COMPOSITES WITH EUTECTIC MICROSTRUCTURE BY HOT PRESSING OF Al_2O_3–Y_2O_3 GLASS MICROSPHERES

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In the work we describe the use of Al_2O_3–Y_2O_3 glass microspheres with high alumina contents prepared by flame synthesis as a precursor for materials with binary eutectic microstructure and high hardness. XRD amorphous microspheres with eutectic composition in a pseudobinary system Al_2O_3–$Y_3Al_5O_{12}$ (YAG) were prepared by feeding a crystalline powder precursor of respective composition into methane-oxygen flame. The microspheres with the mean diameter ≈10 μm were hot-pressed in vacuum under various conditions (temperatures 840-1600°C, pressure 30 or 40 MPa, isothermal dwell 0-120 min). Hot pressing at 1600 °C without isothermal dwell yielded fully dense bulk materials with fine two phase microstructure with Al_2O_3 and YAG phases percolating at submicrometre level and with hardness 15 GPa. Extension of the isothermal dwell resulted in undesirable coarsening of the resulting microstructure.

INTRODUCTION

Significant attention has been paid to preparation of rare earth aluminate-based materials with eutectic microstructures, i.e. the microstructures prepared usually by solidification of a melt with eutectic composition. Such microstructure consists typically of mutually interpenetrating (percolating) network of respective phases, mixed at submicrometre level. Such materials were reported to have excellent high temperature mechanical properties in oxidative environment, good mechanical behaviour, and thermal stability up to near the melting temperature in oxidative environment. For example, flexural strengths of the materials prepared in the system Al_2O_3–YAG were 360-500 MPa from room temperature to 1800°C in air, and compression creep strength at 1600 °C was about 13 times higher than that of sintered composites with the same chemical composition [1]. Especially due to these properties such materials are promising candidates for high temperature applications, such as fiber materials for reinforcement or as bulk materials for machine parts (jet aircraft engines and high efficiency power generation gas turbines components) [2]. Numerous works describe preparation of Al_2O_3/YAG [1-5] $Al_2O_3/GdAlO_3$ [6], $Al_2O_3/RE_3Al_5O_{12}$ (RE = Sm–Lu, Y) [7], Al_2O_3/ZrO_2 [8, 9] ceramics with homogenous ultra fine eutectic microstructure. The described systems were usually prepared by various solidification procedures, using Bridgman method, floating zone melting, edge-defined film-fed growth, micro-pulling down methods or laser floating zone method [9] in bulk form or as fibers.

An alternative route is represented by controlled crystallization of glasses with eutectic composition. Kakegawa et al. describe preparation of very fine-grained glass-ceramics and polycrystalline ceramics with eutectic microstructures through sintering of flakes prepared by rapid cooling of eutectic melts on rollers [10]. However, significant microstructure coarsening was observed during pressureless sintering of the flakes and spark plasma sintering was required to prepare the materials with submicrometre microstructure.

This work reports on successful preparation of materials with eutectic microstructures in the system Al_2O_3–$Y_3Al_5O_{12}$ by pressure assisted densification (hot pressing, HP) of glass microbeads with eutectic composition (60 wt.% Al_2O_3, 40 wt. % Y_2O_3) prepared by flame synthesis. The influence of hot pressing conditions on final density, microstructure, and phase composition of prepared materials is reported.

