PHOSPHATE GLASSES: FORMING, STRUCTURE and PROPERTIES

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Abstract

The structure and some properties of the glasses in the ternary systems (I) $\text{BaO} \cdot \text{B}_2\text{O}_3 \cdot x\text{P}_2\text{O}_5$ ($x=0 \dots 60\text{mol.}\%$) and (II) $\text{BaO} \cdot 2\text{P}_2\text{O}_5(3\text{P}_2\text{O}_5) \cdot x\text{SiO}_2$ ($x=0 \dots 40\text{mol.}\%$) as well as in $\text{SiO}_2\text{-P}_2\text{O}_5$ with molar ratio $\text{SiO}_2/\text{P}_2\text{O}_5=1$ were studied. The structure of glasses were characterised by their Raman spectra and compared with the phases developing in the treatment process. The chemical durability and density also was used to characterise the changes in the structure of glasses. It is shown that glasses are formed by the same structural groupings which are developed in thermal treatment of starting compositions. The changes in the glass structure causes the first 5-10 mol.% addition of other glass formers P_2O_5 or SiO_2 . For these glasses in system I in concentration range of P_2O_5 25-33.3 mol.% there are being formed the weakly connected BPO_4 , BO_3 and BO_4 groups. It is shown that the most promising application by the modification of these glasses of Al_2O_3 are heat resistant coatings for Nb+1%Zr alloys.

1. Introduction

The P_2O_5 containing glasses together with other glass former B_2O_3 or SiO_2 (in the presence of BaO) were studied to obtain high temperature protective coatings. Some structures (and properties) of borophosphate glasses with BaO have been investigated¹⁻³. Structural problems of these glasses become more complicated because of the fact that apart from boron(phosphorus)-oxygen groups the presence of BPO_4 is highly probable⁴.

Silicophosphate glasses in structural investigations may be divided into two groups. Some authors^{5,6} consider that in silicophosphate glasses is formed a common Si-O-P network. Others⁷ propose that groups SiO_4 and PO_4 are very loosely connected and a common network of glasses is not formed. The main problem for the practical use these glasses is that structure of boro- and silicophosphate glasses is formed from units, which do not form stable structure and as follows also properties. Thus is restricting the practical application of these glasses. Usually, e.g.,⁸ to improve the properties of these glasses they are modified by Al_2O_3 .

The present study is about the structure and some properties of the glasses in the system $\text{BaO-B}_2\text{O}_3(\text{SiO}_2)\text{-P}_2\text{O}_5$. In this communication we report a) on the thermal processing of mixtures within the system (I) $\text{BaO} \cdot \text{B}_2\text{O}_3 \cdot x\text{P}_2\text{O}_5$ with gradual increase of $x=0$ to 60mol.% and in the system $\text{SiO}_2\text{-P}_2\text{O}_5$ with molar ratio $\text{SiO}_2/\text{P}_2\text{O}_5=1$, b) on the structure of obtained (I) glasses and glasses within the system (II) $\text{BaO} \cdot 2\text{P}_2\text{O}_5(3\text{P}_2\text{O}_5) \cdot x\text{SiO}_2$ with gradual increase of $x=0$ to 40mol%, c) heat resistant coatings for the oxygen protection of Nb and Nb+1%Zr alloys on the base of these glasses.

Experimental procedure

Glasses were prepared and investigated using methods previously described⁸. Figure 1 shows the glass forming regions and compositions studied in this work for the boro- (I) and silicophosphate (II) systems.

FIGURE 1. Glass formation regions (—) at 1200⁰C and various compositions (●) studied in the system I BaO.B₂O₃-xP₂O₅ (x=0...60mol.%) and in the system (II) BaO.2P₂O₅(3P₂O₅)- xSiO₂ (x=0...40mol%).

The coatings are produced by regular enamel technology using 50% suspension of particles 15-20μm in diameter in mixture of water+isopropanol. The efficiency of coatings have been controlled by the changes of microhardness profile of alloys Nb+1%Zr under the coatings after tests for 100h at temperatures ≥850 ⁰C.

Results and Discussions

The experimental results are interpreted on the assumption that the chemical compounds formed by the constituent parts in the glass melting process determine the structure and properties of the glasses and also the coatings obtained. Tables 1 and 2 summarise experimental results concerning the sequence of chemical compound development in the process of glass formation. The initial reaction of mixture of samples in system (I) and in SiO₂.P₂O₅ start at 300⁰C and form BPO₄ (in system I), and SiP₂O₇ (system II) in two crystalline modifications (cubic and monoclinic), and a changing compositions phase xSiO₂.yP₂O₅. The monoclinic SiP₂O₇ phase ceases to form at 700⁰C. At 1200⁰C when a sufficient quantity of liquid phase is formed the presence of cubic SiP₂O₇ as well as the xSiO₂.yP₂O₅ crystalline phases is present.

