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Vitrification and crystallization in the system of K_2O–B_2O_3–TiO_2

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ABSTRACT

The vitrification and crystallization behavior of melts produced at 1400 °C in the ternary system of K_2O–B_2O_3–TiO_2 is investigated. It is shown that there are two fields of compositions (indicated in mol%) which allow obtaining the glass-ceramic materials with continuous glassy matrix after the cooling of molten compositions. In the first field $[TiO_2] = 25–57$, $[K_2O] = 30–50$ and $[B_2O_3] = 0–25$, the glass-ceramics consisted of the potassium–titanium–borate glassy phase and different crystalline potassium titanates ($K_4Ti_3O_8$, $K_2Ti_2O_5$, $K_2Ti_4O_9$, $K_2Ti_6O_{13}$). The ratio of TiO_2:K_2O in the obtained titanates increases with $[TiO_2]$ and $[B_2O_3]$. In the second field, $[TiO_2] = 7–37$, $[K_2O] = 0–25$ and $[B_2O_3] = 52–93$, the obtained glass-ceramics consisted of a similar vitreous phase, as mentioned above, and TiO_2 crystals. During the cooling of the melts, short whiskers-like crystals of anatase formed in the compositions with relatively low $[TiO_2]$ and relatively high $[K_2O]$, whereas long fiber-shaped crystals of rutile appeared with the compositions characterized with relatively high $[TiO_2]$ and relatively low $[K_2O]$. The possible application of the obtained glass-ceramic materials as a source of fibrous TiO_2, for composite reinforcement, and as solid lubricants is discussed.

1. Introduction

Glass–ceramic materials comprising a vitreous matrix and fibrous single crystals can exhibit superior mechanical properties, important for some special applications. Among such materials there is the group of water-soluble low temperature melting glasses used as solid lubricants or admixtures (up to 30 wt%) to lubricants used in mechanical assemblies of high-load friction. The compressibility of vitreous lubricants influences strongly the modeling of elastohydrodynamic contacts, where pressures and/or temperatures are sufficiently high to induce a glass transition [1–4]. Glassy lubricants are also applied for hot extrusion working of metals, where the extrusion power is decreased without impairing the surface quality [5]. Some borate and phosphate glasses are conventionally used for these purposes. For example, a patent [6] recommended the glass lubricant consisting of (wt%) CaO (2–6), B_2O_3 (18–20), Na_2O (14–18), ZnO (8–12), TiO_2 (8–12) and SiO_2 (balance), as well as another composition containing (wt%): P_2O_5 (45–75), M_2O (10–35) and B_2O_3 (0–45) [5]. Hot calendering glassy lubricants, composed of (mol%) P_2O_5 (40–55), B_2O_3 (up to 9) and M_2O (30–60) (M is an alkali metal), are intended to reduce the wear or seizure of the rolls at high temperatures and pressures, capable of preventing the development of the surface flaws of stainless steel plates; these consist of a water-in-oil type emulsion containing a purified lubricating base oil, surfactant and water-soluble glass [7].

On the other hand, crystalline fiber-shaped TiO_2 and potassium hexatitanate ($K_2O \cdot 6TiO_2$) are used as components of friction materials or admixtures in lubricant compositions due to their excellent mechanical and friction properties [8–10].

From this point of view, glass-ceramics composed of a matrix of low temperature melting glass and crystals that promote decreased friction (TiO_2 and/or $K_2Ti_6O_{13}$), could be very promising materials for use in lubricant compositions. On the other hand, it is well known that the handling of nano-fibers of TiO_2 and potassium titanates, with high aspect ratio (above 3), is associated to carcinogenicity risks [11]; thus, glass-ceramic powders bearing fiber-shaped crystals of a lower aspect ratio would allow decreasing this problem. However, only one publication was found relative to the production of such materials [5], where the glass, containing fiber-shaped TiO_2 crystals, was obtained by fusing batches consisting essentially (wt%): B_2O_3 (45–65), Al_2O_3 (5–30), TiO_2 (5–30) and alkaline earth oxides (3–30); it is noteworthy that the appearance of fiber-shaped rutile was very sensitive to the conditions of the thermal treatment [12].