EXPERIMENTAL

Precursor powder containing 60 wt.% (76.8 mol.%) Al_2O_3 and 40 wt.% (23.2 mol.%) Y_2O_3 was prepared from high purity oxide powders (Al_2O_3 - Taimicron TM DAR, Krahn Chemie GmbH, Germany, Y_2O_3 - Treibacher Industrie AG, Austria). Yttrium oxide was dissolved in concentrated HNO_3, and after mixing the nitrate solution with alumina powder, the suspension was homogenized for 1 h by ball milling in PE jar. Water solution of ammonium hydroxide was then added into the mixture, to precipitate yttrium hydroxide. After calcination at 650°C for 1h, the mixture was pre-reacted at 1600ºC for 4 h in a platinum crucible, crushed, milled and sieved. The powder was then fed into high temperature CH_4–O_2 flame and molten particles were quenched by spraying with distilled water. The prepared glass microspheres were collected, washed with acetone and dried. HP experiments were carried out in vacuum under various conditions (pressure 40 MPa, temperatures 840°C, 950°C, 1000°C, 1300°C and 1600 °C, dwell times 0-120 min). The HP conditions of individual experiments are summarized in Table 1.

The microspheres were characterized by optical microscopy, SEM (Zeiss EVO 40HV at accelerating voltage 20 kV) and TEM (JEOL 1200EX at accelerating voltage 120 kV). Diameter size distribution of particles was determined with the use of SEM micrographs and image analysis software Lucia v. 4.82 (LIM Praha, Czech Republic). Glass transition temperature T_g and the onset of crystallization temperature T_x were determined using DTA analysis of prepared glass microspheres at a DTA-TGA simultaneous analyzer SDT 2960. The phase composition of all three systems, i.e. the precursor powders, the microspheres and bulk hot pressed materials was evaluated by X-ray powder diffraction (STOE Stadi-P, Germany, CuKα radiation, 2θ range 20-80°). The weight fractions of crystalline phases in sintered samples were estimated from X-ray diffraction patterns from integral intensities of diffraction peaks by the method of standard addition [11]. In addition the powders and the microspheres were examinated by IR spectroscopy (FTIR spectrometer Nicolet Magna 750 in the wavenumber range 400-4000 cm^{-1}, by using standard KBr technique). Hardness and fracture toughness of hot pressed specimens was determined by Vickers indentation on polished cross sections at 10 N and 100 N loads, respectively. The microstructure of hot pressed specimens was examined by SEM (Tesla BS300) and FEG SEM (JEOL 7600 F). Density of bulk materials was measured by Archimedes method in mercury. The true skeletal density of both the microspheres and hot pressed specimens (in pulverized form) was measured by liquid pycnometry in hexamethyldisiloxane, as the immersion liquid.

RESULTS AND DISCUSSION

For preparation of bulk materials with eutectic microstructure we selected the system Al_2O_3–Y_2O_3 containing 60 wt.% (76,8 mol.%) Al_2O_3, which corresponds to the eutectic composition in pseudobinary system Al_2O_3–$Y_3Al_5O_{12}$. For flame synthesis of the precursor glass microspheres we used a narrow fraction of starting powder with particle size 25-42 μm. The powder was polycrystalline with YAG and α-Al_2O_3 as major crystalline phases. Accordingly, IR spectra of the powder contained well defined bands corresponding to Al–O and Y–O vibrations in tetrahedral coordination in YAG structure, as well as Al–O vibrations characteristic for octahedrally coordinated aluminium atom in α-Al_2O_3.

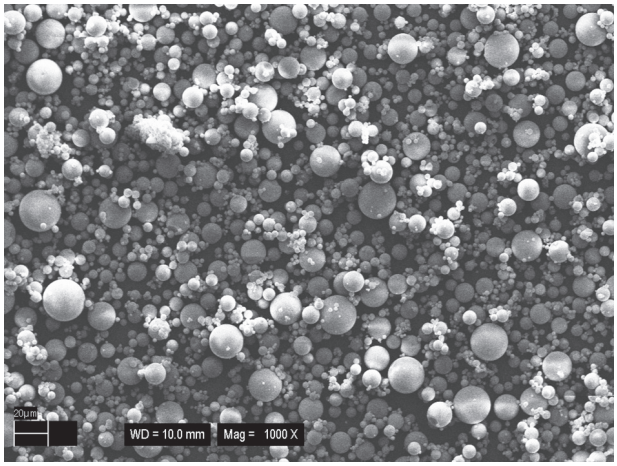


Figure 1. SEM micrographs of prepared glass microspheres.

