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Interaction of Lead Oxide – Germanium Oxide Melts with Platinum and Palladium

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Contact interaction of lead oxide – germanium oxide melts with Pt and Pd was investigated. Good adhesion of these melts to the solid metals was observed.

Keywords: wetting, spreading, platinum, palladium, oxides of lead and germanium.

Introduction

Oxide compounds of PbO-GeO₂ system are provoking interest thanks to their properties [1-4]. An investigation of interaction of oxide melts with Pt and Pd was conditioned by a set of reasons. Nanostructural oxide systems containing ions of rare-earth elements and noble metals are perspective materials for optoelectronics [5]. In addition, noble metals, as crucible materials, can have a substantial effect on properties of synthesized oxide compounds. For example, the color of the glasses based on heavy metal oxides depends on the crucible type used for their obtaining [6]. The intensity of many processes occurring when melts contact with crucible materials can be determined by the wetting. Because of this, the study of contact interaction of PbO-GeO₂ melts with Pt and Pd is of scientific and practical interest.

Results and discussion

“Melt-substrate” contact interaction was investigated by the sessile drop method. The wetting of Pt and Pd by PbO-GeO₂ melts were conducted in air at the separate heating of the sample and the substrate. Photographs of the drops obtained with a Canon EOC 400 Digital were processed using a

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computer. The experimental procedure was similar to described one [7, 8]. The samples were prepared with the use of extrapure-grade PbO and GeO₂.

The contact interaction was studied for each composition at melting temperature because preliminary experiments showed that its increase resulted in the complete spreading of drops within a small time interval.

Figure 1a shows the spreading kinetics of PbO-GeO₂ melt containing 20 mol % of PbO on platinum. According to these data, for 7 sec the contact angle decreased from 65° to 19°. It should be remarked that with increasing τ the value of Θ changed not so sharply. Such change of $\Theta = f(\tau)$ and the values of contact angles ($\tau \geq 20$ sec) are rather unexpected as platinum is a general material for the crucibles in which like oxides are melted. Though, we can note the followings. Firstly, PbO-GeO₂ melts behave similarly on contact interaction with Au and Ag [9]. Secondly, so low values of Θ were also registered on Pt for other oxides [10]. For example, it was established that the contact interaction of LiNbO₃ with Pt, Pt + 10 wt. % of Rh, Pt + 10 wt. % of Ir, Pt + 5 wt. % Au and Ir was characterized by the values of Θ in the range of 12-14°. The exception is the alloy of Pt with Au, on which the contact angle is equal to 28°. Thirdly, there are compounds Pt₃O₄, PtO₂ ($T_m = 723$ K) and PtO ($T_m = 780$ K) in the system Pt-O₂ [11]. PtO and PtO₂ decompose at $T > 773$ K and > 873 K [12], respectively. We calculated the Gibbs energy, ΔG , of reactions $PbO + Pt = PtO + Pb$, $PbO_2 + Pt = PtO + PbO$, $2PbO_2 + Pt = PtO_2 + 2PbO$ and determined that in the range of 773-1273 K ΔG of first reaction is positive in value, while in the case of second and third ones it is small negative. It is not inconceivable that the above causes the good wetting of platinum by PbO-GeO₂ melts.

We obtained analogous results on the contact interaction of Pt with other PbO-GeO₂ melts (Fig. 1, b-d).

At equilibrium [13]

$$\cos \Theta = \frac{\sigma_{sg} - \sigma_{sl}}{\sigma_{lg}}, \quad (1)$$

where σ_{sg} , σ_{sl} , σ_{lg} are the surface tensions at the solid-gas, solid-liquid and liquid-gas boundaries, respectively.

With the work of adhesion

$$W_a = \sigma_{sg} + \sigma_{sl} - \sigma_{lg}, \quad (2)$$

and the work of cohesion

$$W_c = 2\sigma_{lg}, \quad (3)$$

from Eq. (1) – (3) follows that

$$\cos \Theta = \frac{2W_a - W_c}{W_c}. \quad (4)$$

From Eq. (4), according to [13], follows that the value of Θ is determined by the relation between the attractive forces of the liquid to the solid surface and the attractive interaction forces of particles of the liquid. On interaction of liquid with solid, the following cases are possible: wetting ($W_a > W_c/2$) and complete wetting ($W_a > W_c$) [13]. Based on the Eq. (4), it may be concluded that the smaller is W_c

