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Low-melting composite glass solders with low thermal expansion

V.I.Goleus, Yu.S.Hordieiev, A.V.Nosenko

Ukrainian State University of Chemical Technology, 8 Haharina Ave., 49005 Dnipro, Ukraine

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Low-melting composite glass solders based on the lead borosilicate glass with the lead titanate and titanium (III) oxide additions for jointing of the constructional materials with low values of the thermal coefficient of linear expansion at a temperature were investigated. The introduction into the compound of Ti_2O_3 additions powder composition based on low-melting glass made it possible to decrease the TCLE of glass solder from $105 \cdot 10^{-7}$ K^{-1} to $1 \cdot 10^{-7}$ K^{-1} being decreased to $53 \cdot 10^{-7}$ K^{-1} with the introduction of $PbTiO_3$ addition. Concluded that when sintering of powder compositions, the titanium (III) oxide partially dissolves in the glass melt along with the absence of chemical interaction between the glass melt and the lead titanate. The titanium (III) oxide is the most prospective component of the solder powder composition, which minor additions (5 to 8 percent by weight) ensure the highest fluidity of the glass solder as well as the obtainment of ceramic-metal seal agreed as per the TCLE.

Keywords: low-melting glass, composite glass solders, thermal expansion, ceramics, lead titanate, titanium (III) oxide.

Исследованы легкоплавкие композиционные стеклоприпои на основе свинцовоборосиликатного стекла с добавками титаната свинца и оксида титана (III) для соединения конструкционных материалов с низкими значениями температурного коэффициента линейного расширения. Введение в состав порошковой композиции на основе легкоплавкого стекла добавок Ti_2O_3 позволило снизить ТКЛР стеклоприпоя от $105 \cdot 10^{-7}$ К$^{-1}$ до $1 \cdot 10^{-7}$ К$^{-1}$, а при введении добавки $PbTiO_3$ — до $53 \cdot 10^{-7}$ К$^{-1}$. Установлено, что при спекании порошковых композиций происходит частичное растворение оксида титана (III) в расплаве стекла, а также отсутствие химического взаимодействия между расплавом стекла и титанатом свинца. Наиболее перспективным компонентом порошковой припоечной композиции является оксид титана (III), небольшие добавки (5÷8 мас.%) которого обеспечивают наибольшую текучесть стеклоприпоя и получение согласованного по ТКЛР металлокерамического спая.

Легкоплавкі композиційні склоприпої з низьким тепловим розширенням. *В.І.Голеус, Ю.С.Гордєєв, О.В.Носенко.*

Досліджено легкоплавкі композиційні склоприпої на основі свинцевоборосилікатного скла з добавками титанату свинцю та оксиду титану (III) для з'єднання при температурі конструкційних матеріалів з низькими значеннями температурного коефіцієнта лінійного розширення. Введення до складу порошкової композиції на основі легкоплавкого скла добавок Ti_2O_3 дозволило знизити ТКЛР склоприпою від $105 \cdot 10^{-7}$ К$^{-1}$ до $1 \cdot 10^{-7}$ К$^{-1}$, а при введенні добавки $PbTiO_3$ — до $53 \cdot 10^{-7}$ К$^{-1}$. Встановлено, що при спіканні порошкових композицій відбувається часткове розчинення оксиду титану (III) у розплаві скла, а також відсутність хімічної взаємодії між розплавом скла та титанатом свинцю. Найбільш перспективним компонентом порошкової композиції припою є оксид титану (III), невеликі добавки (5÷8 мас.%) якого забезпечують найбільшу плинність склоприпою та отримання узгодженого за ТКЛР металокерамічного спаю.

1. Introduction

Low-melting glasses and composite materials on their base are widely used in the instrument engineering as the solders for jointing of various components of the glass, ceramics, metals and their alloys [1, 2]. When heating to the high temperatures, many materials used in the manufacturing of microelectronic devices are subjected to oxidation, deformation, and rupture. Therefore, when producing the pressure-tight ceramic-metal compounds, the soldering temperature in many cases shall not exceed 450°C. However, low-melting glasses and melts characterized by an adequate fluidity at the specified temperature are also distinguished by excessively high values of the thermal coefficient of linear expansion (TCLE), which are approximately twice as large as the TCLE values of materials being liable for soldering ($50 \div 65 \cdot 10^{-7}$ K^{-1}). Therefore, the substantial thermal stresses occur in the solders formed with the help of such low-melting glasses, which can lead to their fracture.