Table 1. Conditions of hot pressing, Vickers hardness and phase composition of prepared materials.

Sample	Temperature (ºC)	Pressure (MPa)	Hold (min)	Vickers hardness (GPa)	XRD (phases)
A6Y4H1	840	30	50	n.m	YAG, YAP
A6Y4H2	900	30	120	n.m	YAG, YAP
A6Y4H3	1000	40	180	n.m	YAG, YAP
A6Y4H4	1300	40	60	14.6±1.2	YAG, α-Al_2O_3
A6Y4H5	1300	40	180	14.1±1.3	YAG, α-Al_2O_3
A6Y4H6	1600	40	0	14.8±0.9	YAG, α-Al_2O_3
A6Y4H7	1600	40	60	16.3±1.4	YAG, α-Al_2O_3

The OM examination of prepared microspheres showed that the particles were spherical and transparent. The SEM images (Figure 1) revealed a polydisperse system consisting of microspheres with diameters ranging from 1 to 35 μm. The major fraction were microspheres with sizes within the intervals 0-5 μm and 5-10 μm, and only small part accounted for microspheres with larger diameters, i.e. from 10 to 35 μm. The amorphous nature of prepared glass microspheres was confirmed by X-ray powder diffraction (Figure 2). Measured density of prepared microspheres was 3.856 g.cm^{-3}, which is by about 20 % less than the theoretical density (4.216 g·cm^{-3}) calculated by the rule of mixtures from the densities of corresponding crystalline phases (YAG and α-Al_2O_3), also indicating less ordered (amorphous) nature of the structure of prepared microspheres. However, more detailed investigation of the glass microspheres by TEM revealed that they are at least partially crystalline (Figure 3a). Although an unambiguous statistical evidence is not available, it appears that smaller microspheres (between 1 and 10 μm diameter) are amorphous, while larger particles with diameter >10 μm were partially or fully crystalline, containing crystallites of various size and morphology, (Figure 3b). However, the crystal structures do not have to be necessarily harmful, as they can serve as seeds for crystallization of desired eutectic structures. The DTA analysis of the microspheres revealed the presence of three exothermic effects: the first weak effect with maximum at 870°C was interpreted as the glass transition temperature T_G of the aluminate glass, and it is with good agreement with the available published data [12]. Two closely spaced sharp exothermic peaks with the onset T_X at 900 °C and the second maximum at 935.8°C were attributed to crystallization of YAG and $YAlO_3$ (YAP) phases (Figure 4).

The conditions of HP experiments are summarized in Table 1. At first the experiments were aimed at preparation of bulk materials at temperatures where the crystallization, according to the results of DTA could be avoided. They were therefore conducted at the pressure of 30 MPa and at temperatures slightly below T_G (840°C) or in the temperature interval between T_G and T_X. In the latter case densification by viscous flow can be expected. However, the samples prepared under these conditions were white and opaque, with low degree of compaction and with high residual porosity. The SEM investigation revealed the microstructures consisting of organized and only slightly deformed microspheres assembled to a solid body without any indication of stronger compaction or bonding (Figure 5a). The following specimens were therefore subsequently sintered at higher temperatures (1000, 1300 and 1600ºC) under various pressure (30, 40 MPa) and at different holding times (50, 60, 120, 180 min). Prepared samples were white and opaque, and the hardness gradually increased with increasing temperature and time of hot pressing. (Table 1). The highest Vickers hardness 14.8 and 16.3 GPa was measured for the specimens sintered at 1600ºC (sample A6Y4H6 and A6Y4H7, respectively).

