

Influence of a high conductivity additive on the electrical properties of vanadium dioxide-based ceramics

V.R. Kolbunov, A.I. Ivon*, I.M. Chernenko

Radiophysical Department, Dniepropetrovsk National University, UA 49625 Dniepropetrovsk, Ukraine

Received 3 August 2001; received in revised form 15 August 2002; accepted 28 September 2002

Abstract

The influence of copper additive on the electrical resistivity, ρ , and the value of the resistivity jump, ρ_s/ρ_m , in the vicinity of the phase transition temperature $T_t \approx 68^\circ\text{C}$ has been studied for ceramics of composition (wt.%): $x\text{Cu}-(85-x)\text{VO}_2-15\text{VPG}$ (where VPG—vanadium phosphate glass of composition (mol%) $80\text{V}_2\text{O}_5-20\text{P}_2\text{O}_5$). For higher x values, the density of the ceramics increases, and the magnitudes of ρ and ρ_s/ρ_m decrease. The increasing density is associated with the decreasing porosity of the ceramics. To explain the ρ and ρ_s/ρ_m behaviour with variation of x , the percolation theory was used. The percolation of electrical current occurs through the copper and the electrical properties of the ceramics are determined by the additive copper at $x \geq 8$ wt.%. At $x < 8$ wt.%, the basic contribution to the electrical conductivity of the ceramics is given by VO_2 . Vanadium dioxide based ceramics with content of copper in the range 5–8 wt.% have a resistivity jump ρ_s/ρ_m of not less than one order and have more stable behaviour in their electrical parameters after thermocycling through temperature T_t , than do ceramics without copper.

© 2003 Elsevier Science Ltd. All rights reserved.

Keywords: Electrical properties; Resistivity; Resistivity jump; VO_2

1. Introduction

Vanadium dioxide-based materials are interesting due to their sharp changing of physical parameters in the vicinity of phase transition temperature of VO_2 ($T_t = 68^\circ\text{C}$) and in particular to their changing of electrical resistivity. This property allows to create on the basis of VO_2 switching elements, thermistors and other devices.^{1–5} However, low stability of vanadium dioxide at temperature cycles through T_t restricts practical use of such materials. The reason for low stability is mechanical stresses in the interphase region of VO_2 crystals. These mechanical stresses result in the formation of microcracks which decrease the durability of VO_2 crystals and lead to and increase in their resistivity.^{6–8}

Vanadium dioxide-based ceramics (VDBC)⁹ has the resistivity jump in the vicinity of temperature of phase transition of metal-semiconductor in VO_2 . We observed the effect of stabilization of VDBC electrical properties

(electrical resistivity ρ and dielectric constant ε) after thermocycling through temperature T_t .⁸ The dependences $\rho(n)$ and $\varepsilon(n)$ (n —amount of thermocycles) have the plot of saturation after 15–20 thermocycles. However, the resistivity jump in the vicinity of T_t is practically absent. For explanation of such behaviour of VDBC electrical properties the model assuming formation of stable clusters at thermocycling within which the percolation of electrical current into VO_2 takes place was offered.⁸ The sizes of these clusters do not vary during thermocycling. The clusters are isolated from each other by microcracks and are connected electrically by inclusions of a vanadium phosphate glass, which determines a conductivity of ceramics after a long-lived thermocycling. It is possible to assume that stability of VDBC will increase if an additive with high conductivity, which can create the electrical bonds between the earlier mentioned clusters is introduced into the composition of VDBC.

The purpose of the present work is to investigate the influence of additive with high conductivity on electrical resistivity, value of resistivity jump in the vicinity of T_t and stability of these parameters of vanadium dioxide-based ceramics.

* Corresponding author. Present address: Dniepropetrovsk, UA 49050, Ukraine. Tel./Fax: +7-380-0562-465523.

E-mail address: a_ivon@mail.ru (A.I. Ivon).

