On the possibility of using detonation ceramic coatings as microwave energy absorbers

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On the possibility of using detonation ceramic coatings as microwave energy absorbers

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Abstract. The developed absorbing microwave energy coatings of TiO_2 and Al_2O_3/TiO_2 deposited by the detonation method were investigated in this work. Thermal cyclic tests of the obtained samples of different layer thickness on copper substrates were carried out, the phase composition of the obtained coatings was investigated, the effect of high-temperature heating in hydrogen on the phase composition of the coating and its stability was determined. The gas emission was studied on evacuated and degassed experimental model.

1. Introduction

Microwave energy absorbers using organic binding compounds (iron-based coatings of the "Alsifer" type) have found wide application in EVD manufacturing, but a significant disadvantage of this technology is a low adhesive strength of the coatings with the substrate (less than 10 MPa) [1]. Instead of a manual technology of applying absorbing coatings to increase the strength of their adhesion to the substrate a plasma method was proposed for forming the deposition of coatings with a coating layer thickness not more than 170 μm [2]. In order to further increase the adhesive strength as well as decrease the porosity and increase the coating layer thickness and, hence, the absorbing power, the detonation spraying was proposed to be used. The detonation spraying is pulsed in nature and is one of the types of gas-thermal spray coating. To accelerate and heat the particles of the sprayed material, the energy of the explosion of gas mixtures is used [3]. It has been established that detonation coatings of titanium oxide possess good absorbing properties in the wavelength range of 3–8 GHz [4].

The purpose of this work is to study: the formation of cracks in detonation coatings of TiO_2 and Al_2O_3/TiO_2 in the process of high-temperature heating in a hydrogen environment; X-ray phase analysis of the obtained coatings to determine the absorbing phase; gas emission of coatings in the vacuum volume of the evacuated experimental model.

2. Thermal cyclic testing of detonation coatings

Experiments and research were carried out on copper parts of the resonator unit of a high power klystron which were coated with a detonation method with TiO_2 and Al_2O_3/TiO_2 coatings with layer thicknesses of 0.3…2.0 mm. The applied powder material is TiO_2 and composite powder material is Al_2O_3/TiO_2. It is obvious that copper samples and ceramic materials deposited on them have a significant difference in the coefficient of linear thermal expansion (CLTE).

An integral part of the technological process of manufacturing electrovacuum devices (EVD) is the soldering of assemblies which occurs, as a rule, in hydrogen furnaces at a heating temperature of

780…1040°C (exposure at this temperature for 1–3 minutes). In most cases, the manufacturing of the device requires a multistage soldering with the number of steps from 3 to 5. Therefore, a necessary requirement for the samples with detonation coatings is the determination of appropriate number of thermal cycles, at the end of which the integrity and physical properties of the absorbers will remain unchanged.

The experimental studied were carried out as follows. Samples with sprayed coatings were placed into a hydrogen furnace and heated. The rate of temperature rise was 10–15 °C/min., the exposure at maximum temperature was 15 min., the rate of cooling the samples after heating to the specified soldering temperatures did not exceed 20 °/min. With an increase in the coating thickness its reliability decreases, and at temperatures of 1020…1040 °C, corresponding to the soldering temperature by high temperature solders, cracks were formed during the first cycling test (coating layer thickness is 0.6 mm). At the coating thickness layer of 0.6 mm and temperatures of 810…830 °C some insignificant cracks up to 10 μm were detected on the samples after the seventh heating cycle (figure 1(a)). In addition, there was found out an island copper coating on the surface of the ceramic coating under study on the samples after multiple thermal cyclic tests at maximum temperature of 1040°C (figure 1(a)). The copper islands can degrade the microwave energy absorption properties of detonation coatings.

With a thicker coating layer (2 mm) cracks were formed after the first thermal cycle at 830 °C, the size of such cracks increased and amounted to 30 μm (figure 1(b)). Delaminations of coatings and cracks after the thermal cyclic tests of all other investigated coatings of TiO_2 and Al_2O_3/TiO_2 were not detected.