In view of the aforementioned, the composite powder mixtures of glass with the crystalline substances being distinguished by the TCLE low values are generally used for jointing corundum-based ceramics (VK-94, VK-95) with various alloys (29NK, 42N and others) at a temperature of ≤450°C agreed as per the TCLE. According to the data [2–5], $PbTiO_3$ and Ti_2O_3 can be designated as such the most prospective substances having the following average TCLE values: $-10 \cdot 10^{-7}$ K^{-1} and $-194 \cdot 10^{-7}$ K^{-1} in the temperature range from 20 to 200°C.

The objective of the work is to investigate an possibility for producing low-melting composite glass solders based on the lead borosilicate glass with the lead titanate or titanium (III) oxide additions for jointing of the constructional materials with the TCLE low values ($50 \div 65 \cdot 10^{-7}$ K^{-1}) at a temperature of ≤450°C.

2. Experimental

Low-melting glass with the following composition (molecular percent): PbO — 55, ZnO — 5, B_2O_3 — 25, SiO_2 — 15 being preliminary ground in the planetary mill to the specific surface of ~ 2500 cm^2/g were used to manufacture the solder compositions, which compounds are set forth in Table 1 [6]. The crystalline components of the solder compositions of titanium (III) oxide and lead titanate were also ground to the specific surface of 1500÷2000 cm^2/g.

Batch of solder compositions were prepared by mixing of the primary powder components in a ball mill up to producing a homogeneous mixture. The samples for the determination of basic properties of glass solders by the semi-dry pressing method followed by their sintering at a temperature ranging from 420 to 450°C were moulded from the batch materials produced in such a way.

The TCLE of glass solders in the temperature range from 20 to 200°C and their initial softening point (Mg) were determined

Table. Compounds of solder compositions and properties of glass solders

Item No.	Content of the components, wt.%			Properties of glass solders		
	Glass	Ti_2O_3	$PbTiO_3$	TCLE, $\alpha_{20-200} \cdot 10^7$, K^{-1}	Mg, °C	Fluidity L, mm
1	100	–	–	105	330	9.2
2	95	5	–	71	310	8.7
3	92	8	–	50	310	8.5
4	90	10	–	36	310	8.4
5	87	13	–	29	320	8.2
6	85	15	–	26	325	8.0
7	82	18	–	19	325	7.6
8	80	20	–	1	325	7.2
9	90	–	10	95	315	9.0
10	80	–	20	80	320	8.5
11	70	–	30	76	320	8.2
12	60	–	40	69	325	7.6
13	50	–	50	53	325	6.9

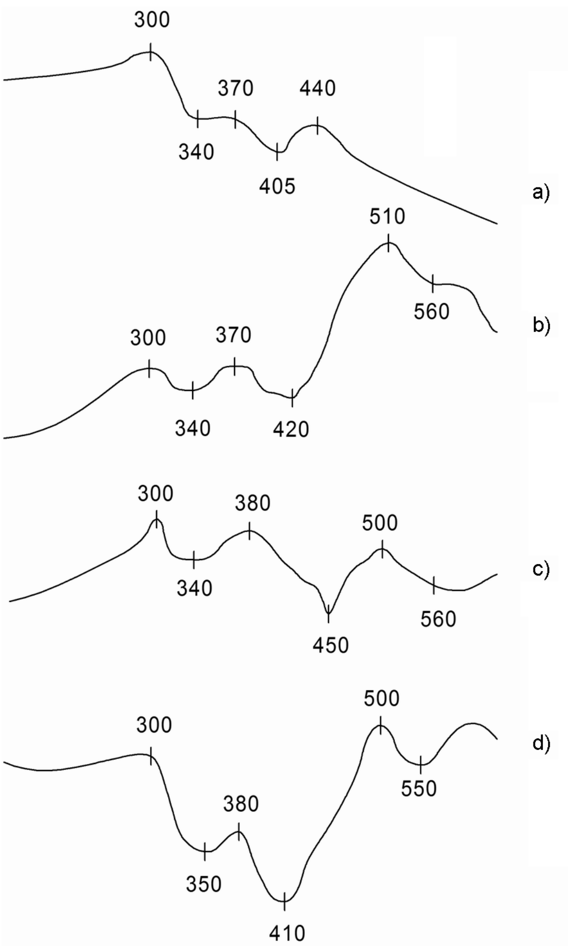

Fig. 1. Thermograms of powders: a) primary glass; b) glass with the addition of 30 wt.% $PbTiO_3$, c) glass with the addition of 50 wt.% $PbTiO_3$; d) glass with the addition of 10 wt.% Ti_2O_3.

