Preparation and Characterisation of Al_2O_3-Y_2O_3 Glass Microspheres

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Abstract: *Al_2O_3-Y_2O_3 microspheres with high alumina content were prepared and characterised. Because Al_2O_3 is not a typical glass former, preparation of aluminate glasses in bulk is difficult due to high melting temperatures and high tendency to crystallisation, which requires high cooling rates. For this reason the studied glasses were prepared in the form of micropsheres with diameters of up to 40 μm, which ensured the quenching rates at the order of magnitude of 1.10^3 K^{-1}. Despite high cooling rates most compositions comprised, apart from fully amorphous microspheres, also microspheres containing crystallites of α-Al_2O_3, YAG (yttrium aluminium garnet, and YAP (yttrium aluminium perovskite). The degree of crystallisation was found to depend from the composition, and diameter of prepared microspheres.*

1. Introduction

Yttrium-aluminate, and generally rare earth aluminate, glasses with high alumina content are considered as potential candidates for various applications ranging from transparent ballistic protections, through infrared transparent windows, to hosts for rare earth elements in materials used for solid state lasers, due to their good mechanical properties, high refraction index and good corrosion resistance. However, the preparation of aluminate glasses in bulk is difficult because these systems have high melting temperatures and high tendency to crystallisation.

The work of Rosenflanz et al. [1] describes preparation 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 $MPa.m^{1/2}$ by pressure-assisted viscous flow sintering of glass microbeads at temperatures above their glass transition region.

Our previously published work describes the synthesis of Al_2O_3 – Y_2O_3 glass microspheres with various Al_2O_3 content in O_2-CH_4 flame and with the use of in-house built experimental equipment, and the attempts to prepare fully dense transparent bulk glass by hot pressing in the temperature interval between Tg and the onset of crystallisation. As yet, all attempts were unsuccessful due to extensive crystallisation during heat treatment as the consequence of the presence of nuclei formed in the synthesised microspheres during cooling. The present work is focused at more detailed characterisation of the microspheres from the point of view of their morphology, size, phase composition, and microstructure by optical microscopy (OM), scanning electron microspcopy (SEM), transmission electron microscopy (TEM) and by X-ray powder diffraction (XRD).

2. Experimental

The compositions of the synthesised specimens (as weighed) are presented in the Table 1. High-purity oxide powders (Y_2O_3 - Treibacher Industrie AG, Austria, Al_2O_3 – Taimicron TM

DAR, Krahn Chemie GmbH, Germany) were used as starting materials. The alumina powder was mixed with yttria dissolved in nitric acid, the mixture homogenised by ball milling, yttrium nitrate converted to hydroxide by the addition of NH_4OH, dried, sieved, and pre-reacted at 1650 °C, and then fed into a modified gas burner axially into the centre of methane-oxygen flame. The microspheres quenched by spraying with water were collected in a sedimentation vessel, dried, and characterised. The morphology was examined by a Nikon Eclipse ME 600 optical microscope and the diameter size distribution determined with the use of the image analysis software Lucia v. 4.82. Detailed morphology was studied with the use of a Zeiss EVO 40 SEM. The internal structure of microspheres was examined by a JEOL 1200EX TEM at the acceleration voltage 120 kV. X-ray diffraction was carried out at the powder diffractometer STOE with CoKα radiation at the wavelength of 1.78897 Å in the 2Θ range 15 – 85°. The weight fractions of crystalline phases were determined from X-ray diffraction patterns from integral intensities of diffraction peaks by the method of standard addition.

3. Results and discussion

Preliminary examination of the prepared aluminates after flame synthesis by OM indicated they were molten thoroughly in the flame, resulting in nearly ideal spherical morphology. The spheres were transparent, and without any obvious traces of crystallisation (Fig. 1a, b). However, the SEM examination revealed striking differences among surface morphologies of microspheres of various compositions and sizes (Fig. 1c, d). In some compositions, especially in those close to the composition of the pseudobinary eutectic YAG – Al_2O_3 (A60, T_m = 1760 °C, Fig. 1c), all micospheres irrespective of their size were smooth, indicating their highly amorphous character.

However, in compositions with higher alumina contents and higher melting temperature (e.g. A75, T_m = 1900 °C), in microspheres with larger diameters SEM revealed regular features suggesting at least partially crystalline nature of these particles.

