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THE PREPARATION OF ALUMINATE GLASS MICROSPHERES BY SYNTHESIS IN CH_4/O_2 FLAME

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ABSTRACT: Binary alumina-rare-earth oxide glasses with high alumina content have been reported recently to have excellent mechanical properties, especially hardness, which is comparable to that of single crystal sapphire. The use of such glasses can be envisaged in transparent ballistic protection, or other applications, which at the same time require good transparency, outstanding mechanical properties, and high chemical durability. However, preparation of such glasses in bulk is difficult due to high crystallisation rates characteristic for the system, which require high cooling rates at the level of 10^3 °C.s^{-1} in order to preserve the matter in glassy state. To by-pass this obstacle, bulk glasses were prepared by hot pressing of quenched glass microspheres at temperatures, which are sufficiently high to facilitate densification by plastic flow, but still low enough to prevent crystallisation of glass. The equipment for flame synthesis of glass microspheres from oxide precursors has been built in-house. Glass microspheres with dimensions < 10 μm and with various compositions from the systems CaO-Al2O3, pure silica, and Y2O3-Al2O3 have been prepared and characterized. Hot pressing of the microspheres yielded bulk non-transparent glasses of respective compositions.

KEY WORDS: glass microspheres, flame synthesis, aluminium oxide, rare earth oxides

1. INTRODUCTION

Rare-earth and calcium-aluminate oxide glasses are of potential technological importance due to their exceptional mechanical and optical properties, including high hardness and elastic modulus, as well as transparency for radiation in mid infrared range. For many optical applications, it is therefore desirable to obtain single-phase glasses with uniform optical properties. Preparation of these glasses in bulk is difficult, because Al_2O_3 is a reluctant glass former, which necessitates the use of high quenching rates, in some instances as high as 10^7 K.s^{-1}. Special ways of preparation are therefore required.

Weber et al. used containerless melting techniques to prepare $Y_3Al_5O^{12}$ and Er_3Al5O_{12} glasses. Containerless melting techniques with the use of an aero-acoustic levitator (AAL) or a conical nozzle levitator (CNL) were used to eliminate heterogeneous nucleation on melting container surfaces and thus to suppress crystallisation on cooling [1]. McMillan et al. prepared CaO-Al_2O3 glasses, containing 50 mol % Al_2O_3 via splat quenching technique [2].

The recent work of Rosenflanz [3] et al. describes a novel process for preparing of high alumina glasses and glass ceramics with aluminate glass matrix and dispersed nanosized crystals of rare earth aluminates, with hardness between 14.4 and 18,3 GPa and the fracture toughness between 2,1 and 4,2 MPa.$m^{1/2}$. Fully dense bulk glasses were obtained by pressure-assisted sintering of glass microbeads. Glass microspheres in the system $Re_2O_3Al_2O_3$ (Re = Y, La, Gd) composition were prepared by flame-spraying technique in a hydrogen-oxygen burner.

Although a score of works describe preparation of alumina-rare-earth and calcium-aluminate oxide

glasses, little is known on mechanical properties of bulk aluminate glasses due to the problems with their preparation in larger volumes.
The present work describes the use of hot-pressing (HP) technique for preparation of bulk aluminate glasses by sintering of glass microspheres with dimensions < 10 μm and with various compositions from the CaO-Al_2O_3 and Y_2O_3-Al_2O_3 systems. The microspheres were prepared by flame-spraying technique. Preliminary results of the work are reported.

2. EXPERIMENTAL

The compositions of the synthesised CaO-Al_2O_3 and Y_2O_3-Al_2O_3 specimens (as weighed) are presented in Table 1. Starting materials were high-purity oxide powders (Y_2O_3 - Treibacher Industrie AG, Austria, Al_2O_3 – Taimicron, Krahn Chemie GmbH, Germany), and $CaNO_3.4H_2O$ p.a.
CaO-Al_2O_3 – precursor powders were prepared by adding the corresponding amounts of $CaNO_3.4H_2O$ solutions in isopropylalcohol to an isopropylalcohol suspension of alumina powder. The suspension was mixed and homogenized for 24 h in a ball mill. Water solution of ammonium hydroxide was then added into the mixture, to precipitate $Ca(OH)_2$. The mixture was stirred for 1h and dried under infrared lamp and calcined in platinum crucible at 1100°C for 4h. At last the calcined mixture was sieved through a 50 μm PE sieve.
Y_2O_3-Al_2O_3 – precursor materials were prepared in a similar manner. Y_2O_3 was converted into nitrate by dissolving it in concentrated HNO_3. The mixture were calcined at 1600°C for 4h.
Glass microspheres were prepared by flame-spraying technique, in which the particulate precursors were fed into a high temperature CH_4-O_2 flame. The molten particles were quenched by spraying them with distilled water. Glass microspheres were then let to settle down in sedimentation tank and collected. A schematic drawing of the apparatus is in Fig. 1.
In this manner prepared glass microspheres were hot-pressed at the pressure of 30 MPa and different temperatures in vacuum, as shown in Tab. 1. The mechanical pressure was applied from the start of the experiment; heating and cooling rates were 10 °C/min.
Properties of oxide precursor glass microspheres and hot pressed bulk glasses were evaluated by optical microscopy, scanning electron microscopy (SEM), X-ray diffraction (XRD), and differential thermal analysis (DTA).

