

Stability of Electrical Properties of Vanadium Dioxide Based Ceramics

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Abstract

The influence of thermocycling process at VO₂ phase transition temperature ($T_t \approx 68^\circ\text{C}$) on the resistivity temperature dependences and dielectric constant (ϵ) of ceramics on a basis of VO₂ and V₂O₅–P₂O₅ glasses has been studied. The differential thermal analysis and dilatometric measurements for tested ceramics has been made. Vanadium dioxide based ceramics exhibits a variation of electrical properties with thermocycling. The resistivity increases, ϵ and electrical resistivity jump ρ_s/ρ_m in the vicinity of T_t decrease with a growth of a number of thermocycles. The reason of such behavior is microcracks formation due to a sharp variation of thermal expansion in the vicinity of T_t . After some repetition of thermocycling process the stabilization of ceramics electrical properties has been observed, but the resistivity jump ρ_s/ρ_m has been disappeared practically. Possible reasons of the stabilization have been discussed. The stabilization of electrical resistivity jump ρ_s/ρ_m ($\rho_s/\rho_m \sim 10^2$ – 10^3) after thermocycling for thin ceramic samples (a thickness ~ 0.4 mm or less) has been shown. © 1999 Elsevier Science Limited. All rights reserved

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1 Introduction

Vanadium dioxide (VO₂) is well known for its phase transition (PT) at $T_t \approx 68^\circ\text{C}$ from a monoclinic semiconducting phase to a tetragonal metal-like phase. This phase transition yields resistivity changes as large as 10^5 for single crystals.¹ This property finds an application for creation of critical thermistors and threshold switches.² The most

important practical results were obtained with VO₂ monocrystals^{1,3} and VO₂ thin films.^{2,4,5} The VO₂-based ceramics and composite materials are of significant interest concerning their application.^{6–9}

We have synthesised the ceramic material on a basis of VO₂ and vanadium phosphate glass (VPG).^{10,11} Soon after the synthesis this ceramic material at the temperature of PT exhibits the resistivity jump $\rho_s/\rho_m \sim 10^3$. Here ρ_s is resistivity in a semiconductor phase (at a temperature $T = 65^\circ\text{C}$), ρ_m is resistivity in a metallic phase (at a temperature $T = 75^\circ\text{C}$). However, after a cyclic heating-cooling through $T_t \approx 68^\circ\text{C}$ (thermocycling process) the value of the resistivity jump decreases and the ceramics resistivity increases. Such behaviour at thermocycling process is known to be usual for VO₂ crystals.¹²

The purpose of the present work is to study the reasons causing resistivity variation of vanadium dioxide based ceramics (VDBC) during thermocycling process and to search the ways for the stabilization of its electrical properties.

2 Experimental

The composition of ceramics in this work having (wt%) 80% VO₂ + 20% VPG has been studied. For the preparation of VPG, reagent-grade H₃PO₄ and vanadium pentoxide (V₂O₅) were mixed and dried at 100°C. Dry mixture was slowly heated to 400°C for dehydration. Dehydrated mixture has been melted at 800°C in air for 1 h and poured into a stainless steel mold. For the preparation of vanadium dioxide (VO₂) vanadium pentoxide (V₂O₅) was used. V₂O₅ was reduced to VO₂ by heating 2 mol V₂O₅ with 1 mol carbon (C) in an inert atmosphere.¹¹ VPG composed of (mol%) 80 V₂O₅ + 20 P₂O₅ has been used in this study. Initial components for vanadium dioxide based ceramics (VO₂ powder and VPG) were milled in a mortar. Then mixture was pressed and pellets obtained have

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been sintered at 900°C in a helium atmosphere for 0.5 h.

Samples for investigation were 12.4 mm in diameter and 2 mm thick. For electrical measurements In–Ga alloy has been used as electrode material. The measurements of d.c. resistivity temperature dependence were made during heating of sample at a rate of 0.5°C min⁻¹. The temperature was controlled, with an absolute error not more than ±0.1°C. Capacitance measurements were made at a frequency 1 MHz with relative error of ±1%. The differential thermal analysis (DTA) and dilatometric measurements were performed with OD-103A instrument. The samples for this measurements were 18 mm long. Thermocycling process through PT temperature was made at a rate of 10°C min⁻¹. Microstructure of VDBC was examined by means of scanning electron microscopy (SEM).