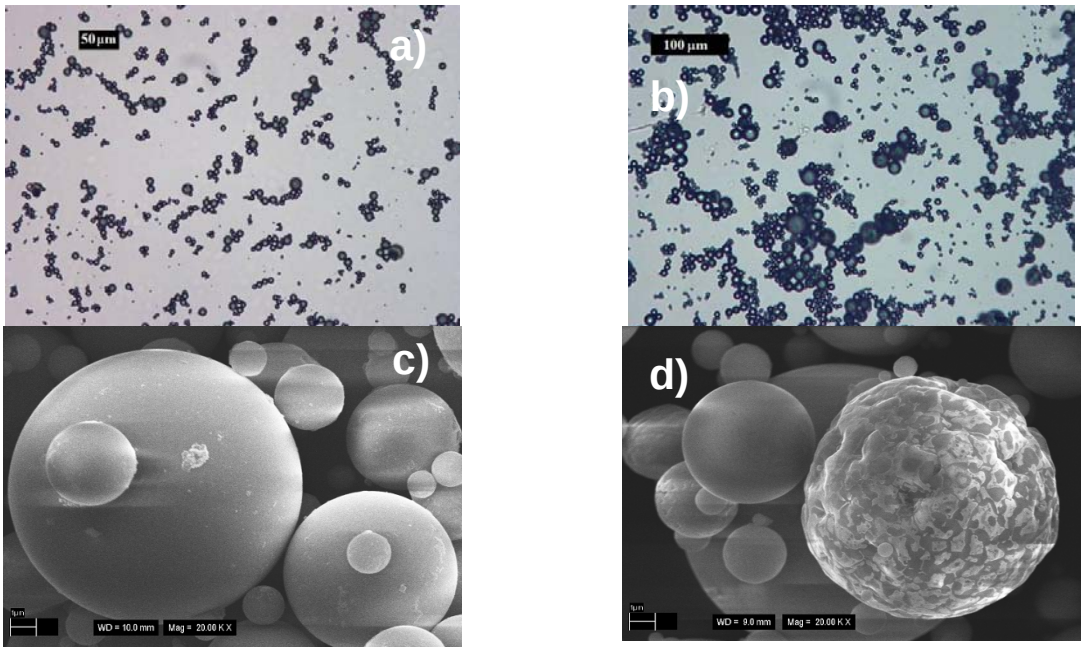

Fig. 1 Optical micrographs of the microspheres A60 (a) and A75 (b), and the detailed SEM micrographs of the same specimens, A60 (c) and A75 (d).

Another distinct feature is different distribution of diameters of prepared microspheres (Fig. 2) with various compositions. As all precursor powders underwent the same treatment,

including sieving through a 40 μm mesh screen, the reason for such behaviour is not clear at the moment. It might be related to a different tendency to agglomeration in powders with different compositions, which then results in different granulometry of powder agglomerates fed to the flame. Generally speaking, the compositions closer to the eutectic showed more narrow distribution of microspheres' diameters, with sizes up to 15 μm, while those further apart contained particles with sizes up to 40 μm.

Sample	Al_2O_3 (wt.%)	Al_2O_3 (mol.%)	T_m/°C	Amorphous phase / wt %	Crystalline phases/wt.%
A43	43	62,6	1925	92	YAG – 100 %
A57	57	74,6	1790	87	YAG - 88 % α-Al_2O_3 - 12 %
A60	60	76,8	1760	94	YAG - 100 %
A63	63	79,0	1775	96	YAG - 56 % YAP - 32 % α-Al_2O_3 - 12 %
A67	67	81,8	1825	89	YAG - 57 % YAP - 14 % α-Al_2O_3 - 16 % trans. Al_2O_3 - 13 %
A75	75	86,9	1900	85	YAG - 26 % YAP - 29 % α-Al_2O_3 - 19 % trans. Al_2O_3 - 26 %

Table 1. The compositions (as-weighed) of prepared microspheres and their basic characteristics: T_m-melting temperature as determined from the phase diagram, the content of amorphous phase, and phase composition of the crystalline fraction.

XRD examination revealed some relations between the composition, granulometry, phase composition and degree of crystallinity of prepared microspheres. Generally, the compositions closer to the eutectic point (A60, A63) were about 95 % amorphous. Several batches of the eutectic composition A60 were even 100 % amorphous. This is easily explained by the lowest tendency to crystallisation in eutectic mixtures, or in compositions close to them. The composition A43, corresponding to stoichiometric YAG, was 92 % amorphous, the rest being crystalline YAG. On the high alumina end of the composition spectra the specimens showed the degree of crystallisation higher than 10 %. The composition of the crystalline part corresponded roughly to the phase diagram, the main crystalline phases being YAG and α-Al_2O_3. The presence of the YAP phase is the result of incomplete YAG formation according to the reaction scheme:

$2Y_2O_3 + Al_2O_3 \rightarrow Y_4Al_2O_9$ (mellilite) T = 900 – 1100 °C (1)

$Y_4Al_2O_9 + Al_2O_3 \rightarrow 4YAlO_3$ (perovskite) T = 1100 – 1250 °C (2)

$3YAlO_3 + Al_2O_3 \rightarrow Y_3Al_5O_{12}$ (garnet) T = 1400 – 1600 °C. (3)

The presence of transition aluminas (δ, θ-Al_2O_3) is related to reaction of alumina with quenching water during flame synthesis of microspheres. The higher extent of crystallisation is related to higher tendency to crystallisation in compositions further from the eutectic, or in those identical to stoichiometric crystalline phases (YAG), and to insufficient cooling rate in larger spheres, which were documented in these compositions.

