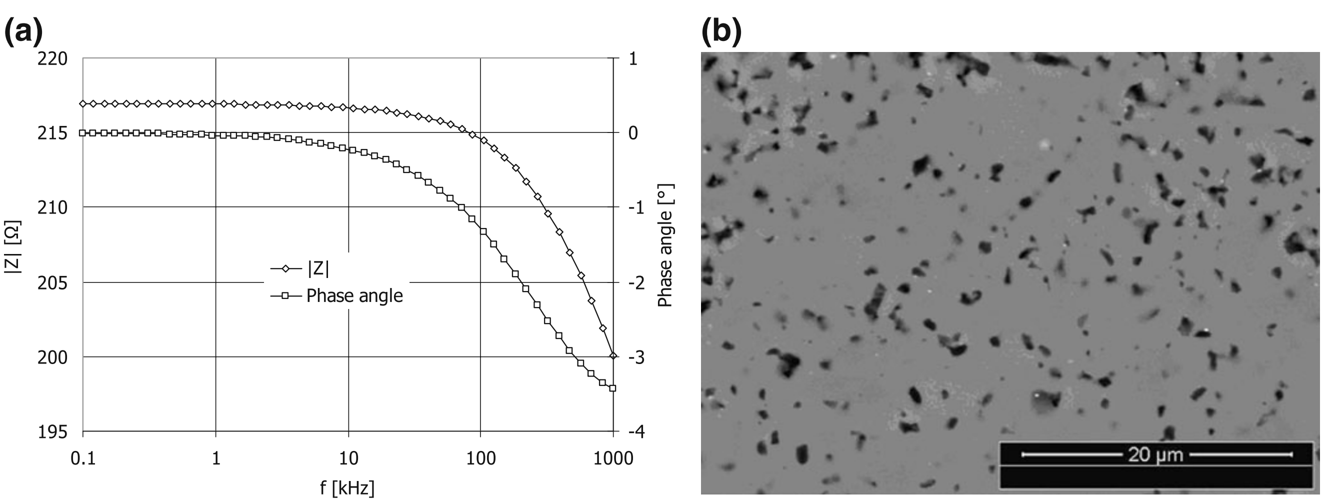

Fig. 7 (**a**) Impedance vs. frequency for polycrystalline SiC fired in an argon at 600°C, (**b**) microstructure (polished cross-section)

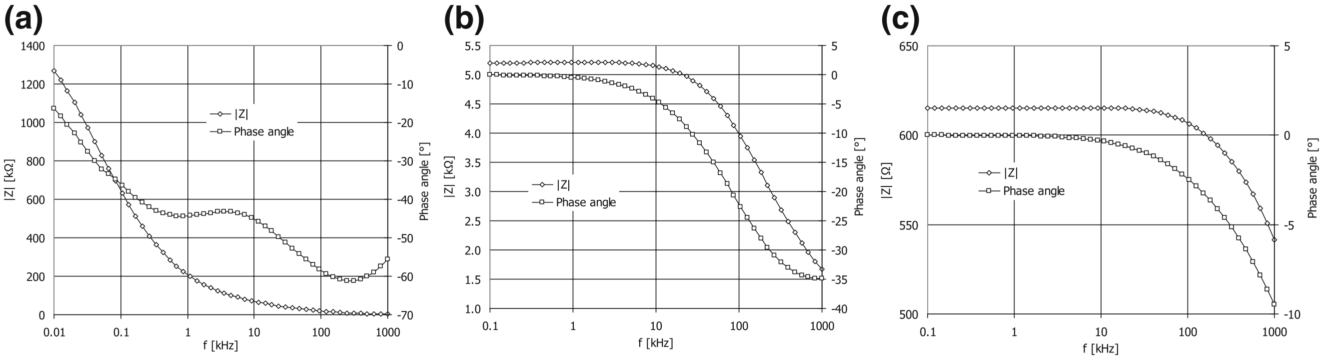

Fig 8 Impedance vs. frequency for (**a**) Polycrystalline SiC, and SiC-B_4C composites with (**b**) 10 wt% B_4C and (**c**) 20 wt% B_4C fired in air at 570°C

TiC the TCR is close to zero, within a temperature range of 293 K to 348 K. An increase of TiC content also results a decrease in SiC-TiC sinter resistivity.

4.2 Impedance spectroscopy for monophase SiC, B_4C sinters and SiC-B_4C, SiC-TiC composite sinters – comparative investigation

The impedance spectroscopy studies were carried out with a Quad Tech 7600 precision meter within a range of 100 Hz to 1 MHz. When alternating electric current flows through a resistor it causes inductive X_L and capacitive X_C reactance to appear. The impedance is given by:

$$Z = R^2 + (X_L - X_C)^2 \quad (3)$$

X_L $2\pi fL$
X_C $1/2\pi fC$

(Z=impedance, L=inductivity, C=capacity, f=frequency, R=resistance).