3 Results and Discussion

Figure 1 shows the typical temperature dependence of resistivity (ρ) for same sample of vanadium dioxide based ceramics (curves 1,3,4) after it was subjected to some numbers of thermocycles. Figure 2 shows the dependences of relative electrical resistivity ρ/ρ_0 of a ceramic sample above and below the PT temperature and value of resistivity jump (ρ_s/ρ_m) on a number of heating-cooling cycles (n). Here ρ_0 is an initial resistivity of a sample, ρ_s/ρ_m defined as the ratio of electrical resistivity at 65°C and 75°C.

The substantial increase of VDBC resistivity and decrease of ρ_s/ρ_m with a number of cycles have been observed. For all samples strongest changes ρ have been observed during some first thermocycles. For a sufficiently large n the stabilization of resistivity takes place. However at the temperature dependence of ρ the jump is practically absent (see Fig. 1, curve 4). The reduction of ceramic samples mechanical durability with the growth of thermocycle number n has also been noticed.

The decrease of vanadium dioxide based ceramics durability during thermocycling is in accordance with the change of volume during metal-semiconductor phase transition in VO₂. Non-uniform heating causes mechanical stresses at the interphase region of VO₂ crystal. These stresses result in the formation of microcracks which reduce VO₂ crystals durability and lead to increase of their resistivity.¹²

For the study of transition heat effect and linear sizes changes of VDBC in a region of temperature T_i the DTA and dilatometric analysis have been made. The results are shown at a Fig. 3. According to the dilatometric measurements (curve 3) the

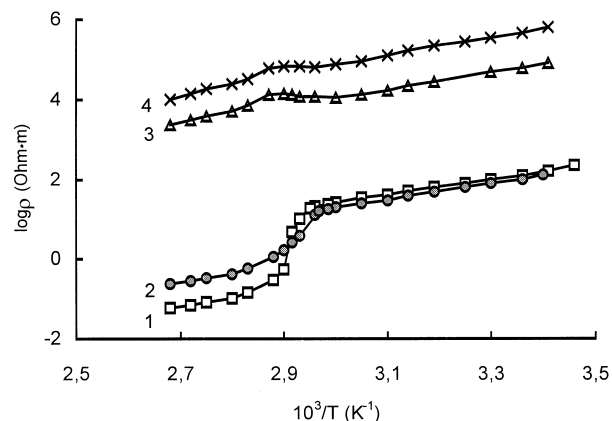


Fig. 1. Resistivity temperature dependences of vanadium dioxide based ceramics (1, 3, 4) without and (2) with epoxy resin impregnant. A number of thermocycles before measurement: 1, 2–0; 3–10; 4–20.

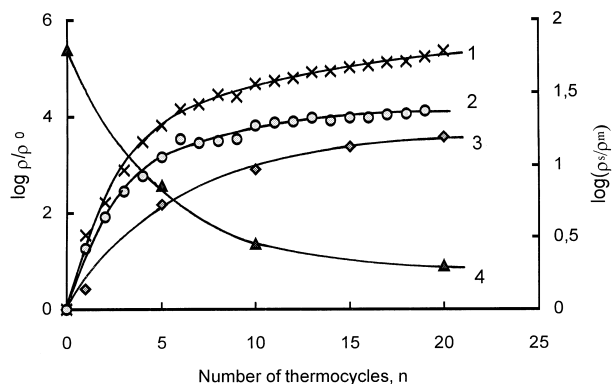


Fig. 2. (1, 2, 3) Dependences of relative electrical resistivity ρ/ρ_0 and (4) value of resistivity jump ρ_s/ρ_m on a number of thermocycles for VDBC (1, 3, 4) without and (2) with epoxy resin impregnant. Relative electrical resistivity measurements are made at (3) 20°C and (1, 2) 90°C.