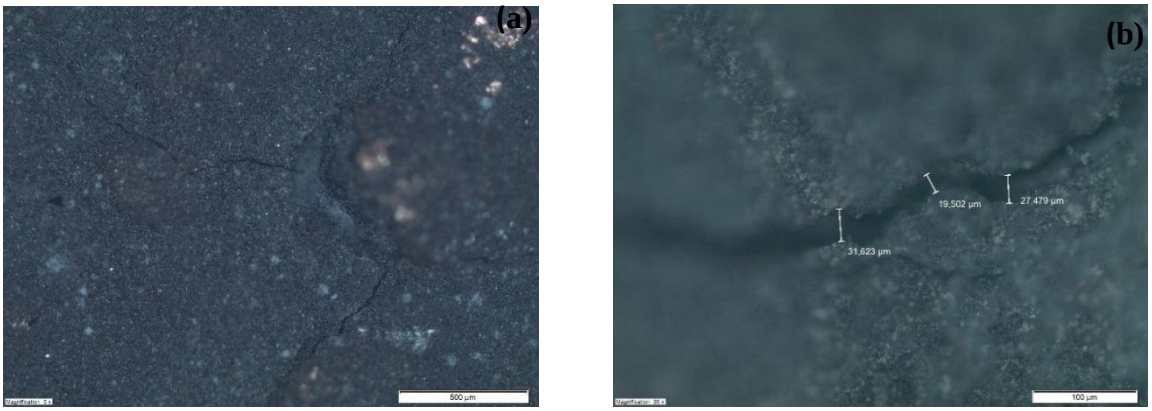

Figure 1. Cracks after the thermal cyclic tests of Al_2O_3/TiO_2 80/20 coatings in a hydrogen environment with a layer thickness of 0.6 mm **(a)** and of TiO_2 coatings with a layer thickness of 2 mm **(b)**.

3. The study of the phase composition

To study the phase composition of the detonation coating of titanium oxide and its stability when heated in hydrogen environment the method of X-ray phase analysis was used (XRPA). Quantitative phase analysis of the detonation coating sample was carried out using X-ray diffractometer DRON-8 (X-ray diffractometer of general purpose, Russia, St. Petersburg) with a cobalt anode (CoKα). A "θ-θ" scanning method was used with a horizontal location of the sample table on a main goniometer axis and a scintillation detector. X-ray photographs were taken at a goniometer radius of 200 mm with a scanning step of 2θ 0.01° and a speed of 1°/min in continuous mode. During X-ray phase analysis diffraction patterns were recorded at different points of the sample and the obtained results of measurements did not differ from each other.

Decoding of diffraction patterns showed that the initial powder of titanium dioxide was rutile (PDF № 01-076-0317) with a tetragonal crystal structure. In the obtained detonation coating titanium dioxide is formed as rutile (PDF № 01-076-0317) by weight 61% and titanium dioxide – as anatase (PDF № 01-075-2551) by weight 39% with tetragonal crystal structures.

The study of the original composite powder material Al_2O_3/TiO_2 80/20 showed that in the powder the original component was titanium dioxide (TiO_2) in the form of a rutile modification (PDF № 01-076-0317) with a tetragonal crystal structure. In this powder material alumina is present in the form of corundum with a modification of α-Al_2O_3 (PDF № 01-071-3629) with a rhombic crystal structure. The original powder material Al_2O_3/TiO_2 87/13 for detonation deposition contains a modification of alumina α-Al_2O_3 (PDF № 01-071-3629) and titanium dioxide (TiO_2) in the form of a rutile modification (PDF № 01-076-0317).

As a result of deposition of the powder material Al_2O_3/TiO_2 80/20 a coating was obtained which contains in its base complex oxides in the form of $Al_6Ti_2O_{13}$ (PDF № 01-078-7549) and Al_2TiO_5 (PDF № 01-070-1434) with orthorhombic crystal structures. In addition, a small amount of titanium dioxide was found in the form of anatase (less than 6% by weight, PDF № 01-075-2551) with a tetragonal crystal structure. The study of this coating showed the absence of absorbing properties of microwave energy in the range of 3–8 GHz [3].

As a result of the detonation spraying of a powder material of Al_2O_3/TiO_2 87/13 a coating was obtained in which X-ray phase analysis revealed the presence of alumina in the form of corundum (PDF № 01-071-3629) with a rhombic crystal structure $\alpha - Al_2O_3$ and alumina with a cubic crystal structure $\gamma - Al_2O_3$ (PDF № 00-050-0741). The presence of titanium oxide in the obtained coating was revealed only in the form of rutile (PDF № 01-076-0317) with a tetragonal crystal structure.

To study the stability of the phase composition of titanium oxide detonation coating we used the comparison of the original obtained radiograph with the radiograph taken after the thermal cycle of the sample. The sample passed a thermal test cycle at a heating temperature of up to 810–830 ^oC in a hydrogen environment with an exposure of two minutes. The comparison of radiographs showed that the number of peaks on radiographs and the magnitudes of their relative intensities remained unchanged. This study showed the stability of the phase composition of titanium oxide detonation coatings after thermal cycling testing in a hydrogen medium simulating soldering processes up to a maximum temperature of 830 ^oC.

4. Investigation of gas emission of detonation coatings

An experimental model (figure 2) was made to investigate gas emission from the pores of detonation coatings. It is a microwave S-band resonator with two copper plugs (resonator walls) soldered into it, on which coatings of TiO_2 with a layer thickness of 0.6 mm and Al_2O_3/TiO_2 87/13 with a layer thickness of 0.7 mm were applied. The magnetic electric discharge pump (MEDP) is built into this model which is a vacuum sensor after evacuation of this model.

