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NEGATIVE THERMAL EXPANSION OF TITANIUM (III) OXIDE

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The aim of this work was to obtain and study the thermal properties of titanium (III) oxide as a possible component of solder powder compositions. Titanium (III) oxide was obtained by solid-phase sintering of titanium (IV) oxide and metallic titanium powders. It has been established that samples of titanium (III) oxide obtained by firing in a high vacuum atmosphere at 1450°C are characterized by negative thermal expansion in the temperature range of 20–425°C. The material exhibits the highest negative thermal expansion coefficient, equal to minus $340 \cdot 10^{-7}$ K^{-1} in the temperature range of 125 to 225ºC. According to the results of X-ray diffraction analysis, Ti_3O_5 is present in the obtained material together with the main Ti_2O_3 crystalline phase. The data of differential thermal analysis showed that the powder of titanium (III) oxide is sufficiently resistant to oxidation upon heating to 620°C; an intense oxidation of Ti_2O_3 with the formation of TiO_2 is observed at higher temperatures. The thermal treatment of the samples in the temperature range of 350–620ºC changes their color: from dark purple to deep blue. The results obtained in this work showed that titanium (III) oxide could be used as an additive allowing tuning the thermal expansion of composite soldering materials. Changing the amount of Ti_2O_3 makes it possible to create composite materials with positive, negative and near-zero coefficients of thermal expansion.

Introduction

Low-melting glasses with a high lead oxide content are widely used as solders in connecting parts of various metals and ceramics in electrical engineering and microelectronics. Glasses with a high lead oxide content have a high coefficient of linear thermal expansion (CTE) in the range of 90–120 10^{-7} K^{-1}, making it impossible to obtain a matched seal with materials with lower CTE values (VK-95 ceramics, alloys 29NK, 42N, and others).

To reduce the CTE value of low-melting sealing glasses, crystalline compounds with a low positive or negative CTE value are introduced into the powder compositions based on them. In this regard, much attention has recently been paid to the search and study of such substances. The properties and structures of known crystalline substances with negative CTE values are shown in Table 1 [1-3]. The properties and structures of known crystalline substances with negative CTE values are shown in Table 1 [1-3].

However, not all of these substances can be used as composite fillers; the list of such compounds is quite limited ($PbTiO_3$, $LiAlSiO_4$, ZrW_2O_8, $NaZr_2(PO_4)_3$). In most cases, this is due to the complexity and high cost of their synthesis and the limited temperature range in which they exhibit a negative CTE value. Furthermore, the potential of these substances to be used as composite fillers is highly dependent on their resistance to the aggressive action of glass melt. Pushkareva et al. [4] report that a promising filler for low-melting sealing and solder glasses can be crystalline titanium (III) oxide, which, according to [5–6], can be obtained by reducing titanium (IV) oxide with coal, hydrogen, calcium, magnesium, or titanium.

Table 1

Crystalline substances with negative CTE value

No.	Chemical compound	Crystal system	CTE, $\alpha \cdot 10^{-7}$, K^{-1}	Temperature, °C
1	$NaZr_2(PO_4)_3$	Hexagonal	–4	20–750
2	$KZr_2(PO_4)_3$	Hexagonal	–17	20–750
3	$BaAl_2B_2O_7$	Hexagonal	–16	20–600
4	$Sc_2W_3O_{12}$	Rhombic	–22	20–800
5	$Y_2W_3O_{12}$	Rhombic	–42	20–830
6	$Lu_2W_3O_{12}$	Rhombic	–68	120–630
7	$NbOPO_4$	Tetragonal	–37	400–700
8	$PbTiO_3$	Tetragonal	–33	20–400
9	$LiAlSiO_4$	Trigonal	–86	20–1000
10	$ZrMo_2O_8$	Cubic	–50	20–300
11	ZrV_2O_7	Cubic	–71	120–230
12	ZrW_2O_8	Cubic	–87	20–160
13	$Zn(CN)_2$	Cubic	–181	0–32

In this regard, this work aimed to synthesise and study the thermal properties of titanium (III) oxide as a possible component of solder powder compositions based on low-melting glasses.