on a quartz dilatometer in accordance with GOST 10978-2014.

The fluidity of glass solder melt (L) was assessed by the diameter of a droplet formed while spreading of a pellet with the diameter of 5 mm and 5 mm high pressed of the experimental batch materials over the surface of VK-95 ceramics within 20 min at a temperature of 450°C.

An X-ray phase analysis of the glass solders was performed on X-ray diffractometer DRON-3M in Co–Kα radiation; with this end in view, the sintered samples were preliminary ground in an agate mortar until passage through sieve No. 0063. The crystalline phases were identified with the help of the ASTM X-ray card catalogue.

The investigation of phase changes proceeding in the batch materials of glass solders while their heating was performed on the derivatograph Q-1500 D in the temperature range from 20 to 600°C at the rate of temperature rise from amouning to 5°C/min.

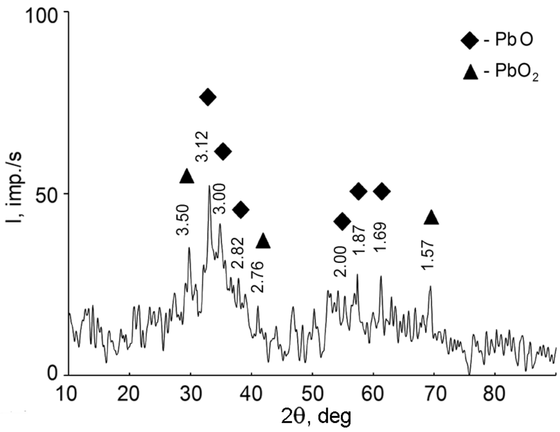

Fig. 2. X-ray diffraction pattern of primary glass after heat treatment at a temperature of 440°C within 1 h.

The IR absorption spectra were recorded on the IRAffinity-1S Fourier transform infrared spectrophotometer (Shimadzu, Japan) in the range of 1600 to 400 cm^{-1}. The samples were prepared by the method of pressing of pellets of the powders under investigation with KBr. Preliminary crushed before passage through sieve No. 0063 powders of: glass, titanium (III) oxide, and sintered glass composition batch were used for the investigation.

3. Results and discussion

Thermographic investigations (Fig. 1) of the powder compositions have shown that the glass transition temperature (t_g) of the primary glass and the compositions based on it is equal to ~ 300°C. Value t_g of the glass solders is lower than their dilatometric softening point (Mg) at an average by 15 to 30°C. Heating of glass powder over the temperature Mg causes its sintering (335 to 370°C) and crystallization at a temperature over 405°C (the exothermic effect with maximum at a temperature of 440°C), which is confirmed by the data of X-ray phase analysis (Fig. 2). Low-intensity diffraction maxima on the X-ray diffraction pattern can be supposedly designated as the lead oxides PbO and PbO_2.

Heating of the powder compositions of primary glass with the additions of Ti_2O_3 (Fig. 1, d) and $PbTiO_3$ (Fig. 1, b; c) over the temperature Mg causes their sintering in the temperature range from 335 to 390°C. The introduction of aforementioned additions into the compound of powder composi-