In the system (I) excess B₂O₃ interacts with BaO at temperatures exceeding 700⁰C yielding metaborate BaO.B₂O₃. The increased NH₄H₂PO₄ content, i.e., increased P₂O₅ content in composition (Fig.1) causes the formation of BPO₄ at 300⁰C along with 3BaO. P₂O₅ and 2BaO.P₂O₅ as well as a ternary compound 2BaO.B₂O₃.P₂O₅. The ternary compound obtained at 900⁰C appears in composition 4 and is rather unstable and disproportionate at 1000⁰C.

It should be noted that the crystalline phases development (system I) results at temperatures 1000-1100⁰C by the formation of BaO.4B₂O₃ in addition to BPO₄. Barium phosphates (samples 4 and 5) form at lower temperatures in range from 300–800⁰C. In the binary SiO₂-P₂O₅ system crystalline phases development results in cubic SiP₂O₇ and xSiO₂.yP₂O₅ formation.

TABLE 1. Crystalline phases identified in the mixtures of investigated samples 1 to 5 of the system(I)

Composition (see fig.1)	Crystalline phases at various temperatures ($^{\circ}\text{C}$)*								
	300	400	500	600	700	800	900	1000	1100
1	BaC,s	BaC,w	BaC,w	BaC,vw	BaB,s	BaB,w	BaB,w	melt	
2	BaC,s	BaC,w	BaC,w	BaC,vw	BaC,vw	BP,w	BP,w	melt	
	BP,w	BP,w	BP,w	BP,w	BP,w	BaB,w	BaB,w		
3	BaC,s	BaC,w	BaC,w	BaC,vw	BaC,vw	BP,w	BP,w	melt	
	BP,vw	BP,w	BP,w	BP,vw	BP,vw	BaB ₄ w	BaB ₄ w		
4	BaC,s	BaC,w	BaC,w	BaC,vw	BaC,vw	BP,w	BP,s	BP,s	melt
	BP,vw	BP,vw	BP,vw	BP,vw	BP,vw	Ba ₃ Pw	Ba ₃ Pw		
5	BP,vw	BP,w	BP,w	BP,w	BP,w	BP,s	BP,s	BP,s	melt
	Ba ₂ P,w	Ba ₂ P,w							

*) Symbols: BaC=BaCO₃; Ba₃B=3BaO.B₂O₃; BaB=BaO.B₂O₃; BaB₂=BaO.2B₂O₃; BaB₄=BaO.4B₂O₃; Ba₃P=3BaO.P₂O₅; Ba₂P=2BaO.3P₂O₅; BP=BPO₄; s=strong; w=weak; vw=very weak.

TABLE 2. Crystalline phases identified in the mixtures of the system SiO₂-P₂O₅ with molar ratio SiO₂/P₂O₅=1

Crystalline phases at various temperatures ($^{\circ}\text{C}$)**										
300	400	500	600	700	800	900	1000	1100	1200	
SP,cub										
SP,mon										
S _x P _y										

**Symbols: SP,cub=cubic SiP₂O₇; SP,mon=monoclinic SiP₂O₇; S_xP_y=changing composition crystalline phase xSiO₂.yP₂O₅.

Figure 2 shows Raman spectra for glassy phases quenched from melt in system (I). The main changes of spectral lines are observed in the ranges of 800-500cm⁻¹ and 1300-900cm⁻¹. Their localisation and intensity change with the increase of P₂O₅ concentration in the glasses.

The spectral lines of glasses BaO.B₂O₃ are the result of the boron-oxygen oscillations in the BO₃ groups. The first 5-10mol.% P₂O₅ addition causes changes in the position of spectral lines to 1100-990cm⁻¹ and 700-620cm⁻¹. They are the result of formation of the bonds in orthophosphate groups³. Increase of P₂O₅ amount to 25-33.3mol.% causes the dominant spectral bands at 1080-920cm⁻¹ and at 520-450cm⁻¹. These indicate on the formation of bonds in BPO₄, BO₃ and BO₄ groups. In this concentration range of P₂O₅ 25-33.3 mol.% the formation of the greatest number of oscillations is observed. This corresponds to glasses with a low stability in this range of P₂O₅. The chemical durability for these glasses is the lowest, i.e., the weight losses considerably increase, Fig.4. At P₂O₅ contents above 40-50 mol.% spectra are somewhat simpler and exhibit relatively broad features. The main oscillations are due to PO₃ groups as well as BPO₄. The chemical durability of these glasses increase (weight losses decrease), Fig. 4.

FIGURE 2. Raman spectra of $\text{BaO} \cdot \text{B}_2\text{O}_3 \cdot x\text{P}_2\text{O}_5$ glasses. The P_2O_5 concentration in mol.% identifies each spectrum.