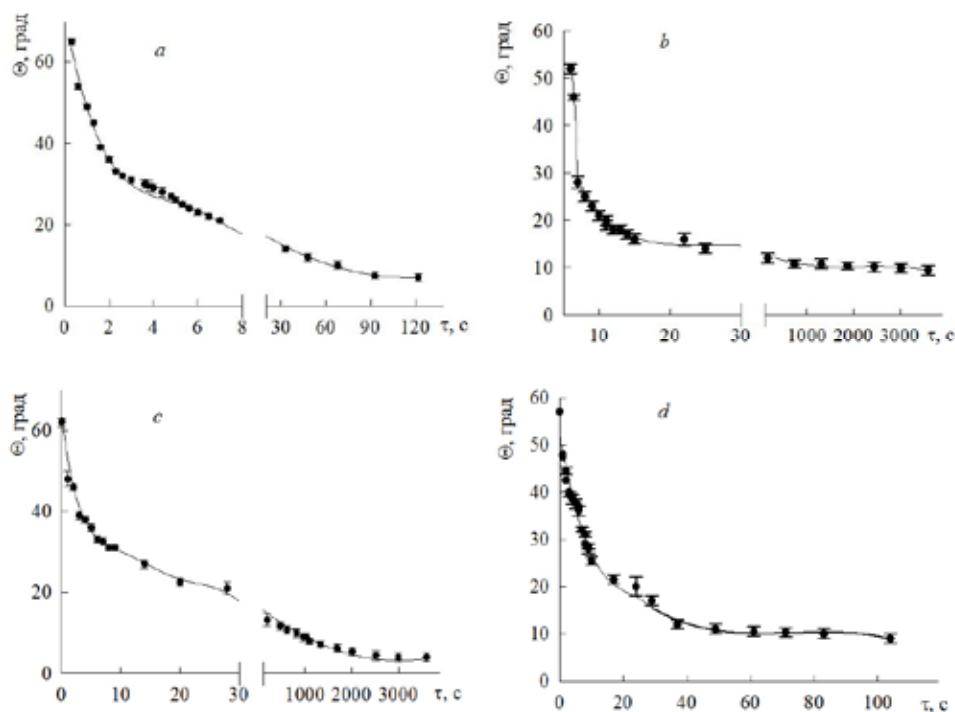


Fig. 1. Spreading kinetics of PbO-GeO₂ melts, containing a) 20, b) 30, c) 40 and d) 60 mol % of PbO, on platinum

and thus σ_{lg} , the better the liquid wets the solid. The surface tension of PbO-GeO₂ melts is likely to be uninvestigated. By virtue of the fact that the surface tension of liquid PbO is smaller than σ_{lg} of melted GeO₂ [14, 15], it is believed that PbO is a surface-active component with respect to GeO₂. Taking into account all things, one might expect the improving wetting as the content of PbO in the melt increases. As illustrated in Fig. 1, the change of content of melt from 20 to 50 mol % of PbO has little effect on the values of Θ .

The study of wetting of refractory metals (W, Mo, Nb) by the alumina-based melts (Al₂O₃-BeO, Al₂O₃-MgO, Al₂O₃-CaO, Al₂O₃-Cr₂O₃, Al₂O₃-ZrO₂, Al₂O₃-TiO₂, Al₂O₃-V₂O₅) showed that initial values of contact angles in all systems increased as the content of added oxide increased, but they passed through a maximum and then decreased [16]. This phenomenon can not be explained by the change of surface tension of the melt because, by Eq. (1), the contact angle augmentation assumes the increase of σ_{lg} while the addition of BeO, TiO₂, V₂O₅, CaO to Al₂O₃ resulted in the reducing surface tension of the melt. The observed change of Θ when wetting the refractory metals by oxide melts was connected with the relevant change of σ_{sl} and adsorptive phenomena at the “solid metal – liquid oxide” boundary. It is not improbable that the behavior of Pt-(PbO-GeO₂) system can be explained in a like manner. In this case it should be considered that the oxide surface is primarily formed by the oxygen anions the size of which is significantly greater than the size of metal cations. As a consequence, the interaction of the metal with some oxide is determined by the reaction of this metal with the oxygen of oxide [13]. In addition, the Pt surface, on being heated in air, is covered with an adsorptive oxygen layer, and then according to V.N. Eremenko’s principle, “similar matter wets similar thing” [17].