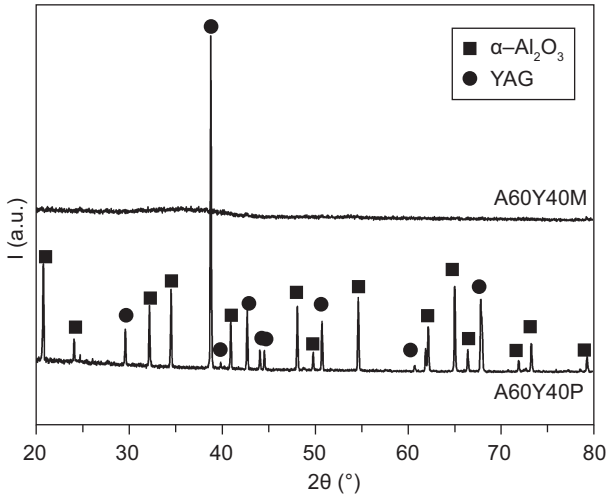
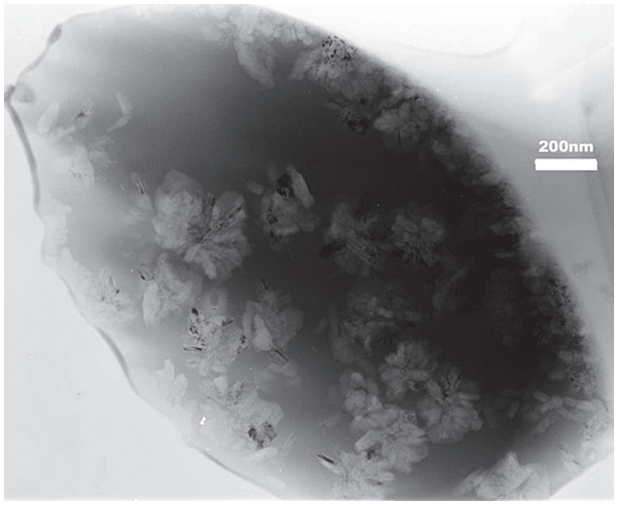


Figure 2. Results of XRD analyses of prepared starting powders and glass microspheres.

a)

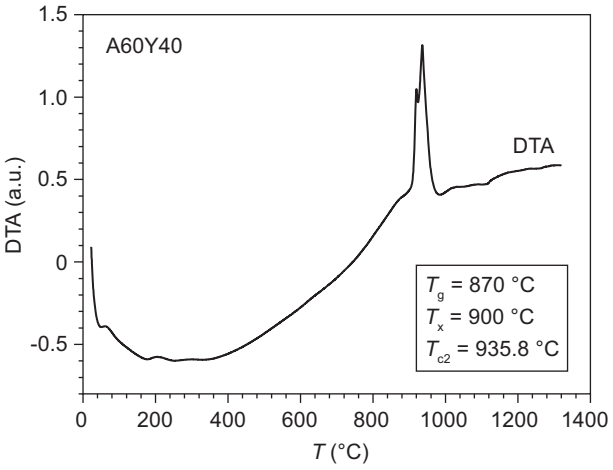


b)

Figure 3. Bright field TEM micrographs of prepared microspheres with angular (a) and dendritic (b) crystallites.

SEM examination of the fracture surface of the sample sintered at 1600ºC and the pressure of 40 MPa without isothermal dwell (A6Y4H6) revealed highly compact microstructure with low residual porosity. Neither the originally present microspheres nor phase boundaries could be distinguished in the SEM micrographs of the fracture surface acquired in secondary electron (SE) mode (Figure 5b). Extension of the isothermal dwell at 1600°C to 60 minutes resulted in significant coarsening of the microstructure, as can be seen from the SEM micrographs of the fracture surface of sample A6Y4H7 (Figure 5c). The ceramics contained micrometre-sized grains with well developed crystal faces. The character of fracture closely resembles the fracture surface of monolithic polycrystalline solid state sintered alumina or YAG.