Materials and Methods

In the work, Ti_2O_3 was obtained by reducing titanium (IV) oxide with metallic titanium. A mixture of powders of titanium dioxide and titanium metal was mixed in amounts corresponding to the following reaction:

$$3TiO_2 + Ti \rightarrow 2Ti_2O_3$$

The molding mass was obtained by moistening a mixture of these powders with a 3% solution of polyvinyl alcohol and then averaging it in a porcelain mortar. Samples were formed from the obtained mass by semi-dry pressing for their subsequent heat treatment. The samples were pressed in two stages on a PSU-10 hydraulic press, the maximum specific pressure of pressing was 50 MPa. The formed samples were subjected to preliminary firing in a laboratory muffle furnace at 550°C for 1 hour to strengthen them and remove the organic binder.

High-temperature firing of the samples was carried out under the conditions of the department of structural ceramics and cermets of the Institute for Problems of Materials Science of the National Academy of Sciences of Ukraine. The samples were fired in an SShVL-01 vacuum furnace, in which the vacuum (~ 10^{-5} mm Hg) was reached with the help of a backing and diffusion pumps, and then they were heated to 1450°C and held at this temperature for 1 hour. The sintered material produced exhibited a saturated dark purple color, as is typical of Ti_2O_3.

Powders with an average particle size of 100 μm obtained by grinding sintered samples in an agate mortar were measured by X-ray phase and differential thermal analysis. X-ray phase analysis of the powders was carried out on a DRON-ZM diffractometer in Co-Kα radiation. Identification of crystalline phases based on diffraction patterns was carried out using an ASTM X-ray file. Phase transformations were investigated using the differential thermal analysis method on a Q-1500D derivatograph in the temperature range of 20-1000°C at the heating rate of 5°C/min. The change in the linear dimensions of the sintered samples during heating was measured with a DKV-5A quartz dilatometer according to GOST 10978-83.

Results and discussion

According to the data of X-ray phase analysis (Fig. 1), in the material, which was obtained by sintering at 1450ºC in a high vacuum atmosphere, in addition to the main crystalline phase Ti_2O_3, there is also a small amount of the Ti_3O_5 phase. The formation of the Ti_3O_5 phase in the sintered composite can be due to the low sintering temperature and the short heat treatment period at this temperature. According to the literature data [5], for the complete reduction of titanium dioxide to

titanium sesquioxide, regardless of the exposure time, the sintering temperature should not be lower than 1550ºC.

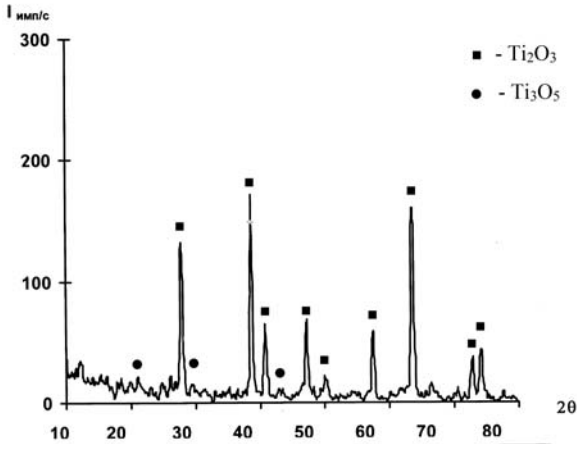

Fig.1. X-ray diffraction pattern of Ti_2O_3 powder

The results of derivatographic studies of the Ti_2O_3 powder are shown in Fig.2.