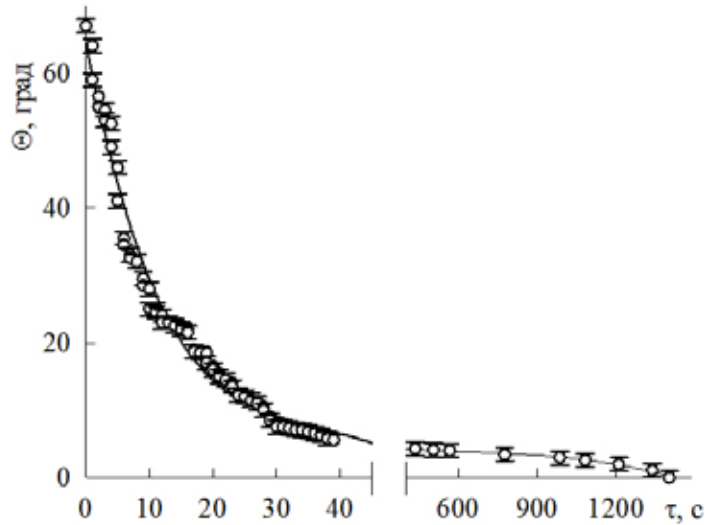


Fig. 2. Spreading kinetics of Pb+ 80 mol % of GeO₂ melt on palladium

We can also point out the possibility of brittle failure of Pt on interaction with melts. This question was detailed in the monograph [18].

Fig. 2 shows results on the contact interaction of Pd with PbO + 80 mol % of GeO₂ melt. From this figure we observe that for ~ 30 sec the melted drop is practically spreading over the palladium. In the course of time (~ 800 sec) a complete spreading takes place.

There is one compound PdO ($T_m = 1150$ K) in the palladium-oxygen system [11]. A desorption of oxygen from polycrystalline palladium in the range of temperatures from 500 to 1300 K was investigated in [19]. The obtained results argue for a strong interaction in the palladium-oxygen system.

We established that after experiment the drop composed of Pb + 80 mol % of GeO₂ turned red-orange instead of practically transparent. It can give an indication of “melt-substrate” chemical interaction [6].

A relation between the Gibbs energy of chemical reactions at the phase interface ($\Delta_r G$) and contact angles in the metal-oxide systems was considered in [20]. The author pointed out that this relation could be conditioned by an influence of chemical interaction on the work of adhesion. In analyzable models the contact angle depends on a degree of reaction product conversion; the correlation between $\Delta_r G$ and Θ was found only for the case that the three-phase system attained the equilibrium state. In a general way, nonequilibrium systems likewise can be considered. In this case the value of Θ will be determined immediately by the degree of reaction product conversion rather than by $\Delta_r G$ [20].

The drop of PbO + 80 mol % of GeO₂ was found to spread on Pd after a precursor layer which was arranged in front of the conditional three-phase contact line. A detailed analysis of this phenomenon was given in [21] and we will not discuss it here. It should be noted that this phenomenon was observed on spreading PbO-GeO₂ melts over silver [22].