sharp elongation of ceramic sample occurs during the transition to a metallic phase of VO₂. This elongation is usually registered at temperatures corresponding to the beginning of endothermic DTA peak when T_i is attained in the surface area of a sample. The relative elongation of vanadium dioxide based ceramics near T_i is $\Delta l_i/l = (1.24 \pm 0.12) \times 10^{-3}$. The study of DTA curves after various numbers of thermocycles allows us to make a conclusion that the intensity of endothermic peak is practically constant. It is illustrated by the data of Fig. 3 (curve 4) where the dependence of a relative area of this peak S/S_0 on a number of thermocycles n is given (S and S_0 are areas of endothermic peak at $n \neq 0$ and $n = 0$, respectively).

Thus the thermocycling process does not destroy the phase transition in VDBC. Increase of ρ and decrease of resistivity jump ρ_s/ρ_m are apparently caused by microcracks formation in ceramics.

Figure 4 shows the microstructure of vanadium dioxide based ceramics. VDBC structure includes

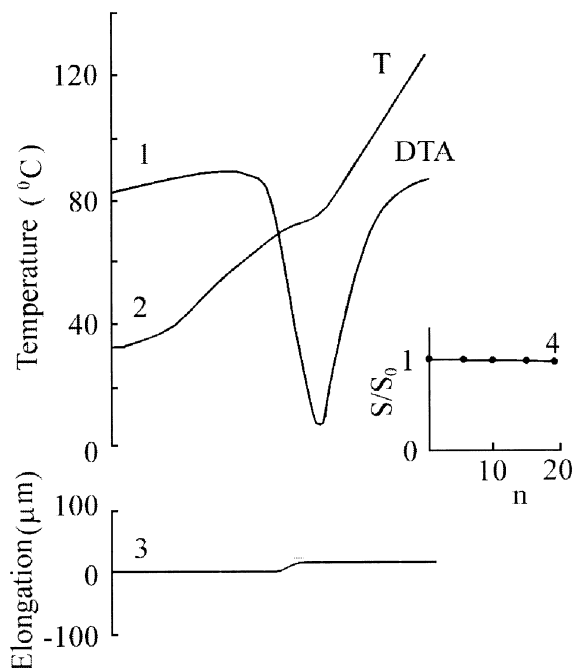


Fig. 3. Results of (1) DTA and (3) dilatometric analysis for vanadium dioxide based ceramics: 2, the temperature curve; 4, dependence of endothermic peak relative area on a number of thermocycles

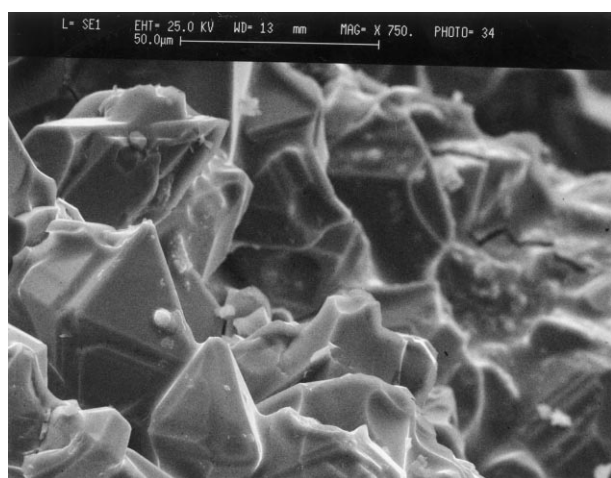


Fig. 4. Microstructure of ceramics on a basis VO_2 and $\text{V}_2\text{O}_5\text{-P}_2\text{O}_5$ glasses.

the following components: chaotically oriented VO_2 crystallites (size of crystallites is in a range 30–50 μm); inclusions of VPG and pores which are actually emptinesses formed between VO_2 crystallites during their growth. The crystallites of VO_2 form a random net in ceramics. The volume content of pores is 30–40%. This content exceeds the percolation threshold $x_c = 0.25$ in a 3-dimensional case.^{13,14} This is the reason for the open porosity of a sample and samples of ceramics are therefore pervious for liquids. That allows to prepare a composite material by the impregnation of VDBC by impregnant.