Tab. 1: The composition of prepared glass samples and their basic characteristic: T_m-melting temperature as determined from phase diagram, T_g-glass transition temperature, T_x- onset of crystallisation, THP-hot pressing temperature, n.m.= not measured, n.d.= not detected

Sample	Al_2O_3 (wt.%)	CaO (wt.%)	Y_2O_3 (wt.%)	T_m/°C	XRD	T_g/°C	T_x/°C	THP/°C
A49C51	49.3	50.7	0	1405	amorphous	n.d.	n.m.	850
A76C24	75.7	24.3	0	1727	semi-cryst	n.m.	n.m.	0
A79C21	79.4	19.6	0	1752	semi-cryst.	n.d.	917	0
A60Y40	60	0	40	1760	amorphous	870	910	900
A75Y25	75	0	25	1900	semi-cryst.	876	909	-

3. RESULTS AND DISCUSSION

Glass microbeads prepared by flame synthesis were transparent: some compositions were XRD amorphous, others, especially those with very high alumina contents were partly crystalline. This indicates that flame-spraying technique can be used for preparation of glass microspheres in glass systems, which request high melting temperatures (>1700°C), and high cooling rates (700 °C/s). Fig. 2 presents the scanning electron micrographs of glass CaO-Al_2O_3 and Y_2O_3-Al_2O_3 microspheres. Glass microbeads with particle diameter between 1 and 10μm resulted from the flame synthesis. Fig. 3 and Fig. 4 show the XRD patterns of some selected precursor powders (black line) and of the glass CaO-

Al_2O_3 and Y_2O_3-Al_2O_3 microspheres (red line) ofthe same composition as the precursor powder. As the XRD-patterns show, that precursor powders are crystalline, and usually consist of α-alumina and respective (calcium or yttrium) aluminates of various compositions, especially grossite in CaO-Al_2O_3 and ytrium aluminium garnet $Y_3Al_5O_{12}$ in Y_2O_3-Al_2O_3 powders.

CaO-Al_2O_3 microspheres of the composition A79C21 were partially crystalline, containing crystalline grossite phase. Partial crystallisation of grossite may be due to too high a temperature of the flame, which does not allow sufficiently fast cooling of the formed microbeads. The microbeads of the composition of A60Y40 were XRD amorphous.

Fig. 5a shows the fragments of a A49C51 pellet obtained by hot pressing at the temperature of 850 °C and the pressure of 30 MPa (the pressure was applied at temperature 300°C), for 22 min. The final product was XRD amorphous, virtually fully dense (99.8 % of glass skeletal density) and with characteristic glassy fracture. The colour was gray due to penetration of carbon from graphite hot pressing die into the sintered material), and non-transparent.

The Fig. 5b presents the photograph of the pellets A60Y40 obtained by hot pressing at 840 and 900°C, respectively. The first hot pressing experiment with dwell time below the T_g was not successful: the specimen was soft and porous. Increase of the hot pressing temperature to the interval between T_g and T_x. (Tab. 1) as determined from DTA curves of the prepared microspheres resulted in dense specimens. All prepared pellets were white and opaque. The reason for the opacity is not clear at the moment. Possible hypothesis include the presence of light scattering residual porosity, partial crystallization of glass in the course of hot pressing and incorporation of water during quenching into glass structure.