The effect of TiO_2 crystallization was not addressed in the glasses previously investigated in the system of R_2O–RO–B_2O_3–TiO_2 [13–17]. The crystallization of potassium titanates was noted only in the K_2O–Fe_2O_3–TiO_2 glass-forming system [18,19], for

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which the presence of Fe_2O_3 limits their application as lubricants in iron based mechanisms. The binary alkali-dititanate glasses [20] tend to complete crystallization and can only be obtained by a very fast cooling of melts. On the other hand, it was found that the slow cooling of the TiO_2 solution (30 wt%) in potassium metaborate ($K_2O \cdot B_2O_3$) and diborate ($K_2O \cdot 2B_2O_3$) melts, resulted in crystallization of potassium hexatitanate ($K_2O \cdot 6TiO_2$); whereas, the melts obtained at 1060 °C in the system of $K_2O \cdot 4B_2O_3$–TiO_2 formed crystalline TiO_2 during the cooling [21,22].

It is important to note that the cited research [21,22] presented only materials of some selected compositions that did not form a continuous glassy matrix, which is required for glassy (glass-ceramic) lubricants. The goal of this research was to define the range of compositions in the ternary system of K_2O–B_2O_3–TiO_2, which would allow obtaining glass-ceramic materials, consisting of a continuous glass–matrix and fiber-shaped crystals of TiO_2 or potassium titanates, able for use as solid lubricants. The selected system is preferable over the system of K_2O–TiO_2–P_2O_5 because the latter tends to form $KTiOPO_4$ during the cooling [23].

2. Experimental

The raw materials were TiO_2, K_2CO_3 and H_3BO_3 (CTR Scientific, chemical grade purity +99%). The prepared batches were heat treated in an electric furnace (Lindbergh-Blue M BF51433) in a platinum crucible. The stages included 400 °C for 1 h, to decompose the H_3BO_3 and to reduce B_2O_3 looses during the fusion [16], and fusion at 1400 °C for 2 h. The melts were quenched on a stainless steel plate; according to the result of the fusion, the obtained materials were classified as (1) transparent glasses, (2) partially crystallized glasses with continuous glassy matrix (glass-ceramics), and (3) unmelted mixtures or materials that did not containing continuous glassy matrix.

The structure of the partially crystallized glasses was investigated by scanning electron microscopy (SEM, Philips XL30ESEM), equipped with an X-ray micro-analyzer for energy dispersive spectroscopy (EDS, EDAX Pegasus). The samples were cut with a diamond disc, polished with diamond paste and carbon coated to make the surfaces conductive. The phase composition of glass-ceramic powders (grain size of 0.10–0.25 mm) was analyzed by X-ray diffractometry (XRD, Philips ŃPert-MPD) and identified with the ICDD/2002 standard base of data. The temperature of glass transition, of the glass-ceramic materials produced, was analyzed by differential thermal analysis (DTA, BAHR STA503) using powdered samples of 0.5 g (particle size in the range 0.10–0.25 mm) by heating up to 1100 °C at 10 °C/min.

Friction parameters were determined with a rehometer (TA, AR2000); a device was designed in which a cylindrical cavity (diameter of 41 mm) on the stainless steel base (M316) was filled with a powder of solid lubricant (particle size in the range of 0.10–0.15 mm), to obtain a homogeneous layer of 0.45 mm of the thickness. The powder was pressed by the load cell shaft which had a stainless steel (M316) pad (40 mm of diameter) under a normal load of 20 N at room temperature (23 °C). Previous to each test, the steel surfaces in contacting the powdered solid lubricant were ground with 320-grid sandpaper. Tests were conducted at a constant shaft rotational speed of 1 rps during 0.3 h. The normal load was kept constant by the apparatus during the time of testing. The readings of friction torque were digitally collected and further divided by radius of the contact area to calculate the friction force.

The water resistance of the produced glass-ceramic materials was investigated with powdered samples (particle size in the range 0.315–0.500 mm) to determine the time necessary for completed dissolution of a vitreous phase in distilled water at 96 °C (powder/H_2O weight ratio of 0.1).