A resistor performs best, when its impedance is independent from the current frequency, then it have resistive characteristic. Impedance spectroscopy within a range of 100 Hz to 1 MHz was used, to evaluate impedance characteristics of the samples.

Relationship between impedance and frequency for a resistive element of B_4C is presented in Fig. 6(a). The figure shows that the impedance of B_4C is independent from the frequency. In investigated frequency range, the phase angle between the voltage and the current is zero. The B_4C element in the investigated frequency range has a strictly resistive character. The microstructure of B_4C presented in Fig. 6(b) seems to be almost without porosity.

Relationship between impedance and frequency for a resistive element of SiC fired in argon is presented in Fig. 7. The figure shows that the impedance of the SiC is almost independent from the frequency. The phase angle between voltage and current is small, and in the investigated frequency range it was −3.5°. The microstructure of SiC fired in argon presented in Fig. 7(b) is almost nonporous.

Relationship of impedance and frequency for resistive air-fired elements of SiC and SiC-B_4C composites with B_4C content of 10 and 20 wt.% are presented in Fig. 8(a),

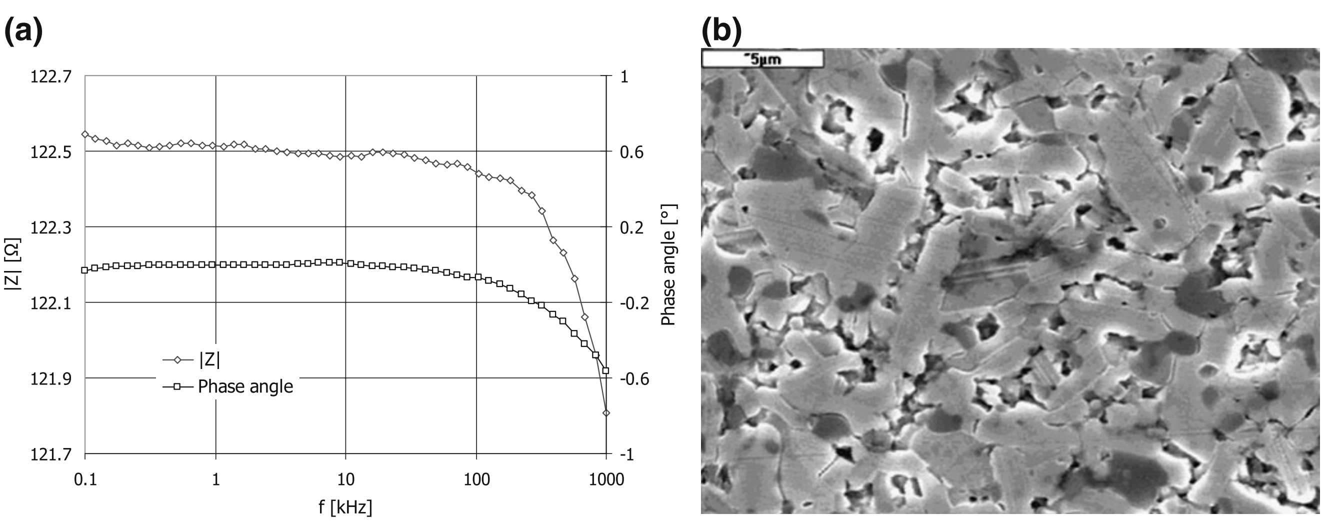

Fig. 9 (**a**) Impedance vs. frequency, (**b**) microstructure (polished cross-section) for SiC-B_4C with 40 wt% B_4C, fired in air at 570°C