In the present work the epoxy resin as impregnant has been used. The typical resistivity temperature

dependence of VDBC composite is shown in Fig. 1 (curve 2). The comparison of this dependence with a similar dependence for a non-impregnated sample (see Fig. 1, curve 1) shows that after the filling of pores by impregnant the resistivity of vanadium dioxide based ceramics below T_t practically does not change, but above T_t it grows essentially. As a consequence the samples of impregnated ceramics have smaller value of resistivity jump ρ_s/ρ_m . The dependence of resistivity on a number of thermocycles n (see Fig. 2, curve 2) for impregnated VDBC is similar to the appropriate dependence for ceramics without impregnant. The only difference is that the resistivity jump disappears after the fewer number of thermocycles.

The data submitted above show that process of microcracks formation in ceramics impregnated with epoxy resin is stronger. It is caused probably by the space restriction for VO_2 crystallites during phase transition caused by epoxy resin in impregnated ceramics. Therefore the destroying action of stresses is amplified. It is necessary to note that filling of pores does not result in stabilization of ceramics electrical properties but the mechanical properties are stabilized. The impregnated VDBC keeps its high mechanical durability after great number of thermocycles.

The result obtained in the present work can be explained if to take into account the contribution of vanadium dioxide to electrical conduction of ceramics. The electrical resistance of a random network formed by VO_2 crystallites in ceramics defines this contribution. At non-uniform heating the sharp thermal expansion of ceramics in the vicinity of T_t leads to microcracks formation. The microcracks break off the bonds in VO_2 crystallites network and therefore microcracks decrease the contribution of VO_2 to electrical conduction of ceramics.

For description of such behavior the percolation theory^{13,14} can be used. In accordance with it the infinite cluster defines conductivity of disorderly system above the percolation threshold.¹⁴ Such cluster is an infinite random network formed by the component with high conductivity. The infinite cluster is absent below the percolation threshold. The high conductive component forms the finite clusters (isolated clusters) which are isolated from each other by the component with low conductivity. Therefore low conductive component defines the conductivity of disorderly system below the percolation threshold.

Vanadium dioxide is a high conductive component in ceramics, but microcracks, pores and inclusions of VPG are the low conductive components. The resistivity jump ρ_s/ρ_m in the vicinity of T_t will observe if vanadium dioxide defines the

electrical conduction of ceramic sample. It takes place if a percolation of electrical current into VO₂ crystallite network has been realized, i.e. this network is the infinite cluster or it consists from the isolated clusters with average size more than a size of ceramic sample in the direction of electrical field. Absent or weak ρ jump shows that VO₂ crystallite network consists from isolated clusters with average size less than a sample sizes.

The microcracks break off current percolation paths in VO₂ crystallite network resulting in the decrease of average size of VO₂ clusters. As consequence, the resistivity of ceramics increase with growth a number of thermocycles. The weak dependences of VDBC relative resistance on a number of thermocycles which is observed at large n (see Fig. 2) shows that process of percolation path destruction has a saturation. It is confirmed also by the study of dielectric constant (ϵ) of vanadium dioxide based ceramics (see Fig. 5). At large n values a weak dependence of ϵ on n takes place, too.

It is necessary to note that dielectric constant of VDBC is especially high at temperatures above T_i . It is a characteristic feature of heterogeneous materials consisting of the high conductivity grains which are separated by thin insulating layers.¹⁵ For such materials low-frequency dielectric constant is approximated by expression $\epsilon \approx \epsilon_s l_g / l_s$,¹⁵ where l_g is average grains size, ϵ_s and l_s are dielectric constant and average thickness of layers. In vanadium dioxide based ceramics with l_g it is possible to connect the average size l_c of isolated clusters within the limits of which the percolation over VO₂ crystallites takes place, l_s —with average thickness of microcracks l_m . The observed reduction of ϵ with the growth of n is apparently caused by the reduction of isolated clusters average size. After repeated thermocycling the average size of isolated clusters attains some constant meaning l_{c0} , that testifies to the end of microcracks formation process in