2. Experimental

As an additive with high conductivity the finely divided powder of copper was used. Vanadium dioxide-based ceramics with composition (wt.%): $x\text{Cu}-15\text{VPG}-(85-x)\text{VO}_2$ ($x=0-15$) was the object of investigation. Here VPG—vanadium phosphate glass of composition (mol%) $80\text{V}_2\text{O}_5-20\text{P}_2\text{O}_5$. The samples of VDBC were obtained using technology which was described earlier.⁹ The specimens were 10 mm in diameter and 2 mm thick. During the gravity test the weight of specimens was measured with precision ± 0.0001 g and their sizes—with precision ± 0.025 mm. The electrodes for electrical measurements were obtained using vacuum pulverization of indium or electrodeposition of copper. The results in both cases were identical. The temperature dependences of resistivity were recorded when heating a ceramic specimen with velocity not more than $1^\circ/\text{min}$. The value of the resistivity jump in the vicinity of T_t (ρ_s/ρ_m) was determined as the ratio of values of electrical resistivity of ceramics at the temperature of 65°C (ρ_s) and 75°C (ρ_m) accordingly.

Thermocycling was performed by means of cyclic heating of a ceramic specimen up to 90°C with subsequent cooling to 25°C . For quantitative assessment of the stability of electrical parameters of ceramics during thermocycling relative change of electrical resistivity ρ_{10}/ρ_0 and relative change of the jump of resistivity $[\lg(\rho_s/\rho_m)]_0/[\lg(\rho_s/\rho_m)]_{10}$ after 10 thermocycles were used. Here index 0 corresponds to the initial value of parameter, index 10 corresponds to the value of parameter after 10 temperature cycles.

3. Results and discussion

The data of investigation of influence of the additive of copper on density of vanadium dioxide-based ceramics are represented in Fig. 1. Values of density d_e were

defined as the ratio of mass of an examined ceramic specimen to its volume which was calculated by specimen sizes (the curve 1). Curve 2 for theoretical density d_t is calculated assuming that ceramics are a three-phase mixture of vanadium dioxide ($d_v=4.34\text{ g cm}^{-3}$), vanadium phosphate glass ($d_v=2.8\text{ g cm}^{-3}$) and copper ($d_{\text{Cu}}=8.9\text{ g cm}^{-3}$). The calculation yielded such relation:

$$d_t = (0.15/d_g + x/d_{\text{Cu}} + (0.85 - x)/d_v)^{-1}.$$

The dependence of ratio d_e/d_t as the function of the content of copper in ceramics x are also represented in Fig. 1 (curve 3).

As Fig. 1 shows increase in the content of copper leads to increase in the density of ceramics. The distinction between experimental d_e and theoretical d_t values of density are bound substantially with considerable porosity of vanadium dioxide-based ceramics. It is confirmed by data of electron microscopy obtained earlier for vanadium dioxide-based ceramics without the additive of copper.⁸ According to these data the ceramics consists of VO_2 crystallites, inclusions of vanadium phosphate glass and pores.

The porosity of VDBC can be estimated using the ratio d_e/d_t as $(1-d_e/d_t) 100\%$. As Fig. 1 shows with the growth of copper the ratio d_e/d_t increases, and consequently, the porosity of ceramics decreases. It explains the increase of density when adding the copper to the composition of ceramics. The diminution of ceramics porosity with increase of copper is confirmed also by optical microscopy.

The data of investigation of influence of the additive of copper on temperature dependence of VDBC electrical resistivity is represented in Fig. 2. It is visible that in interval of the content of copper from 0 to 12 wt.% the resistivity jump in the vicinity of T_t takes place, however its value and values of resistivity considerably depend on the content of copper.

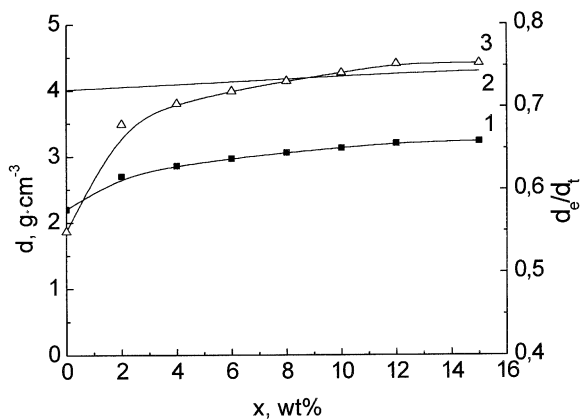


Fig. 1. Dependences of VO_2 -based ceramic density on the content of copper: 1—experiment (d_e), 2—calculation (d_t), 3—ratio d_e/d_t .