References

1. Bush A.A. Monokristally s segnetoelektricheskimi i svyazannymi svoystvami v sisteme PbO-GeO₂ i vozmozhnye oblasti ikh primeneniya (Single crystals with ferroelectric and related properties in the PbO-GeO₂ system and potential fields of their application) / A.A. Bush, Yu.N. Venevtsev. Moscow: NIITEKHIM, 1981. 70.
2. Umesaki N. Neutron scattering from PbO-GeO₂ glasses / N. Umesaki, T.M. Brumier, A.C. Wright, A.C. Hannon, R.N. Sinclair // Phys. B. 1995. № 213-214. P. 490-492.
3. Sigaev V.N. Structure of lead germanate glasses by Raman spectroscopy / V.N. Sigaev, I. Gregora, P. Pernice, B. Champagnon, E.N. Smelyanskaya, A. Aronne, P.D. Sarkisov // J. Non-Cryst. Solids. 2001. V. 279. P. 136-144.
4. Denisov V.M. Stable and metastable phase equilibria in the liquid-state and solid-state PbO-GeO₂ system / V.M. Denisov, V.P. Zhreb, L.T. Denisova, M.S. El'berg, V.A. Storozhenko // Inorganic Materials. 2011. V. 47. № 13. P. 1428-1449.
5. Belushkin, A.N. Study of structural aspects of forming optical properties of GeO₂-Eu₂O₃-Ag nanosystem / A.N. Belushkin, S.E. Kichanov, D.P. Kozlenko, E.V. Lukin, B.N. Savenko, S.K. Rakhmanov, G.P. Shevchenko, V.S. Gurin, G.E. Malashkevich, V. Haramus, D.K. Pogorelyi, K.M. Podurets // FTT. 2010. V. 52. № 7. P. 1278-1282.
6. Lesal D. Heavy metal oxide glasses: preparation and physical properties / D. Lesal, J. Pedlikova, P. Kostka, J. Bludska, M. Poulain, J. Zavadil // J. Non-Cryst. Solids. 2001. V. 294. P. 288-295.
7. Denisov V.M. Contact interaction of bismuth-oxide-based melts with solid metals and oxides / V.M. Denisov, V.P. Chentsov, S.I. Shalaumov, N.V. Korchemkina, N.V. Buzovkina / Izv. Akad. Nauk SSSR, Neorg. Mater. 1991. V. 27. № 4. P. 763-765.
8. Antonova, L.T. Contact interaction of bismuth oxide based melts with silver, silicon and germanium / L.T. Antonova, V.M. Denisov, E.A. Pastukhov, N.V. Maznyak, A.V. Inyakin // Rasplavy. 2006. № 2. P. 7-13.
9. Denisov, V.M. Contact interaction of PbO-GeO₂ melts with gold and silver / V.M. Denisov, O.V. Kuchumova, L.T. Denisova, S.A. Istomin, G.M. Zeer // Rasplavy. 2011. № 3. P. 15-19.
10. Maltor H. Adhesion of crystallized LiNbO₃ melt to various crucible materials / H. Maltor, Th. Berthold // J. Cryst. Growth. 2001. V. 231. № 1-2. P. 1-3.
11. Kazenas, E.K. Isparenie oksidov (Evaporation of Oxides) / E.K. Kazenas, Yu.I. Tsvetkov. Moscow: Nauka, 1997. 543.
12. Tret'yakov, Yu.D. Neorganicheskaya khimiya. Khimiya elementov (Inorganic chemistry. Chemistry of Elements). V. 1 / Yu.D. Tret'yakov, L.I. Martynenko, A.N. Grigor'ev, A.Yu. Tsyvadze. Moscow: Khimiya, 2001. 472.
13. Summ B.D. Fiziko-khimicheskie osnovy smachivaniya i rastekaniya (Physico-chemical principles of wetting and spreading) / B.D. Summ, Yu.V. Goryunov. Moscow: Khimiya, 1976. 231.
14. Denisov V.M. Stroenie i svoystva rasplavlennykh oksidov (Structure and properties of molten oxides) / V.M. Denisov, N.V. Belousova, S.A. Istomin, S.G. Bakhvalov, E.A. Pastukhov. Yekaterinburg: Ural. Otd. Ross. Akad. Nauk, 1999. 498.
15. Fiziko-khimicheskie svoystva okislov (Physicochemical Properties of Oxides): Reference-book / Ed. by G.V. Samsonov. Moscow: Metallurgiya, 1978. 472.

16. Mitin, B.S. Wetting of refractory metals by liquid oxides / B.S. Mitin, E.F. Grits / Adgeziya rasplavov (Adhesion of Melts). Kiev: Naukova dumka. 1974. P. 80-83.

17. Eremenko, V.N. Zmochuvannya ridkimi matalami tverdikh poverkhon' tugoplavkikh spoluk (Wetting of Solid Surfaces of Refractory Compounds by Rare Metals) / V.N. Eremenko, Yu.V. Naidich. Kiev: Izdatel'stvo Akademii Nauk Ukr. SSR, 1958. 60.

18. Dmitriev, V.A. Vysokotemperaturnoe razrushenie platinovykh metallov i splavov (High-temperature Erosion of Platinum Metals and Alloys) / V.A. Dmitriev. Moscow: Ruda i metally, 2003. 176.

19. Samsonov, A.N. Investigation of oxygen desorption from polycrystalline palladium. Thermal desorption of O₂ from chemisorption layer of O_{адс} on decomposition of PdO surface oxide and in the process of oxygen emission from the palladium bulk / A.N. Samsonov, E.A. Suprun // Kinetica i kataliz. 2010. V. 51. № 3. P. 435-446.

20. Ivanov A.V. A relation between the Gibbs energy of chemical reaction and contact angles in the liquid metal – oxide systems / A.V. Ivanov // Vestn. Mosk. universiteta. 2. Khimiya. 2002. V. 43. № 5. P. 311-314.

21. De Gennes P.G. Wetting: statics and dynamics / P.G. De Gennes // Rev. Mol. Phys. 1985. V. 57. P. 827-863.

22. Denisov V.M. Contact interaction of PbO-GeO₂ melts with silver / V.M. Denisov, O.V. Kuchumova, L.T. Denisova, S.A. Istomin, S.D. Kirik, A.A. Shubin, L.A. Irtyugo // Rasplavy. 2010. № 1. P. 3-8.

Взаимодействие расплавов оксидов свинца – оксидов германия с платиной и палладием

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Исследовано контактное взаимодействие расплавов оксидов свинца – оксидов германия с платиной и палладием. Установлено, что наблюдается хорошая адгезия таких расплавов к твердым металлам.

Ключевые слова: смачивание, растекание, платина, палладий, оксиды свинца и германия.