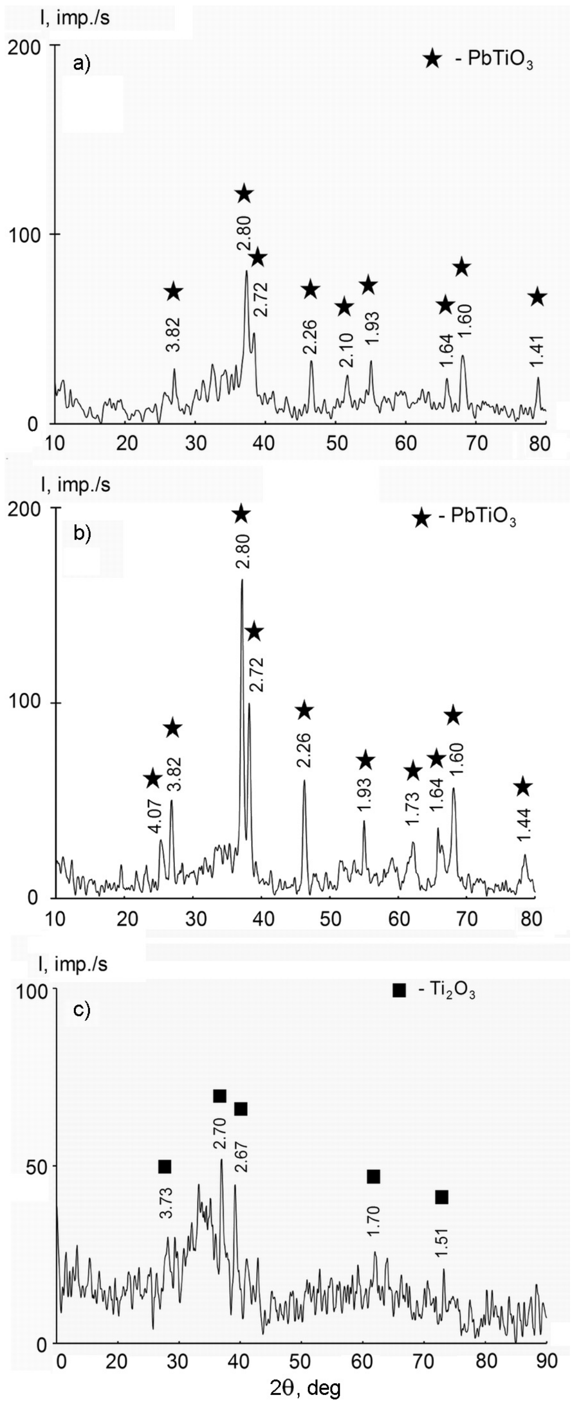

Fig. 3. X-ray diffraction patterns of the glass solders based on the powder compositions with the content of: a) 30 wt.% $PbTiO_3$; b) 50 wt.% $PbTiO_3$; c) 20 wt.% Ti_2O_3.

tion also promotes a shift of the glass crystallization interval to the higher-temperature region (ranging from 450 to 530°C). In view of the fact that the glass crystallization as a rule decreases the spreadability of glass smelt over the ceramic surface, it can be assumed that a temperature ranging from 420 to 450°C is the most acceptable temperature for obtainment of junctions being based on the experimental glass.

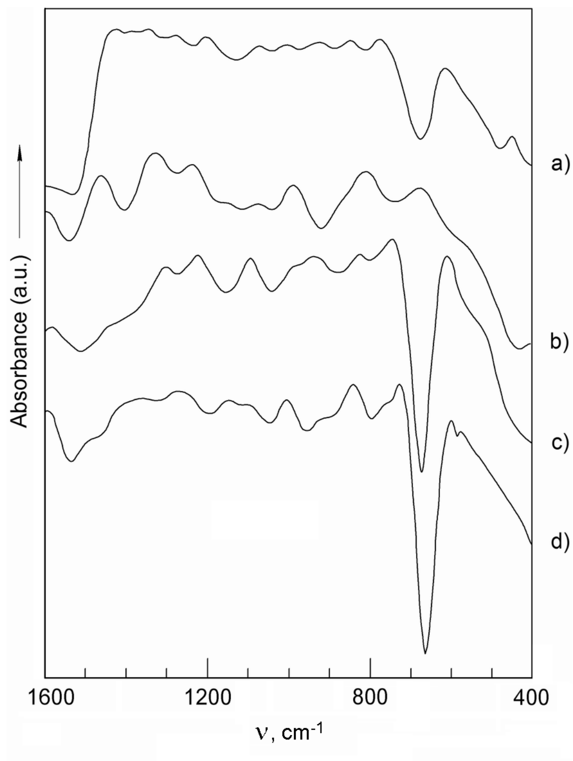

Fig. 4. IR absorption spectra: a) primary glass; b) glass solder with 20 wt.% Ti_2O_3; c) titanium (III) oxide.