ceramics. Such behaviour can be explained if to take into account that at sufficiently large content of microcracks in ceramics VO₂ crystallites have an opportunity to expand into microcracks during phase transition thus reducing the stresses. The process of microcracks formation will be stopped when the change of an isolated cluster average size at PT does not exceed half of microcrack average size l_m . This requirement yields

$$L_{c0} \approx 0.5l_m / (\Delta l_t / l) \quad (1)$$

It is suggested that at large n dielectric constant ϵ_c of VDBC is $\epsilon_c \approx l_{c0} / l_m$ (here $\epsilon_m = 1$ is assumed for microcracks). Then from (1) we obtain such relationship:

$$\epsilon_c \approx (2\Delta l_t / l)^{-1} \quad (2)$$

This relationship gives $\epsilon_c \approx 400$ for the meaning of $\Delta l_t / l$ found in our experiment. Obtained value of ϵ_c is in accordance with VDBC dielectric constant above T_i at large n (see Fig. 5).

The absence of jump at a temperature dependence of resistivity at large n is caused by occurrence of percolation in a VO₂ crystallites only in limits of clusters which are isolated from each other by microcracks. It is necessary to note that resistivity of vanadium dioxide ceramics usually does not exceed 10⁵–10⁶ Ohm m and its activation energy is ~ 0.3 – 0.4 eV above and below T_i . Vanadium phosphate glasses¹⁶ have the same meanings of activation energy. This allows us to assume that conductivity of studied material after repeated thermocycling is determined by VPG inclusions. Apparently VPG inclusions form the electrical connection between VO₂ clusters isolated by microcracks.

It is necessary to expect the occurrence of resistance jump at PT temperature when a ceramic sample is polished up to thickness about the average size of isolated cluster l_{c0} . It is confirmed by the data of Fig. 6 obtained for VDBC impregnated by

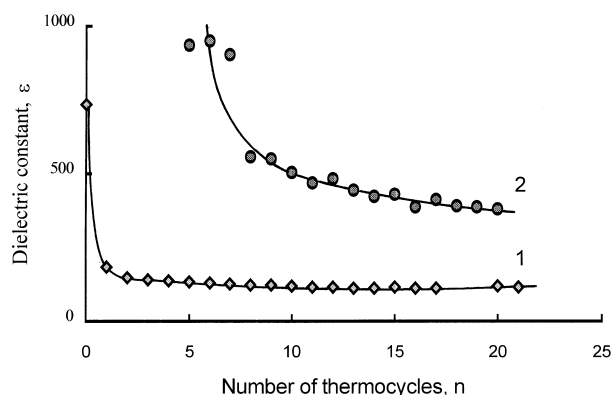


Fig. 5. Dependences of dielectric constant of VDBC on a number of thermocycles at (1) 20°C and (2) 90°C.

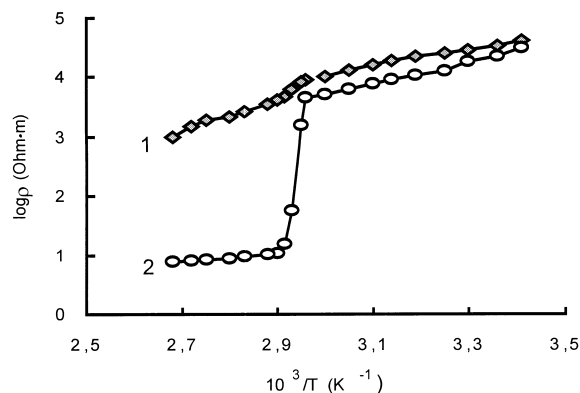


Fig. 6. Resistivity temperature dependences of VO₂-based ceramics after 20 thermocycles. Samples thickness are (1) 0.6 mm and (2) 0.25 mm.

epoxy resin and subjected to repeated thermocycling. As it is seen the jump of ρ for the initial sample of ceramics is practically absent but after polishing up to thickness of ~ 0.25 mm it appears.