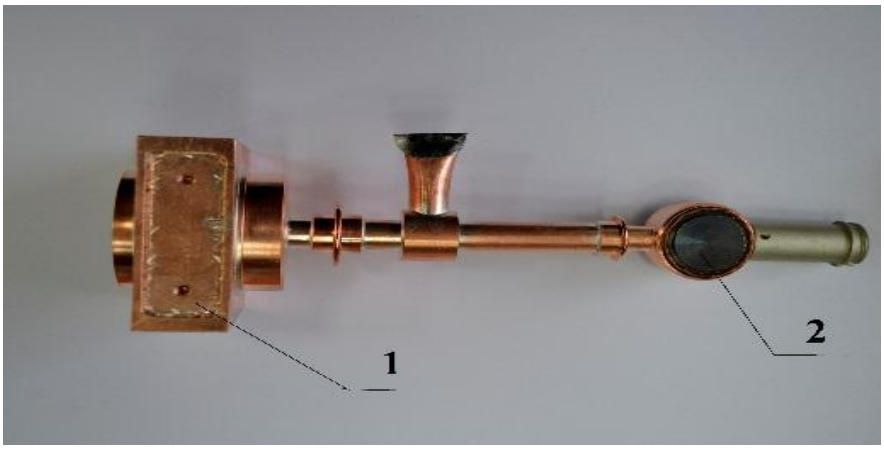

Figure 2. The experimental model for investigating vacuum properties of detonation coatings: 1. a part of the resonator unit with soldered parts with detonation coatings applied on them; 2. the magnetic electric discharge pump (MEDP).

The experimental model was evacuated according to the mode of technological process of evacuating a power EVD and unsoldering. The gas emission from the pores of detonation coating of the sealed experimental model was investigated by the value of MEDP maximum current surge at the moment of its activation after different exposure periods according to the developed method described in reference [5]. The condition of the shell tightness of the experimental model is fully achieved. A significant increase in the exposure time is almost equal to the sensitivity increase of such measurements.

Changes in MEDP maximum current after the exposure time of 12 days were not detected. Consequently, the detonation coatings, obtained from Al_2O_3/TiO_2 and TiO_2 materials in vacuum, do not emit gasses from the porous structure of the applied material. The accuracy of pressure measurement was $2 \cdot 10^{-6}$ Pa which corresponds to a gas flow less than 10^{-15} m^3Pa/s taking into account the exposure time of 12 days and the volume of the experimental model.

5. Results and discussion

Thermocyclic tests in hydrogen at maximum temperatures of 810–830 ^oC for detonation coatings from TiO_2 and composite materials Al_2O_3/TiO_2 on copper substrates showed that with coatings layer thicknesses up to 0.6 mm and the number of thermal cycles not exceeding 6, there are no visible coating defects. Tests at temperatures above 1000^{o}C lead to the destruction of detonation coatings on copper substrates.

The main microwave energy-absorbing phase in the wavelength range of 3–8 GHz in detonation coatings of titanium dioxide (TiO_2) and composite materials Al_2O_3/TiO_2 87/13, obtained by sintering and subsequent crushing, is titanium oxide in the form of a rutile modification. After treating the detonation coatings in hydrogen environment at temperatures of 810–830 ^oC the phase composition of titanium oxide coatings does not change.

Gas emission from detonation coatings inside the vacuum volume after pumping a sealed experimental model using MEDP was not detected.

6. Conclusions

Detonation coatings deposited from TiO_2 and composite materials Al_2O_3/TiO_2, can be used for further research as intravacuum absorbers of microwave energy on real EVD samples. Detonation coatings of TiO_2, Al_2O_3/TiO_2 have high adhesion strength with the substrate and the strength of the coating material itself, which allows: to exclude the appearance of free foreign particles of the coatings in the EVD; improve the reliability of the coatings of microwave-energy absorbers in microwave EVDs.

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References

[1] Pavlova M A, Rybkin V N and Nemogay I K 2009 *Elektronnaya tekhnika. Ser.1 SVCH-tekhnika* **503** 42–5
[2] Ilyin V N, Potapov Yu A, Smirnov V A and Drozdov S S 2002 *Scientific and technical conference "Electronic devices and devices of new generation": collection of conference materials (Saratov)* 75
[3] Ulyanitsky V Yu, Nenashev M V, Kalashnikov V V, Ibatullin I D, Ganigin S Yu, Yakunin K P, Rogozhin P V and Shtertser A A 2010 *News of the Samara Scientific Center of the Russian Academy of Science* **12** 569–75
[4] *Application № 2019106447 RF* – Priority 6.03.2019
[5] Korepin G F 1999 *Elektronnaya tekhnika. Ser.1 SVCH-tekhnika* **2** 42–3