The formation of possible products of chemical interaction between the glass melt and the crystalline fillers at the indicated temperature was assessed according to the data of X-ray phase analysis (Fig. 3) and IR spectroscopy (Fig. 4). As it follows from the data of Fig. 4, the crystalline-phase composition of the experimental glass solders consists only of the crystalline substances being found in the powder compositions, that is the lead titanate and titanium (III) oxide. At the same time, it is necessary to take note of low intensity of the diffraction maxima on the X-ray diffraction pattern of glass solder No. 8 containing 20 percent by weight of Ti_2O_3 (Fig. 3, c) making it possible to assume that the titanium (III) oxide has partially dissolved in the glass melt.

The data of spectral absorption of the IR rays (Fig. 4) make it possible to assess changes in the anion framework structure of the primary glass (Fig. 4, a) when its melt interacts with the crystalline titanium (III) oxide (Fig. 4, c).

Partial dissolution of titanium (III) oxide in the glass melt (Fig. 4, b) results in the decrease of total intensity of bands in the region of 1300 to 1500 cm^{-1} and their shift closer to 1200 cm^{-1} probably being associated with the valence vibrations of the boron-oxygen linkages between [BO_3] and [BO_4] groups. The presence of an absorption band with the maximum of 1083 cm^{-1} is indicative of the increase of [BO_4] groups due to transition of [BO_3] into [BO_4] [7—9]. The appearance of a new absorption peak with the maximum of 742 cm^{-1} characteristic of the vibration of Ti–O linkages in [TiO_4] groups is indicative of partial dissolution of the crystalline filler in the primary glass melt. Therefore, partial dissolution of Ti_2O_3 in the glass melt promotes strengthening of the structural framework of the primary glass due to the formation of [BO_4] and [TiO_4] tetrahedrons [10–12].

The presence of basic absorption bands in the regions of 800 to 900 cm^{-1} and 550 to 650 cm^{-1} stipulated mainly by the deformation vibrations of Ti–O linkages in [TiO_6] groups is observed in the IR spectra of glass solder and crystalline titanium (III) oxide [10, 11].

Therefore, in view of the data of X-ray phase analysis and IR spectroscopy, the glass solders under investigation can be considered as the composite materials, which properties are additively dependent on the content of glassy and crystalline phases in their composition being assessed by the weighted average values.

The results of experimental determination of glass solder properties are indicative of the fact that the introduction of the lead titanate and titanium (III) oxide additions into their composition promotes a considerable decrease in the TCLE values and the fluidity of solders under investigation (Table).

At the same time, it has been established that the TCLE experimental values are reasonably approximated by the equation of straight line in dependence on the content of the lead titanate in their composition (Fig. 5, line *1*). Besides, these values are also equal to the weighted average values being obtained of the TCLE values of primary glass and the lead titanate (Fig. 5, line *2*). Therefore, it can be concluded that the TCLE values of glass solders with the lead titanate additions are additively dependent on the content of glassy and crystalline phases in their composition. This is an indirect proof of the absence of chemical interaction between the glass melt and the lead titanate crystals at the sintering temperatures of powder composition.

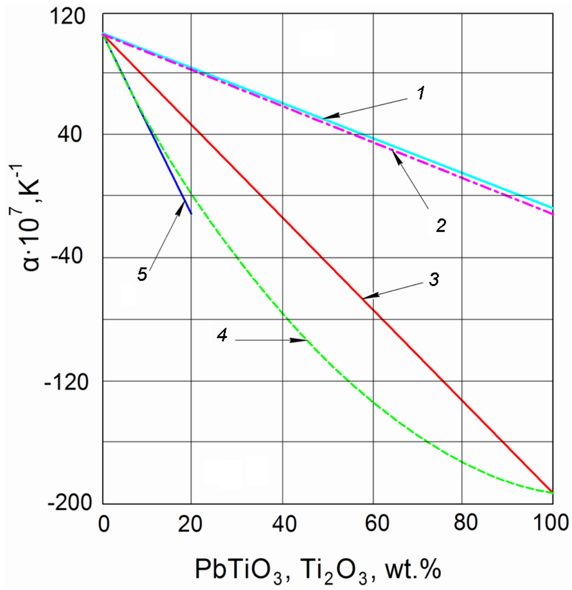

Fig. 5. The TCLE of glass solders in dependence on the content of $PbTiO_3$ (*1*, *2*) and Ti_2O_3 (*3*, *4*, *5*) in the powder compositions.