The results of FEG SEM examination of polished cross section of the specimen A6Y4H6 with the use of a low angle backscattered electron detector applied to enhance phase and composition contrast revealed the existence of a very fine microstructure consisting of two phases percolating at submicrometre scale and characteristic for eutectic composites (Figure 6a). Gray phase was attributed to α-Al_2O_3, while the white parts



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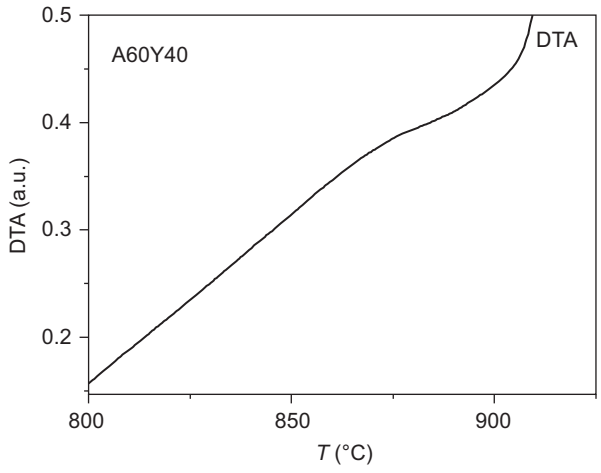
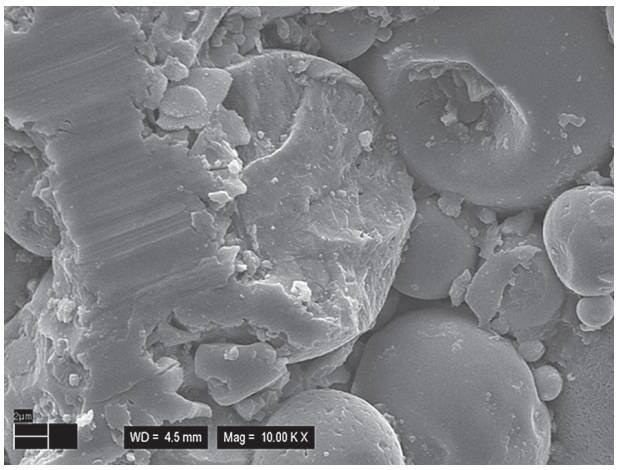


b)

Figure 4. Results of DTA analysis of prepared glass microspheres.



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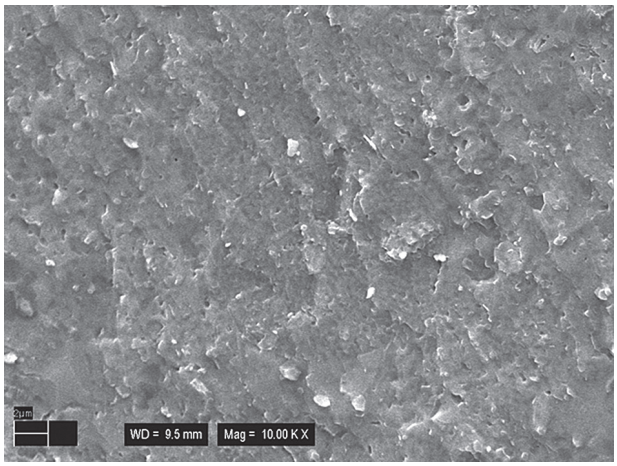