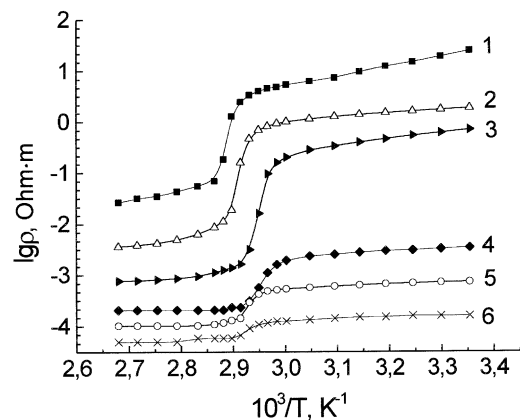


Fig. 2. Temperature dependences of electrical resistivity of VO_2 -based ceramics with the different content of copper (wt.%): 1—0; 2—4; 3—6; 4—8; 5—10; 6—12.

The data of investigation of such dependence is given in Fig. 3. As it follows from these data, with increase of copper in vanadium dioxide-based ceramics the values of electrical resistivity ρ and resistivity jump in the vicinity of temperature T_t ρ_s/ρ_m diminish. If the additive of copper has a content more than 12 wt.% ρ tends to be a certain limiting value, and the ρ_s/ρ_m value tends to unit. It should be noted also that when the content of copper covers intervals from 0.5 to 3 wt.% larger values of the resistivity jump appear if compared with ceramics without the additive of copper. Such behaviour of ρ_s/ρ_m correlates with the sharp increase of ceramic density in interval of the content of the additive of copper from 0 to 3 wt.% (Fig. 1).

To explain electrical properties of vanadium dioxide-based ceramics it is necessary to allow for features of its microstructure. The contribution of the different components into VDBC electrical conductivity are interlinked with these features. According to data of microstructural investigations⁸ an electrical bond between VO₂ crystallites can be formed two ways. In the first case, it is direct contact, which is formed between crystallites when baking ceramics. In the second case, the contact is formed by VPG inclusions, which function as electrical bonds between VO₂ crystallites. These bonds are high-ohmic enough because VPG electrical resistivity exceeds VO₂ resistivity in a semiconductor phase by not less than 2–3 orders.¹⁰ Pores and the microcracks disrupt electrical bonds between VO₂ crystallites.

The electrical bonds between VO₂ crystallites are random. For this reason the vanadium dioxide-based ceramics are a disordered heterogeneous material. For explanation of electrical properties of such material the percolation theory ideas can be used.^{11,12}

According to the percolation theory VDBC electrical conductivity can be considered as conductivity of a three-dimensional random resistor network. Resistors which have a random value of electrical resistance are

included in bonds of such network. VO₂ crystallites are located in the nodes (sites) of network. Distance between nodes of the network are equal to the medial size of VO₂ crystallites. The values of electrical resistances between network nodes are determined by electrical bonds between VO₂ crystallites. If direct contact between adjacent VO₂ crystallites takes place, the value of electrical resistance of bond is determined by a conductivity of vanadium dioxide. If VPG gives the electrical bond between VO₂ crystallites, the value of electrical resistance of bond is determined by glass conductivity. The pore or the microcrack breaks off the electrical bond between adjacent VO₂ crystallites. This is equivalent to the inclusion of the resistor with infinite electrical resistance in this bond of the network.

Taking into account the earlier mentioned, two reasons may explain the decrease of VDBC resistivity caused by the introduction of copper into the composition of ceramics (Fig. 3). Firstly, the additive of copper diminishes porosity of ceramics (Fig. 1). It increases the amount of electrical bonds between network nodes in which VO₂ crystallites are located and therefore gives increasing of ceramics conductivity. Secondly, the additive of copper provides low-impedance electrical bonds between adjacent nodes of network, that also promotes the decrease of ρ .

Vanadium dioxide-based ceramics are interesting for practical use as a material having electrical properties such as the properties of crystalline vanadium dioxide. It will take place when the contribution of vanadium dioxide into electrical conductivity of ceramics will be more than contribution of other components (vanadium phosphate glass, copper, pores and cracks). According to the percolation theory results¹² it takes place, if the fraction of network bonds with the electrical resistance determined by a vanadium dioxide exceeds a percolation threshold x_c ($x_c=0.25$ in a three-dimensional case¹²) In this case the VO₂ crystallites, which have direct contact or are linked by copper, form an infinite cluster where one is part of a random resistor network. Practically all electric current of ceramics flows in this cluster.