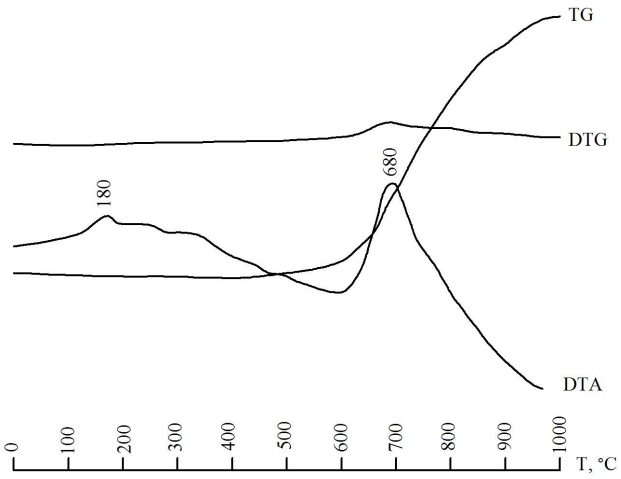

Fig. 2. Changes in TG, DTG and DTA during heating of Ti_2O_3 powder

The course of the DTA curve shows that when the Ti_2O_3 powder is heated to a temperature of 1000°C, two exothermic reactions occur in it. A small exothermic effect at a temperature of 180°C is due to possible modification transformations of α-Ti_2O_3↔β-Ti_2O_3 [5-6]. The second exothermic effect, which is observed in the temperature range of 600–1000°C, is characterized by a maximum at a temperature of 680°C and is accompanied by an increase in the sample weight. The TG and DTG show that the weight gain starts at temperatures above 620°C and reaches 10.9 wt% at 1000°C.

X-ray phase analysis of the powder heat-treated at 680–700°C (Fig. 3) showed that it consists mainly of rutile, and the increase in weight of the studied samples is associated with the oxidation of Ti_2O_3 to TiO_2, which occurs most intensely at 680°C.

Accordingly, titanium (III) oxide powder is quite stable against oxidation when heated to 600–620°C. Furthermore, following additional heat treatment in the temperature range of 350–620°C, the colour of the investigated samples changed from dark purple to intense blue. According to the authors of [7, 9], this may be caused by the formation of the Ti_3O_5 compound on the surface of the studied samples of sintered materials, as an intermediate product of the oxidation of Ti_2O_3 to TiO_2.

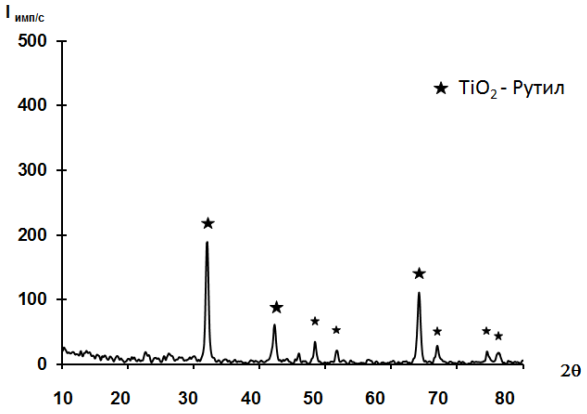

Fig. 3. X-ray diffraction pattern of Ti_2O_3 powder heated to 700°C

Dilatometric studies in the temperature range from 20 to 520°C showed that the resulting sintered Ti_2O_3 sample, unlike most glassy and ceramic materials, does not expand, but contracts (Fig. 4) when heated to 400–425°C. It should be noted that changes in the relative linear dimensions of the investigated sample, both during heating and cooling, are described by an S-shaped curve.

The results of the calculation of CTE values, which were obtained using the DTA curve, are shown in Table 2.

The investigated Ti_2O_3 sample exhibits negative thermal expansion when heated to 425°C, with the maximum negative value in the temperature range 125-225°C. Such reversible compression-expansion of the produced material appears to be related with the

probable modification transformation of α-$Ti_2O_3 \leftrightarrow \beta$-$Ti_2O_3$ at 180°C and subsequent surface oxidation of $Ti_2O_3 \leftrightarrow Ti_3O_5$ above 350°C. This is confirmed by a change in the trend of the dilatometric and differential thermal curves at 350°C, as well as a change in the color of the sample from dark violet to deep blue.