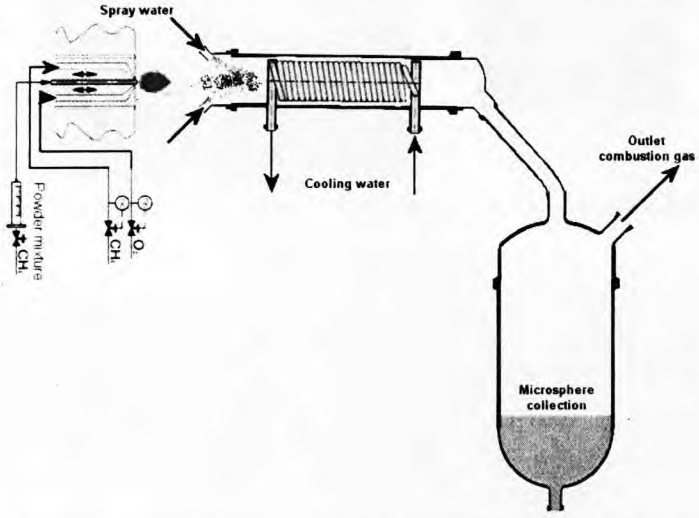

Fig. 1: Schematic of the apparatus for preparation of glass microspheres, by flame-spraying technique.

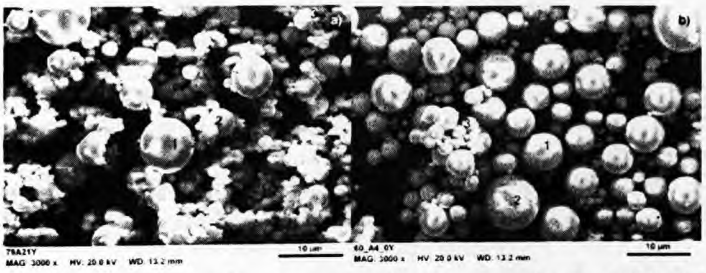

Fig. 2: SEM micrographs of microspheres prepared by flame synthesis: A79C21 (a), A60Y40 (b)

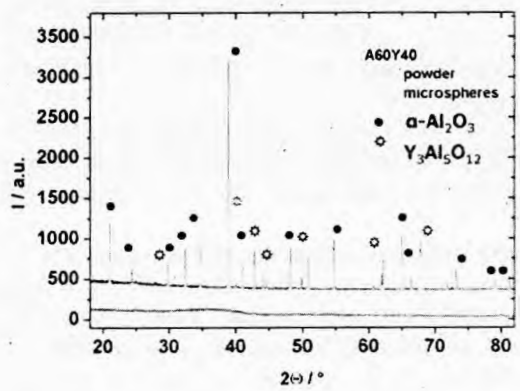

Fig. 3: The results of X-ray powder diffraction analysis of A60Y40 starting powder and microspheres

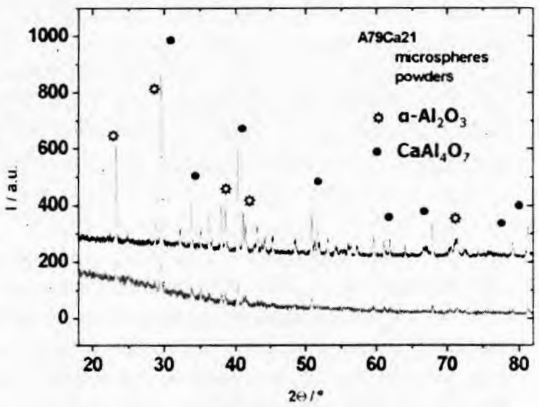

Fig. 4: The results of X-ray powder diffraction analysis of A79C21 starting powder and microspheres

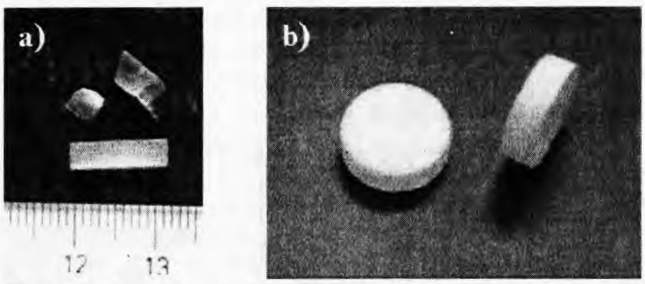

Fig. 5: Photographs of hot pressed bulk glasses. A49C51 (a), A60Y40 (b)

4. CONCLUSIONS

In the paper we report successful preparation of calcium-aluminate and yttrium-aluminate microspheres by flame-spray synthesis. Microspheres were amorphous, or partially crystalline. Hot pressing of microspheres in the temperature interval between Tg and onset of crystallisation yields bulk opaque glasses with low residual porosity. Possible reasons for the lack of transparency include the presence of light scattering residual porosity, partial crystallisation of glass in the course of hot pressing and incorporation of water during quenching into glass structure.

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5. REFERENCES

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