The additive of copper in the range 0–3 wt.% decreases porosity of ceramics and increases amount of bonds with low electrical resistance between VO₂ crystallites. It makes the resistor network of an infinite cluster more heavy-bodied. VO₂ crystallites which earlier did not give the contribution to a conductivity of ceramics are included in this network. Therefore, contribution of vanadium dioxide to ceramics conductivity is growing. It explains higher values of ρ_s/ρ_m in interval of the content of copper 0–3 wt.% compared with the ceramics without the additive of copper (Fig. 3). The further increase of copper leads to the decrease of the resistivity jump value ρ_s/ρ_m as well as to the decrease of ceramics resistivity ρ .

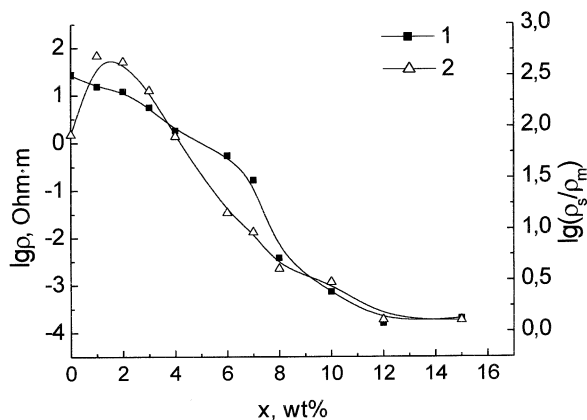


Fig. 3. Dependences of electrical resistivity ρ (1) and value of the jump of resistivity ρ_s/ρ_m (2) on the content of copper for VO₂-based ceramics.

It follows from Fig. 1, that the density of ceramics is changing insignificantly with growth of x when the content of copper is more than 3 wt.%. It allows the conclusion, that the reason of observed behaviour ρ and ρ_s/ρ_m (Fig. 3) is not the decrease of porosity but the increase of copper content in ceramics.

According to the optical microscopy data the copper is present in VDBC in the form of inclusions which are located between VO_2 crystallites or coat their surface. When the copper content increases these inclusions integrate in clusters. Such clusters are in-parallel with some parts of infinite cluster formed by VO_2 crystallites and shunt these parts of infinite cluster. The shunting effect of copper is more developed below T_t , when the vanadium dioxide is in more high-ohmic semiconductor phase. Fig. 2 shows that when x is increasing in interval of the additive of copper $x > 4$ wt.% the change of ceramics resistivity is more at $T < T_t$ than at $T > T_t$. It explains diminution of the resistivity jump ρ_s/ρ_m when the content of copper is increasing (Fig. 3).

Fig. 3 shows that the sharp decrease of ceramics resistivity takes place when the content of the additive of copper is about 8 wt.%. Such behaviour suits to the change of the resistivity in the vicinity of percolation.^{11,12} Therefore, it is possible to conclude that the final clusters of copper are integrating in the infinite cluster when the copper content is about 8 wt.% or more and in ceramics where there is percolation over copper component. The network of the infinite cluster with percolation over the copper component of ceramics shunts the network of the infinite cluster with percolation in VO_2 crystallites. Therefore at $x > 8$ wt.% the additive of copper gives basic contribution to conductivity of vanadium dioxide-based ceramics. It explains low values of ρ and practically absence of resistivity jump ρ_s/ρ_m when content of copper is large (Fig. 3).

The data of investigation of influence of the additive of copper on the stability of VDBC electrical parameters during cyclic heating and cooling of ceramics through the temperature T_t are shown in Fig. 4. It is possible to see that increase of copper content decreases the relative change of resistivity ρ_{10}/ρ_0 and the relative change of resistivity jump $[\lg(\rho_s/\rho_m)]_0/[\lg(\rho_s/\rho_m)]_{10}$ after thermocycling. It allows to conclude that VDBC electrical parameters are stabilized when the additive of copper is introduced in the composition of ceramics.