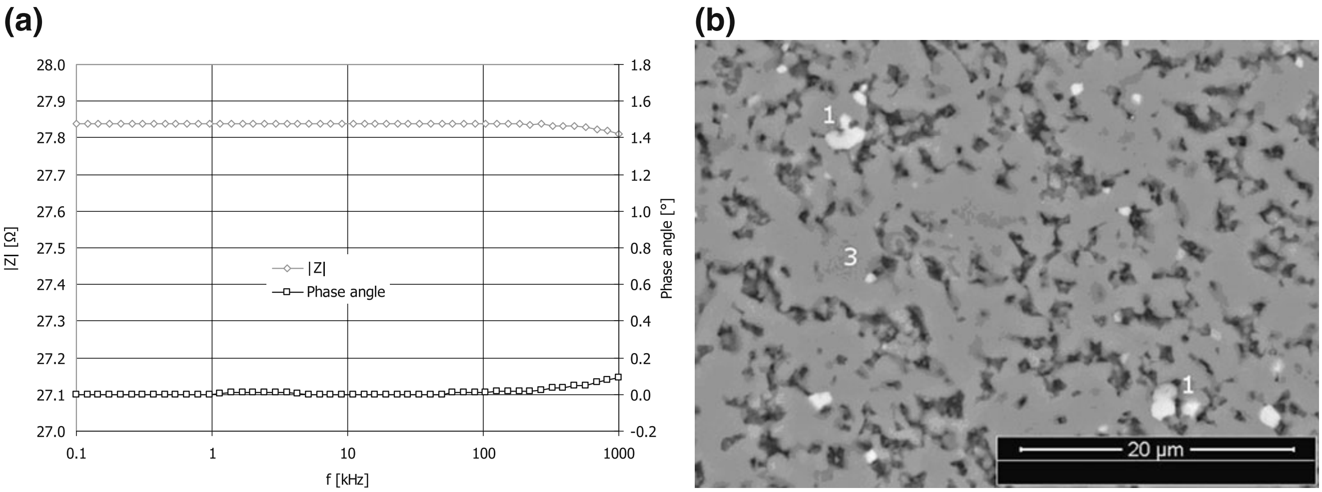

Fig. 10 (**a**) Impedance, vs. frequency, (**b**) microstructure (polished cross-section) for SiC (2)-TiC (1) sinter with 15 wt.% TiC fired in argon at 600°C

(b), (c). The impedance of the SiC sample fired in air exhibits a high dependence from the frequency, see Fig. 8 (a); it has a capacitive character. The phase angle between voltage and current was as high as 60°. Based on this result, it may be assumed that oxidation occurs at grain boundaries resulting in an increase in the electric capacitance of the samples. The impedance for the SiC-B_4C sinter exhibits higher independence from the frequency than the monophase SiC sinter fired in air, see Fig. 8(b) and (c). With 40% of B_4C in the composite, the impedance is independent of frequency, see Fig. 9(a). This means, that SiC-B_4C composites are more resistant to oxidation than monophase sinter SiC. The microstructure of SiC-B_4C for 40 wt% B_4C presented in Fig. 9(b) shows very low porosity.

Relationsip of impedance and frequency for SiC-TiC composite sinters with a 15 wt% content of TiC is presented on Fig. 10(a), and their microstructure on Fig. 10(b). The impedance of the resistive element with 15% TiC is practically independent from the frequency. The element with 30% TiC exhibits an inductive character for frequencies above 10 kHz, see Fig. 11. The phase angle between the voltage and current is 6° at 1 MHz.

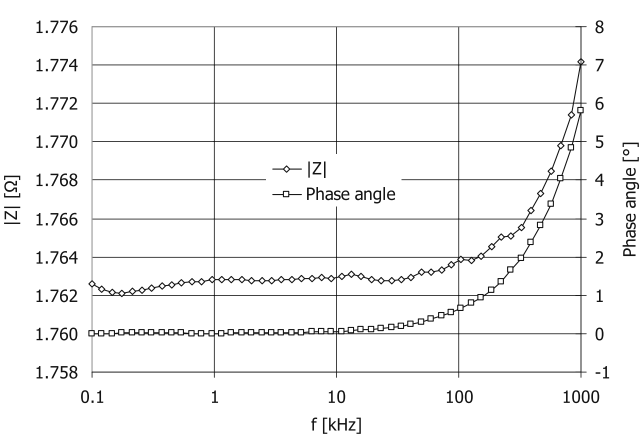

Fig. 11 Impedance vs. frequency for SiC-TiC sinter with 30 wt.% TiC fired in argon at 600°C

5 Conclusion

Among the investigated materials, monophase B_4C sinter is the most resistant to oxidation. Firing samples in air to 570°C during the thermal treatment process of electrodes does not affect their electrical parameters. B_4C material can be use as a resistor in applications where a low TCR value is not necessary, for example in power resistors and suppression resistors. Within the investigated frequency range from 100 Hz to 1 MHz, B_4C element have a resistive characteristic, so it can be applied wherever non-inductive resistors are needed.

Monophase SiC sinter is resistant to oxidation at temperatures up to 500°C, at higher temperatures it oxidizes at grain boundaries. The non-oxidized SiC element have almost resistive characteristic. Its phase angle is −3.5°. Within investigate temperature, the TCR for this material is in range from 100 to 120 ppm/K. It can be use for non-inductive resistors.

SiC sinter fired in 570°C is oxidized, and it shows capacitive character. The phase angle between the current and voltage is −60°. This eliminates this material from application as a volume resistor.