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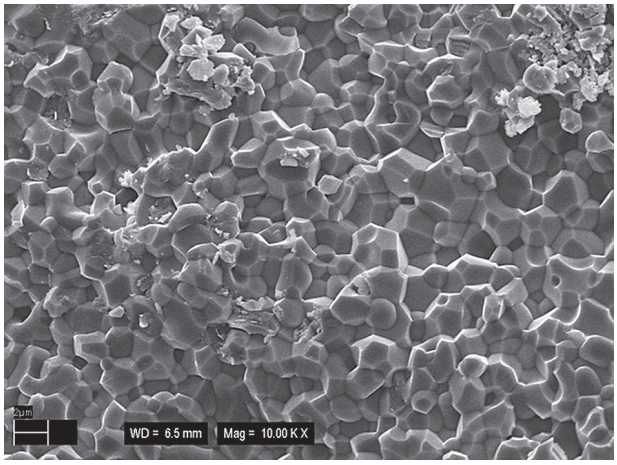
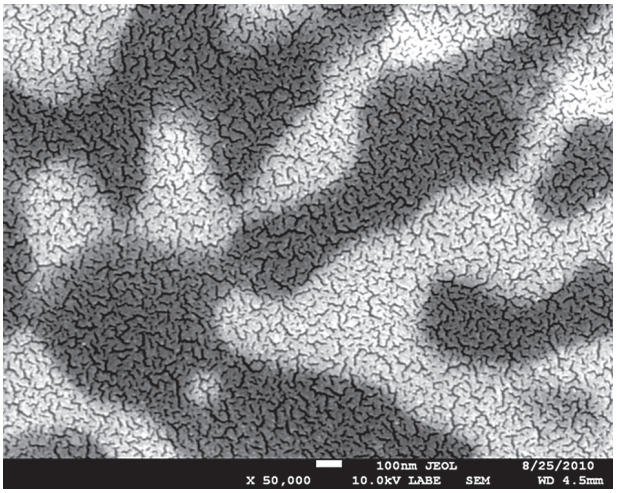


c)

Figure 5. SEM micrographs of fracture surfaces of materials densified under various conditions. The conditions of hot pressing are shown in parentheses - a) A6Y4H1 (840ºC, 30 MPa, 50 min); b), A6Y4H6 (1600ºC, 40 MPa, 0 min); c) A6Y4H7 (1600ºC, 40 MPa, 60 min).

represent YAG. The phase composition was confirmed also by the results of X-ray diffraction, as will be discussed in more detail below. At lower magnification (Figure 6b) the outlines of original microspheres could be discerned in some cases. The micrograph indicates also rather inhomogeneous nature of the composite, where the areas with characteristic eutectic microstructure (e.g. the circular part in the middle of the micrograph) are surrounded by the areas of continuous YAG phase with isolated grains of α-Al_2O_3.

The XRD examination of hot pressed specimens revealed some trends in phase development. The materials sintered at lower temperatures (840, 900, 1000ºC) contained YAG and $YAlO_3$ phase with perovskite structure (YAP) as major crystalline phases. No α-Al_2O_3 was detected. The samples densified at higher temperatures (1300, 1600°C) contained YAG and α-Al_2O_3. The results



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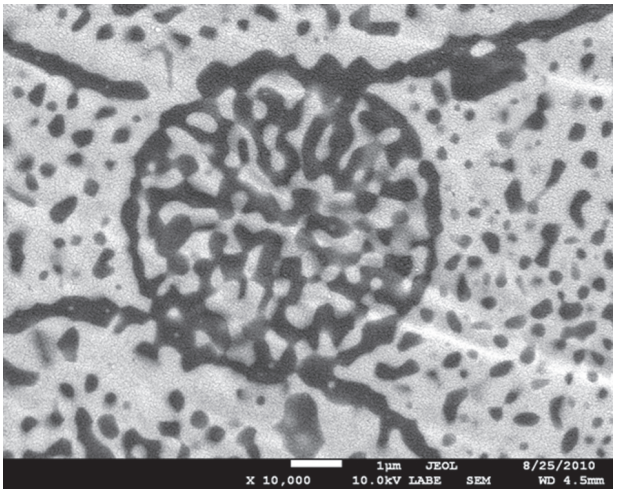

b)

Figure 6. FEG SEM micrographs of the A6Y4H6 sample densified at 1600ºC and 40 MPa, without isothermal dwell - a) detailed view of the microstructure; b) overall view showing phase and compositional inhomogeneity of the prepared material.