The study of resistivity temperature dependence for the same sample with different thickness has shown that after repeated thermocycling the resistivity jump appears at thickness of about 0.3–0.4 mm or less. It gives a right to believe that for VO₂-based ceramics investigated in the present work the average size of stable isolated clusters within the limits of which percolation in VO₂ crystallites takes a place is ~ 0.4 mm. This meaning exceeds approximately (one order) the sizes of VO₂ crystallites in VDBC (see Fig. 4).

The obtained data allow us to assume that it is possible to ensure stability of electrical properties of VO₂-based ceramics during thermocycling if the thickness of a sample will not exceed the size of stable VO₂ clusters. It is confirmed by results given at Fig. 7. It can be concluded that for thin VDBC samples the relative change of resistivity on number of thermocyclings n is significantly less than for thick samples (see Fig. 2) and the value of a jump ρ_s/ρ_m does not decrease with n and even grows weakly. The last is probably caused by the fact that the data are obtained during heating of ceramic sample. In this case the value of ρ_s/ρ_m registered for small n is less because destruction of a part of current percolation paths in a network of VO₂ crystallites takes place at transition through T_t (for the same reason the large value of ρ_s/ρ_m during cooling is registered at small n). However, it is necessary to note that the behaviour of ceramic samples with thickness that do not exceed the average size of stable VO₂ clusters can also be explained by the quasi absence of thermal gradient in thin samples. The addition investigation is necessary to answer the question what from two aforesaid reasons is the essential reason for stability of electrical properties of the thin ceramic samples.

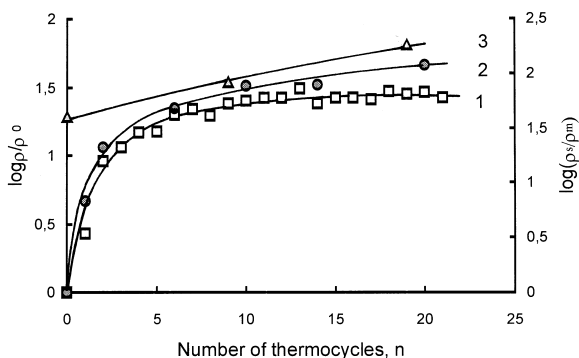


Fig. 7. (1, 2) Dependences of relative electrical resistivity ρ/ρ_0 and (3) value of resistivity jump ρ_s/ρ_m on a number of thermocycles for VO₂-based ceramics with epoxy resin impregnant. ρ/ρ_0 measurements are made at (2) 20°C and (1) at 90°C. Thickness of a sample is 0.3 mm

4 Conclusion

Ceramics on a basis VO₂ and V₂O₅-P₂O₅ glasses exhibits the sharp volume expansion at transition to a metallic phase of vanadium dioxide. The relative elongation of VO₂-based ceramics in the vicinity of phase transition temperature ($T_t \approx 68^\circ\text{C}$) is $\Delta l_t/l = (1.24 \pm 0.12) \times 10^{-3}$. A sharp volume change is a cause of microcracks formation into VDBC. Microcracks destroy the electrical current percolation paths into VO₂ crystallite network of ceramics. This process leads to unstability of VO₂-based ceramics electrical properties at cyclic heating-cooling through T_t . Unstability exhibits as resistivity increase and decrease of dielectric constant and electrical resistivity jump ρ_s/ρ_m in the vicinity T_t with growth of a number of thermocycles.

After a sufficiently large number of thermocycles the stabilization of VO₂-based ceramics electrical properties takes place. However the resistivity jump ρ_s/ρ_m is practically absented. It appears after polishing of ceramic samples up to thickness of ~ 0.4 mm or less.

The behaviour of ceramic samples at a large number of thermocycles can be explained by the completion of microcracks formation process and the appearance of the stable clusters within which the electrical current percolation into VO₂ crystallites takes place.

The stability of ρ_s/ρ_m value ($\rho_s/\rho_m \sim 10^2 - 10^3$) for thin samples of VO₂-based ceramics at thermocycling can be explained by the small thickness of a sample that do not exceed the average size of the stable VO₂ crystallites clusters or by the quasi absence of thermal gradient in such samples.

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