The Raman spectra (Fig.3) of glasses with molar ratio $\text{SiO}_2/\text{P}_2\text{O}_5=1$ show the formation of the bond $\text{P}=\text{O}$ with the oscillation at 1330 cm^{-1} . After the thermal treatment of these glasses this oscillation decrease and a band at 330 cm^{-1} appears This is characteristic for group SiO_6 ^{5, 6}.

FIGURE 3. Raman spectra of glasses with molar ratio $\text{SiO}_2/\text{P}_2\text{O}_5=1:1$ -quenched from melt; 2- annealed at 500°C 7 h, 3- annealed at 700°C 7 h.

The density dependence (Fig.4) on SiO_2 content in these glasses by presence of BaO shows that in the presence of other oxide glass building agent over 5-10 mol.% causes the shift of those characteristics away from linearity. It indicates the changes in the glasses structure and as follows from⁹ to the formation of $\text{P}-\text{O}-\text{Si}$ links.

It can be imagine that the introduction of small amounts (up to 5%) of SiO_2 in to the Ba methaphosphate glasses may form diploid structure of tetrahedral SiO_4 between linear poliphosphate (type A, see scheme). In this case there is a crosslinks between linear poliphosphate. A bound glass

structure is formed. The density of glasses increases. At SiO_2 content above 10-15mol.% the structure of type B (see scheme) may form with three bridging oxygens, i.e., structural links are weakened⁹.

FIGURE 4. The chemical inertness of the glasses in system $\text{BaO} \cdot \text{B}_2\text{O}_3 - (0 \dots 60 \text{ P}_2\text{O}_5)$ and the density of the glasses in system II:1-in across section by $\text{BaO}/\text{P}_2\text{O}_5=1/2$ and 2- by $\text{BaO}/\text{P}_2\text{O}_5=1/3$.

The most promising application area of investigated glasses are coatings. Therefore to optimise coatings output formed on surface Nb-Zr alloys (as well as on Fe-Co alloys) formed by temperatures 1050...1150°C in vacuum at $p=10^{-3}$ – 10^{-4} Pa of the given glasses several factors must be taken into account. Amongst these as a primary are: chemical durability of basic glasses, adhesion to the surface of substrata in vacuum in the temperature range $\geq 850^\circ\text{C}$, insignificant interaction with the substrata. Therefore the glasses in the system $\text{BaO}-\text{SiO}_2(\text{B}_2\text{O}_3)-\text{P}_2\text{O}_5$ were modified by Al_2O_3 . When the molar ratio in the glasses is $\text{Al}_2\text{O}_3:\text{SiO}_2:\text{P}_2\text{O}_5 \sim 1$ forms a strong bonded glass structure. This allows to develop vitreous heat resistant coatings with the following ingredients in composition (wt.%): BaO 33...40, MgO 0...15, Al_2O_3 17...25, B_2O_3 0...5, SiO_2 12...26 and P_2O_5 . The coatings by the melting temperature have an excellent adhesion to surface of Nb-Zr alloys in vacuum. Optimal thickness of coating is 40-50 μm . During the melting process between metall and coating a 4-6 μm thick dense crystalline diffusion interlayer (mainly from oxygen free NbP crystals) is formed. The structure of this zone differs from the glassy coating and metal. The changes of microhardness profile under the glassy coatings after tests for 100h at temperatures $\geq 850^\circ\text{C}$ in oxygen environment

shows (Fig. 5) that diffusion of oxygen in substrata could be observed in very short zone as a result of coatings technological process.

FIGURE 5. Microhardness profile for glassy coatings - Nb+1%Zr after tests

These shows that both the formed vitreous coating as well as the crystalline interlayer formed are effective barriers to oxygen diffusion, thus protecting Nb-Zr alloy at elevated temperature (above 750 °C).

Conclusions

The compounds developing in the glass melting process of P_2O_5 containing systems (I) $BaO \cdot B_2O_3 \cdot xP_2O_5$ ($x=0 \dots 60$ mol.%) and (II) $BaO \cdot SiO_2 \cdot P_2O_5$ -system by molar ratio of $SiO_2/P_2O_5 \leq 1$ were studied. It is shown that glasses are formed by the same structural groupings which are developed in thermal treatment of starting compositions. Introduction of 5-10mol.% of the others glass builders (P_2O_5 or B_2O_3) in the compositions of the glasses I and II causes considerable changes of structure. For practilly application it is important to modify these glasses by Al_2O_3 . Conducted tests proved that glasses at the precence of Al_2O_3 and by molar ratio of $Al_2O_3:SiO_2:P_2O_5 \sim 1$ are promising materials for heat and oxygen corrosion resistant protective coatings on Nb-Zr alloys at temperatures above 750°C.

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