The TEM examination confirmed completely amorphous character of smaller microspheres, revealing heterogeneous nucleation and growth of nanosized crystals from the surface of larger ones into their interior. In some cases polycrystalline microspheres with the grain size of about 200 nm and the microstructure resembling polycrystalline α-Al_2O_3 or YAG were observed. Detailed TEM investigation of the present crystalline phases by electron diffraction is in progress.

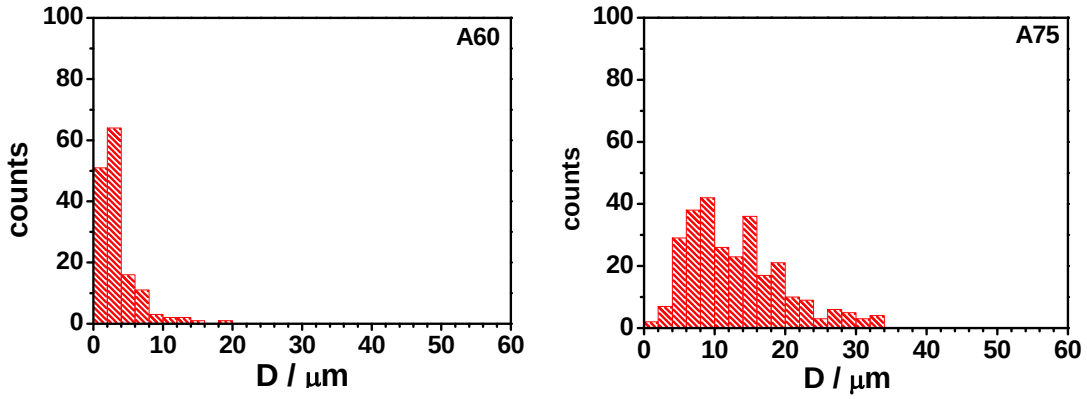

Fig. 2 Distribution of diameters of microspheres of the eutectic composition A60 and the composition A75 at high alumina end of prepared compositions.

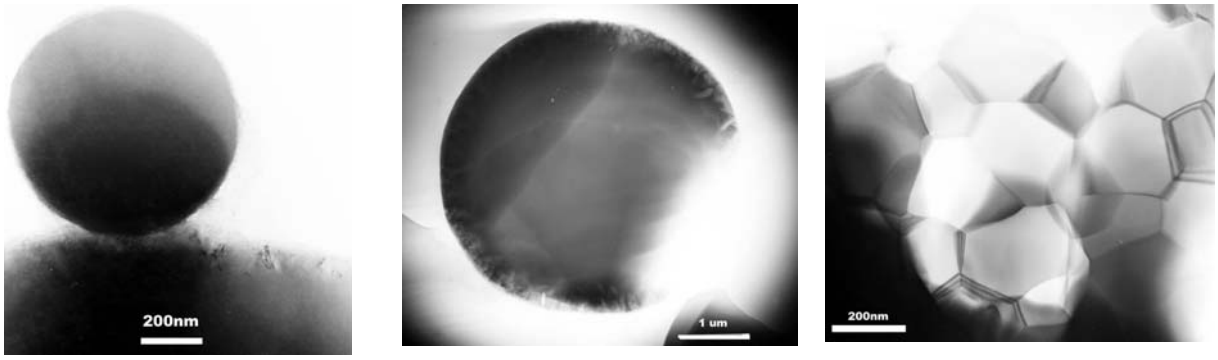

Fig. 3 TEM micrographs of prepared glass microspheres: a), A43, small, completely amorphous microsphere, b), A75, larger microsphere with surface crystallization, c) A57, polycrystalline microsphere with microstructure resembling polycrystalline α-Al_2O_3 or YAG.

4. Conclusions

Amorphous yttrium aluminates of various compositions and with high alumina contents were prepared by flame synthesis from powder precursors, and characterised by OM, SEM, TEM and XRD. The methods confirmed spherical morphology of prepared specimens, with diameters up to 40 μm. Spheres with smaller diameter were completely amorphous, while those with lager diameter were often partly, or completely crystalline, containing nanocrystals of YAG, YAP, or α-Al_2O_3 growing from the surface to the spheres' interior. In some case completely polycrystalline spheres were observed with microstructures resembling polycrystalline α-Al_2O_3 or YAG. In addition, transition aluminas were detected in microspheres with higher alumina contents.

Acknowledgement

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