3. Results

Fig. 1 presents the results of the fusions carried out of selected compositions in the K_2O–B_2O_3–TiO_2 system. It was noted that complete vitrification was only obtained with compositions of low [TiO_2] and high [K_2O] or [B_2O_3], which were not promising to form rutile (anatase) or potassium titanates containing glass-ceramics after regulated crystallization of the glasses obtained. However, there were two fields of composition where the cooled melts formed a continuous glassy matrix bearing crystalline phases, the composition ranges were (in mol%): the field A, [TiO_2] = 35–57, [K_2O] = 30–50 and [B_2O_3] = 0–25; and field B, [TiO_2] = 7–37, [K_2O] = 0–25 and [B_2O_3] = 52–95. The XRD patterns and micrographs of some as-quenched samples obtained in the fields A and B are reported in Figs. 2 and 3 and Figs. 4 and 5, respectively.

The materials obtained with the compositions from the field A were partially crystallized glasses (Fig. 3) consisting of a glassy phase bearing different crystalline potassium titanates (bulk crystallization): composition No. 6 ($0.30K_2O$–$0.15B_2O_3$–$0.55TiO_2$) contained only potassium hexatitanate; whereas for No. 10 ($0.35K_2O$–$0.10B_2O_3$–$0.55TiO_2$) and No. 7 ($0.35K_2O$–$0.20B_2O_3$–$0.45TiO_2$) the crystalline phases were a mixture of $K_2Ti_2O_5$, $K_2Ti_4O_9$ and $K_2Ti_6O_{13}$. For composition No. 8 ($0.40K_2O$–$0.20B_2O_3$–$0.40TiO_2$), the resulting material showed $K_2Ti_2O_5$; whereas for No. 9 ($0.45K_2O$–$0.20B_2O_3$–$0.35TiO_2$) only a small amount of $K_4Ti_3O_8$ was detected (Fig. 2). Further increases on the [K_2O] above 45 mol% favored the formation of transparent glasses.

The EDS analysis of vitreous phases for the compositions from field A, showed the presence of all oxides of the system investigated; the molar ratio of K_2O:TiO_2 varied in the range of 7–9 and indicated that B_2O_3 was the main component of the glassy phases. According to DTA data (Table 1), all possible crystallization processes in partially crystallized glasses with compositions from field A, were entirely completed during melting and cooling; the temperature of glass transition of vitreous phases varied in the range of 530–550 °C.

The as-quenched samples of compositions from field B (Fig. 1) were partially crystallized glasses consisting of continuous glassy matrix and TiO_2 crystalline phase. Relatively large fiber-shaped ru-

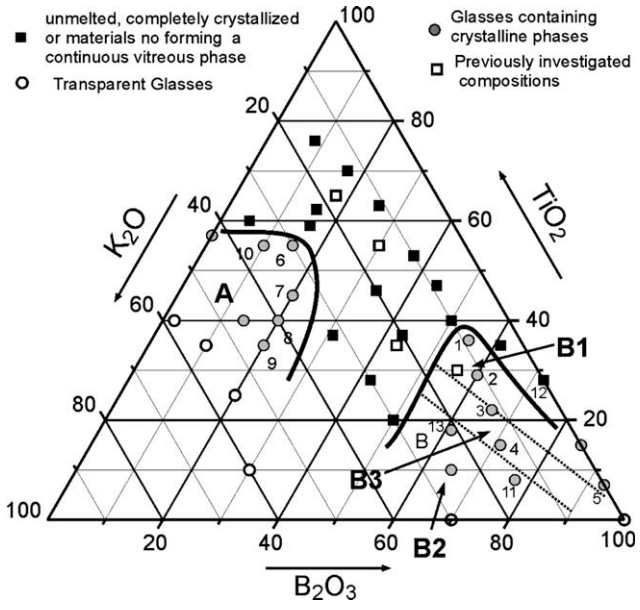

Fig. 1. Vitrification–crystallization diagram of the K_2O–B_2O_3–TiO_2 system. The continuous curves indicate the fields of formation of glass-ceramic materials with continuous glassy matrix (A and B) by quenching of melts. Compositions in mol%.