SiC resistivity to oxidation can be improved by adding B_4C. Composite SiC-B_4C sinters are more resistant to oxidation than monophase SiC sinter. With 40% of B_4C, the element is completely resistive. This type of resistive element can be used when low TCR is not necessary, for example as power resistors, suppression resistors and in any application that requires non-inductive resistors.

Composite sinters SiC-TiC, can be use for making resistors working in temperatures up to 300°C. Above this temperature, electrical parameters of this material change due to slow surface oxidation. SiC-TiC material with 15% TiC, within temperature range from 20°C to 75°C, exhibits TCR close to zero, and its impedance is independent from the frequency. This material can be used for making non-inductive resistors with low TCR.

Acknowledgments The authors wish to thank the measurement laboratory staff, and Mr Andrzej Cichocki for help in the research and in editing this paper.

References

1. F. Thevenot, Boron carbide – a comprehensive review. J. Europ. Ceram Soc. **6**, 205–225 (1990)
2. J. Lankford, Comparative study of the temperature of hardness and compressive strength in ceramics. J. Mat. Sci. **18**, 1666–1674 (1983)
3. L. Stobierski, *Carbide ceramics*. Uczelniane Wydawnictwa Naukowo-Dydaktyczne AGH, 2005 (in Polish)
4. L. Stobierski, *Węglik krzemu: budowa własności i otrzymywanie*. Ceramika 48, PAN, Kraków (1996), 80, 92 (in Polish)
5. L. Jaworska, L. Stobierski, A. Twardowska, D. Królicka, Preparation of materials based on Ti–Si–C system using high temperature–high pressure method. J. Mater. Process. Technol. **162–163**, 184–189 (2005)
6. J. Lis, R. Pampuch, J. Stobierski, *Preparation and Properties of New Structural Ceramics in the Ti-Si-C System. Proc. Int. Symp. of Advanced Materials for Structural and Tribological Application* (Vancouver, Canada, 1995), Aug. 21-23
7. Y. Tkachenko, V. Britun, E. Prilutskii, D. Yurchenko, G. Bovkun, Structure and properties of B_4C - SiC composites. Powder Metall. Met. Ceram. **44**(3–4), 196–201 (2005)
8. The Circuits and Filters. *Handbook*, 2nd edn, 10. 1. Resistor, ed. by W.-K. Chen (CRS Press and IEEE Press, Chicago, USA, 2001), p. 274
9. W.F. Knippenberg, Growth phenomena in silicon carbide. Phil. Res. Rept. **18**, 161 (1963)
10. W.J. Choyke, L. Patrick, Exciton radiation and phonon spectrum of 6H SiC. Phys. Rev. **2**(6), 127 (1962)
11. G.A. Slack, R.I. Scace, Nitrogen incorporation in SiC. J. Chem. Phys. **42**, 805 (1965)
12. M. Ikeda, H. Matsunami, T. Tanaka, Site effect on the impurity levels in 4H, 6H, and 15 R SiC. Phys. Rev. B **22**, 2842–2854 (1980)
13. G. Pensyl, W.J. Choyke, Electrical and optical characterisation of SiC. Phys. B **185**, 264 (1993)
14. Y. Tajima, W.D. Kingery, Solid Solubility of aluminium and boron in silicon carbide. J. Am. Ceram. Soc. **65**, C 27–C 29 (1982)
15. A. Suzuki, H. Matsunami, T. Tanaka, J. Electrochem. Soc. **124**, 241 (1977)
16. M.H. Anikin, A.A. Lebedev, A.L. Syrkin, A.V. Suvorov, Sov. Phys. Semicond. **19**, 69 (1985)
17. V.S. Ballandovich, G.N. Violina, Yu. M. Tairow, *Fiz. Tekhn. Poluprov.* **15**(1981) 498/503; *Soviet Phys. – Semicond.* **15**(1981) 283/6
18. Yu. A. Vodakov, N. Zhumaev, B. P. Zverev, et al., *Fiz. Tekh. Poluprovodn. (Leningrad)* **11**, 373 (1977); *Soviet Phys. – Semicond.* **11**, 214 (1977)
19. C. S. Brooks, M. A. DeCrescente, D. A. Scola, The wetting of silicon carbide surfaces. *J. Colloid Interface Sci.* **27** (1968), p.773-788
20. D. Emin, Electronic Transport in Boron Carbides. Boron–rich solids, AIP Conf. Proc. No. 140, 189 (1986)
21. D. Emin, Structure and single-phase regime in boron carbides. Phys. Rev. B **38**, 6041–6055 (1988)
22. I. Cadoff, J.P. Nielsen, Titanium-carbon phase diagram. J. Metals **5**, 1564 (1953)
23. T.G. Utkina, J.C. Karimow, Anomalies of electrical properties of disordered titanium carbide. *Solid State Phys.* **28**(10) (1986)