indicate preferential crystallization of YAG and formation of the YAP phase as an intermediate product in the formation of YAG. The α-Al_2O_3 crystallizes only after yttrium is consumed by formation of YAG. The results are in agreement with the results of Blosi et al. [13], who reported crystallization of YAP, YAG and YAM in the temperature interval 800-900 ºC, as well as stability of all these phases up to 1200º C. They also conclude that YAG and YAM start to crystallize at a lower temperatures than YAP, but being thermodynamically favoured over YAP they are stable to higher temperatures [13, 14]. Guo et al. [15] report on formation of YAP and YAG in the interval 850-880 ºC, with complete conversion to YAG at 1060°C. They also propose that the temperature of 1150°C is necessary to obtain pure crystalline YAG. Similarly, Huang et al.[16] observed complete disappearance of YAP in samples sintered at 1200ºC. The total content of crystalline phases increased with increasing temperature and time of isothermal dwell as documented by growing intensity of diffraction peaks in Figure 7.

Pressure-assisted sintering of glass microspheres prepared by flame synthesis was shown to be a suitable method for preparation of very fine polycrystalline YAG/α-Al_2O_3 composites with the two phases percolating at submicrometre scale. Such microstructure cannot be achieved by conventional pressureless or pressure-assisted sintering of mixed polycrystalline powders. Although the method represents a relatively simple way of obtaining such microstructures and does not require any sophisticated experimental equipment, there are still several questions that need to be addressed:

1. fluctuation of chemical composition of individual microspheres resulting in variation of phase composition within the composite,
2. presence or absence of crystal seeds in microspheres of various diameters, which also influences the phase composition and microstructure of the composite.

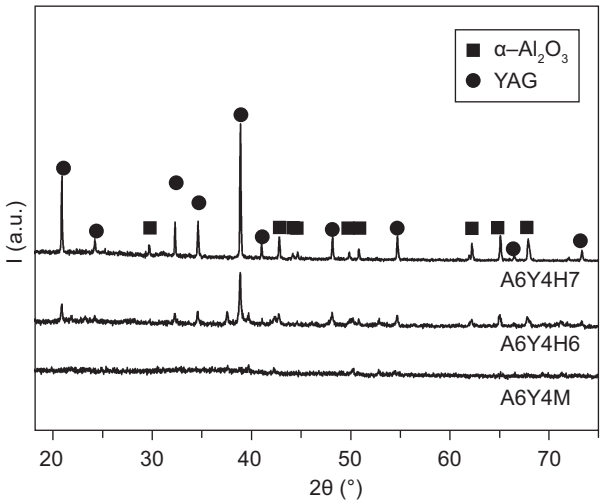

Figure 7. The results of XRD analysis of glass microspheres and the materials A6Y4H6 and A6Y4H7 after hot pressing.

This is reflected also in the results of hardness measurement, where individual values of hardness measured for the same material varied widely, depending on the location of the indent. As a solution, preparation of precursor powder for flame synthesis by sol-gel method is proposed. Generally, the powders prepared in this way are highly homogenous and contain highly uniform particles. Resulting reduction of particle size of starting powder could facilitate the preparation of completely amorphous glass microspheres with no crystal seeds, and thus higher homogeneity of the composite.

CONCLUSIONS

The work reports on an alternative method of preparation of ceramics in the system YAG/α-Al_2O_3 with eutectic microstructure. Nearly fully dense materials with hardness up to 16.3 GPa can be prepared by conventional hot pressing of Al_2O_3–Y_2O_3 glass microspheres with eutectic composition prepared by flame synthesis from powder precursors, showing a simple way for preparation of two phase microstructures percolating at submicrometre scale. The presence of crystal seeds in glass microspheres influences the crystallization of the system and impairs the homogeneity of the final microstructure. Extension of isothermal dwell beyond the optimum time results in significant coarsening of the microstructure, which then resembles the microstructure of Al_2O_3–YAG composites prepared by conventional sintering from powders.

Acknowledgement

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