Alternatively, while sintering of the glass solders containing the titanium (III) oxide additions, it partially dissolves in the glass melt. Therefore, the actual content of crystalline Ti_2O_3 in the indicated glass solders is considerably less than in its primary powder composition. So, the dependence of the TCLE experimental values (Fig. 5, line *4*) of the glass solders on the content of Ti_2O_3 is notable for a considerable deviation from the rule of additivity (Fig. 5, line *3*). For these glass solders the TCLE experimental values can be equal to the weighted average values only in case if the TCLE is calculated according to an additive formula with a double content of Ti_2O_3. The data of Fig. 5 show that a straight line *5* having been obtained in accordance with such formula gives a reasonable approximation for the dependence of the TCLE experimental values of the glass solders on the content of Ti_2O_3 (up to 20 percent by weight) in the compound of powder composition.

It has been established that to produce a ceramic-metal seal agreed as per the TCLE ($50 \div 65 \cdot 10^{-7}$ K^{-1}), the amount of Ti_2O_3 (5 to 8 percent by weight) introduced into the compound of powder composition should be considerably less than the amount of $PbTiO_3$ (40 to 50 percent by weight). Besides, it is necessary to take note of the fact the indicated amount of titanium (III) oxide addition as compared with the lead titanate addition causes a minor decrease in the fluidity of glass solder over the surface of ceramics (Fig. 6).

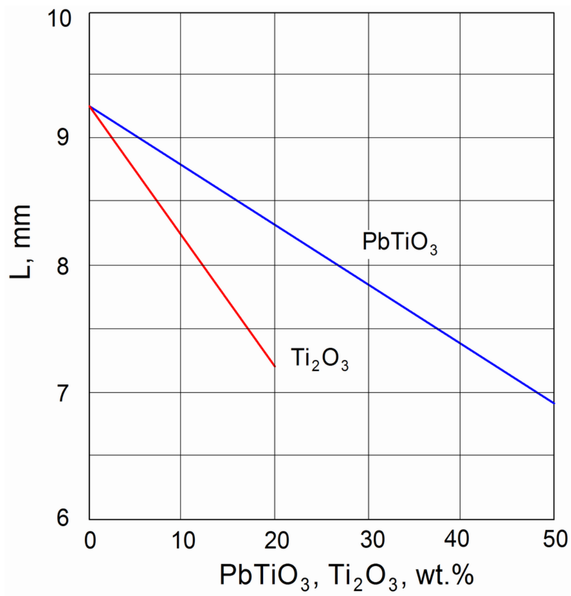

Fig. 6. Fluidity of glass solders in dependence on the content of $PbTiO_3$ and Ti_2O_3 in the powder compositions.

It has also been established that the glass solders with Ti_2O_3 addition are characterized by the least fluidity with equal content of the crystalline fillers in the powder compositions (Fig. 6). This is connected with partial dissolution of titanium (III) oxide in the glass melt as in case with the TCLE. If we assume that 40 to 50 percent by weight of Ti_2O_3 remains in the glass solder after heat treatment of the powder composition, the fluidity of glass solders containing $PbTiO_3$ will be commensurable with the fluidity of glass solders obtained from the powder compositions with a double content of titanium (III) oxide. Therefore, the fluidity of glass solders under investigation is first of all determined by the content of the residual glassy phase irrespective of the type of crystalline additions.

4. Conclusions

The experimental investigations have established an possibility for obtainment of the ceramic-metal seals between the constructional materials with the TCLE low values ($50 \div 65 \cdot 10^{-7}$ K^{-1}) from the powder compositions based on low-melting lead borosilicate glass with the titanium (III) oxide or the lead titanate additions at a temperature of ≤450°C. It has been noted the titanium (III) oxide is the most prospective component of the powder composition, which minor addition ensures the highest fluidity of the glass solder and obtainment of ceramic-metal seal agreed as per the TCLE.

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