It is known that the change of ρ and ρ_s/ρ_m during thermocycling is linked with the formation of microcracks in ceramics.^{7,8} The microcracks disrupt electrical bonds between VO_2 crystallites. It leads to the destruction of the infinite cluster network with percolation in VO_2 crystallites. The infinite cluster with percolation in VO_2 crystallites is disintegrating in clusters of final sizes which are isolated from each other by microcracks and are connected by high-ohmic inclusions of a vanadium

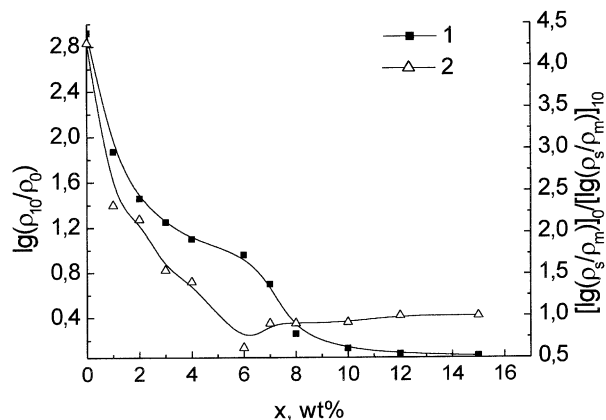


Fig. 4. Relative change of electrical resistivity ρ_{10}/ρ_0 (1) and relative change of the jump of resistivity $[\lg(\rho_s/\rho_m)]_0/[\lg(\rho_s/\rho_m)]_{10}$ (2) after 10 thermocycles as function of the content of copper in VO_2 -based ceramics.

phosphate glass. In this case VPG additive determines ceramics conductivity. Therefore for ceramics without the additive of copper the process of thermocycling leads to rapid increasing of resistivity and disappearance of resistivity jump in the vicinity of temperature T_t . The additive of copper probably creates low-impedance electrical bonds between final clusters. It conserves the contribution of VO_2 in conductivity of ceramics and explains more stable behaviour of parameters ρ and ρ_s/ρ_m during thermocycling.

As Fig. 4 shows the value of ρ_s/ρ_m after 10 thermocycles exceeds similar value before thermocycling if the content of copper in ceramics is 5–8 wt.%. As Fig. 5 shows such behaviour of ratio ρ_s/ρ_m is associated with the fact that during thermocycling of ceramics resistivity change in temperature interval $T < T_t$ is more than in interval $T > T_t$. It may be caused by expansion of VDBC in the vicinity of temperature T_t , when the VO_2 crystallites transfer into a metallic phase.⁸ The expansion probably recovers a part of electrical bonds between VO_2 crystallites, which are torn by microcracks in

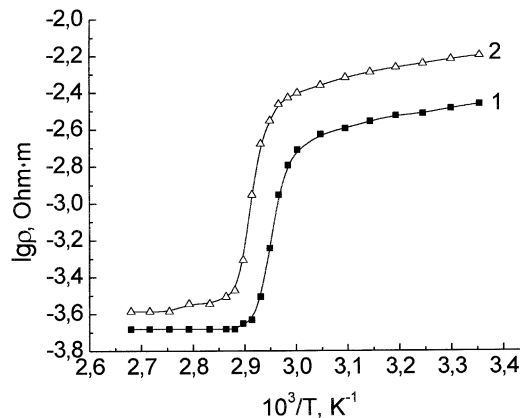


Fig. 5. Temperature dependences of electrical resistivity of VO_2 -based ceramics with 8 wt.% of copper before (1) and after (2) 10 thermocycles.

temperature interval $T < T_1$. The inclusions of coppers which are located between VO_2 crystallites and on their surface promote this process. Therefore additives of copper in interval 5–8 wt.%, which give the value of resistivity jump ρ_s/ρ_m in the limits 1–2 orders and increase the stability of electrical parameters of vanadium dioxide-based ceramics, probably is most acceptable for practical usage of this material.

4. Conclusion

The density of vanadium dioxide based ceramics of composition (wt.%): $x\text{Cu}-15\text{VPG}-(85-x)\text{VO}_2$ (VPG—vanadium phosphate glass of composition (mol%) $80\text{V}_2\text{O}_5-20\text{P}_2\text{O}_5$) is increasing, resistivity ρ and value of resistivity jump ρ_s/ρ_m in the vicinity of temperature of phase transition T_1 in VO_2 are decreasing when the value x grows.