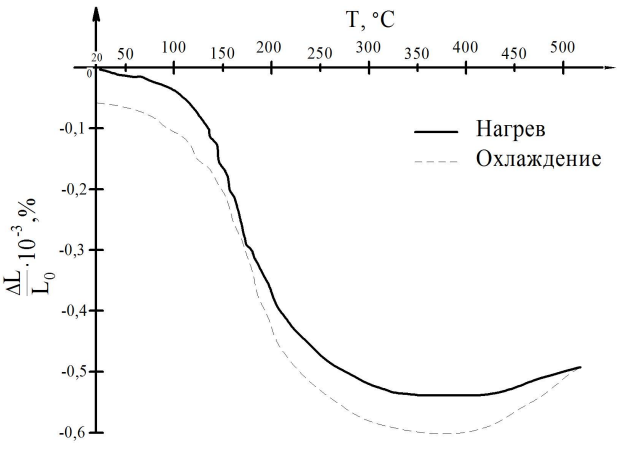

Fig.4. Dilatometry curve of Ti_2O_3 sample
—— - heating; – – – - cooling

Table 2

LCTE values of sintered Ti_2O_3 in various temperature ranges

No.	LCTE, $\alpha \cdot 10^{-7}$, K^{-1}	Temperature range, °C
1	–65	25–125
2	–340	125–225
3	–93	225–325
4	–1	325–425
5	57	425–520

In order to establish the possibility of using titanium (III) oxide as a component of solder powder compositions, we studied its effect on the thermal expansion coefficient of solder glass obtained in the $PbO–ZnO–B_2O_3–SiO_2$ system. This low-melting glass is characterized by a low softening temperature (310°C) and a high CTE value ($\alpha_{20–200} = 98 \cdot 10^{-7}$ K^{-1}), which does not allow obtaining a matched junction with VK-95 ceramics, the CTE of which is $\alpha_{20–200} = 58 \cdot 10^{-7}$ K^{-1}. The research results showed that the addition of 4 wt.% titanium (III) oxide to the powder composition reduces the thermal expansion coefficient of the solder glass from $98 \cdot 10^{-7}$ K^{-1} to $55 \cdot 10^{-7}$ K^{-1} without affecting the fusibility of glass solder. Depending on the Ti_2O_3 content in the solder powder composition, the solder softening temperature was 300–315°C, and the soldering temperature was 390–410°C.

Conclusions

It has been established that in the sintered sample of Ti_2O_3, obtained by firing at 1450ºC a mixture of titanium dioxide and titanium metal powder in a high vacuum atmosphere, in addition to the main crystalline phase Ti_2O_3, there is also a small amount of Ti_3O_5. It is noted that titanium (III) oxide powder obtained by grinding a Ti_2O_3 sample is sufficiently resistant to oxidation when heated to 620°C. At higher temperatures, intense oxidation of Ti_2O_3 to TiO_2 is observed. Dilatometry showed that the investigated material had negative thermal expansion in the temperature range of 20–425ºC and may thus be employed as a component of solder powder compositions based on low-melting glass.

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НЕГАТИВНЕ ТЕПЛОВЕ РОЗШИРЕННЯ ОКСИДУ ТИТАНУ(III)

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Метою цієї роботи було отримання і дослідження теплових властивостей оксиду титану(III), як можливого компонента порошкових композицій для спаювання. Оксид титану(III) був одержаний твердофазним спіканням порошків оксиду титану(IV) і металевого титану. Встановлено, що зразки оксиду титану(III), отримані випалом в атмосфері високого вакууму при температурі 1450°С, характеризуються негативним тепловим розширенням в інтервалі температур 20–425°С. В температурному інтервалі 125–225°С матеріал характеризується найбільші негативним значення коефіцієнта теплового розширення, рівним мінус 340·10^{-7} К$^{-1}$. За даними рентгенофазового аналізу в одержаному матеріалі крім основної кристалічної фази Ti_2O_3 присутні домішки Ti_3O_5. Методом диференційно-термічного аналізу встановлено, що порошок оксиду титану(III) досить стійкий до окислення при нагріванні до 620°С, при більш високій температурі спостерігається інтенсивне окислення Ti_2O_3 до TiO_2. При термічній обробці досліджуваних зразків в інтервалі температур 350–620°С, візуально встановлено зміна їх забарвлення від темно-фіолетового до насиченого синього кольору. Отримані в даній роботі результати показують можливість застосування оксид титану(III) в якості добавки регулюючої теплове розширенням композиційних матеріалів для спаювання. Змінюючи кількість Ti_2O_3, можна створювати композиційні матеріали з позитивним, негативним і майже нульовим коефіцієнтом теплового розширення.

Ключові слова: негативне теплове розширення, оксид титану(III), матеріали для спаювання, композиційні матеріали.

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Keywords: negative thermal expansion; titanium (III) oxide; soldering materials; composite materials.

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