The reason of density increasing is diminution of porosity of ceramics when the content of copper x is increasing.

The behaviour of ρ and ρ_s/ρ_m with a variation of the content of copper in VDBC is possible to be explained using the percolation theory if electrical conductivity of ceramics is considered as conductivity of random resistor network with the VO_2 crystallites in the nodes of this network.

The crystallites of VO_2 give the basic contribution to electrical conductivity of ceramics in interval of the content of the additive of copper $0 \leq x \leq 8$ wt.%. According to the percolation theory notions the electrical conductivity of ceramics in this interval of the additive of copper is determined by the network of the infinite cluster, the electrical resistances between nodes of which are determined by conductivity of VO_2 .

The percolation in copper component of VDBC takes place if $x > 8$ wt.%. The network of the infinite cluster with percolation in copper component shunts the network of the infinite cluster with percolation in vanadium dioxide and electrical properties of VDBC are determined by the additive of copper.

The temperature cycling in the vicinity of phase transition temperature T_1 destroys low-impedance electrical bonds between VO_2 crystallites as a result of micro-cracking. The introduction of the additive of copper increases amount of low-impedance electrical bonds between VO_2 crystallites. It explains the increasing of stability of electrical parameters of vanadium dioxide based ceramics at thermocycling with increasing copper content.

References

1. Francois, B., Pierre, M. and Pierre, D., Three Conductivity State Circuit Element. US Patent 4,054,940, 18 Okt. 1977.
2. McHugh, J. P., Nalepa, P. J., Miller, R. C. and Dawson C. W., Method for Preparation of VO_2 Current Inrush Limiters for Incandescent Lamps. US Patent 4,056,378, 1 Nov. 1977.
3. Tosaki, H., Arima, H., Ikegami, A. and Kamata Y., Critical Temperature Sensitive Resistor Material. US Patent 4,603,008, 29 Jul. 1986.
4. Taketa, Y. and Furugochi, R., Switching and oscillation phenomena in $\text{SnO}_2\text{-VO}_x\text{-PbO}$ ceramics. *Appl. Phys. Lett.*, 1977, **31**(7), 405–406.
5. Pan, Y., Wu, G. Z. and Yi, X. S., Artificial thermistors prepared by incorporating V_2O_3 and VO_2 into polymer matrices. In *Proceedings of the International Conference Electronic Ceramics and Applications. Electroceramics V, Book 2*, ed. J. L. Baptista, J. A. Labrincha and P. M. Vilarinko. University of Aveiro, Aveiro, 1996, pp. 195–198.
6. Bruckner, W., Opperman, H., Reihelt, W., Terukow, J. I., Tschudnowski, F. A. and Wolf, E., *Vanadiumoxide: Darstellung, Eigenschaften, Anwendung*. Akademie-Verlag, Berlin, 1983.
7. Miller, V. I., Bondarenko, V. M., Perelyaev, V. A., Alekseyunas, A. A., Gechyauskas, S. I. and Sheikin, G. P., Synthesis and some properties of single-crystal and polycrystalline vanadium dioxide. *Liet. Fiz. Rinkinys*, 1977, **17**(5), 639–642.
8. Ivon, A. I., Kolbunov, V. R. and Chernenko, I. M., Stability of electrical properties of vanadium dioxide based ceramics. *J. Eur. Ceramic Soc.*, 1999, **19**(10), 1883–1888.
9. Ivon, A. I., Kolbunov, V. R. and Chernenko, I. M., Vanadium dioxide ceramics. *Inorganic Materials*, 1996, **32**(5), 555–557.
10. Murawski, L., Chung, C. H. and Mackenzie, J. D., Electrical properties of semiconducting oxide glasses. *J. Non-Cryst. Sol.*, 1979, **32**, 91–104.
11. Kirkpatrick, S., Percolation and conduction, I. Transport theory of percolation processes. *Rev. Mod. Phys.*, 1973, **45**, 574–610.
12. Shklovskii, B. I. and Efros, A. L., *Electronic Properties of Doped Semiconductors*. Springer-Verlag, Berlin, 1983.