Materials Science-Poland, *Vol. 28*, *No. 2*, *2010*

Fabrication of magnesium aluminum silicate glass ceramics by sintering route

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Magnesium aluminum silicate (MAS) glass ceramic material was prepared by the sintering route. A three-stage heat treatment, consisting of calcination, nucleation and crystallization, was developed with MgF_2 as a nucleating agent. The effect of the percentage chemical composition and the sintering temperature on the density of the compacted material was also studied. The thermal stability of MAS was measured by thermogravimetry (TG), differential thermal analysis (DTA). TG/DTA studies revealed that the powder exists as $MgO–Al_2O_3–SiO_2–H_2O$ in solid state, and then transforms to $MgO–Al_2O_3–SiO_2$ via some metastable intermediates above 300 °C. The microstructure and phases were analyzed by X-ray diffractometry (XRD). XRD analysis revealed the formation of various phases such as magnesium silicate, fluorophlogopite, nobergite, siliminite etc. at various processing temperatures.

Keywords: *magnesium aluminum silicate; machinable glass; particle size distribution*

1. Introduction

Magnesium aluminum silicate (MAS) glass ceramic systems are of technological importance because of their usefulness in high voltage applications and in an ultra high vacuum. These materials not only posses peculiar machinability features but also have superior electrical insulation properties, ultra high vacuum compatibility, high thermal stability, low thermal conductivity and good mechanical strength [1]. MAS materials are also being used in nuclear technology [2, 3], in the production of prototype components, used in medicines for the axles of mechanisms providing energy for implanted cardiostimulators and are also used in the production of welding jets or as holders for welded components [4–7]. The properties of MAS glass ceramics such as hardness, machinability, and conductivity depend upon the composition and microstructure. Machining of these materials can be carried out to precise tolerances and

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surface finish with conventional tools. The explanation underlying the good machinability of MAS lies in the unique microstructure of an interlocking array of platelike mica crystals, dispersed uniformly throughout the glass matrix. MAS glass ceramic materials have been prepared by controlled crystallization in which a large number of tiny crystals rather than few bigger single crystals have been grown [2, 8]. Radonig ey al. [9] studied the effect of fluorine content and its source on the crystallization of MAS materials. The predominant crystalline phases identified in their study were fluorite, norbergite or fluorophlogopite, depending on the heat treatment, the fluorine concentration, etc. General preparation methods have been discussed in the literature [2, 4] but due to special nature and technological importance of the material, the crucial preparation process has either been too vaguely addressed or is missing entirely. Therefore, the preparation of these materials is of special importance. In the light of this fact, preparation of machinable MAS glass ceramic was undertaken using a sintering route.

2. Experimental

Materials. High purity chemicals, silica (Fluka), aluminum oxide (BDH), magnesium oxide (Merck), potassium carbonate (Riedel-de-Haen), boron oxide (BDH), magnesium fluoride (BDH), orthophosphoric acid (BDH) and acetone (BDH) were used as raw materials.

Preparation. Magnesium aluminum silicate (MAS) glass ceramic specimens were prepared by utilizing SiO_2, Al_2O_3, MgO, K_2CO_3, and B_2O_3 as given in Table 1.

Table 1. Magnesium aluminum silicate glass ceramic specimen's designation and composition

Specimen	Chemical composition (wt. %)					
	SiO_2	Al_2O_3	MgO	K_2CO_3	B_2O_3	MgF_2
MAS -1	36.62	12.73	16.87	13.93	1.91	17.91
MAS -2	37.57	13.19	16.49	14.26	1.97	16.49
MAS -3	37.72	13.23	16.05	13.98	2.48	16.54
MAS -4	38.51	13.51	16.38	14.27	2.53	14.78
MAS -5	36.34	24.82	13.23	11.32	3.53	10.76

Three-stage schedules, i.e. calcination, nucleation and crystallization processes were used. In the first stage, initial charge was mixed thoroughly and calcined at 950 °C for 24 h according to a pre-determined heating schedule. Approximately 4–7 wt. % MgF_2 was added to the calcined charge and milled in a planetary ball mill for 40 h. The fine ball milled charge was seasoned in 5% H_3PO_4 acid solution in an acetone medium for 72 h. Compacts of MAS ($61\times16\times5$ mm^3) were made using a hydraulic press of the load capacity of ca. 25 t/in^2 (1 t/in^2 = 15.44 M Pa).

Sintering. The compacts were sintered in a two-step heating program. In the former step, the compact was heated up to 600–630 °C for 2–4 h to ensure good nucleation and to initiate the crystal growth. In the latter step, heating was carried out at different heating rates, in the range of 15–60 °C/h, up to sintering temperatures of 950–1080 °C. The sample was kept at the sintering temperature for a sufficiently long time to achieve the desired crystal growth.

Characterization. The crystallinity of MAS specimens was determined by X-ray diffraction on a Rigaku Geiger flux instrument using CuKα radiation. For measurement of the weight loss, combined TG–DTA thermal analysis was performed using a Netzsch STA-409 thermoanalyzer. The particle size distribution of the powder specimens was measured by a laser particle size analyzer (SK-Laser Micron PRO-7000S). The density of MAS specimens was measured using an Ultra Pycnometer 1000 (Quantachrome). Porosity was measured by radiographic techniques, using a realtime radiography Instrument (Model Isvolt HS Panta SeiFert). Before making the measurements, the sample surface was polished with 3μ alumina powder to obtain a good reflective surface. The micro-structural features and porosity of the sintered specimen MAS-5 were observed using a scanning electron microscope (SEM, LEO 4401). The specimen was fully polished, placed on an aluminum stud, dried in air and then it was coated with thin gold film for the SEM observation.

Effect of acids and bases. The sintered specimens were treated with 5% hydrofluoric and hydrochloric acids for 24 hrs at 95 °C, in order to observe the effect of these acids. The effect of 5% sodium hydroxide and sodium carbonate was also studied, for 6 h at 95 °C. The samples were weighed, to check for any loss in weight, after washing off acids and bases.

3. Results and discussion

Thermal analysis (TG/DTA) was conducted and the representative thermograms of specimen MAS-5 are shown in Fig. 1. A total weight loss 9.14% was observed after heating up to 900 °C. Two peaks in the DTA data were observed. The former peak is an endothermal minimum, which is connected with glass transformation. The exothermal maxima (second peak) correspond to the separation of the crystalline phase. The position of the minimum on the DTA curve is basically determined by the chemical composition of the separated phase or by its transformation temperature. The exothermal crystallization peak, its position and shape are characterized by the crystallization process [10]. All the volatiles were completely removed at 900 °C. The particle size distribution curve of specimen MAS-5 powder is shown in Fig. 2. This curve revealed that the particle size distribution is <10μm with a median particle size of around 5.3 μm. Experimental results confirmed that a smaller particle size and the particle size distribution that has a narrow profile is essential for good sinterability. It was also found that specimen MAS-5 sintered at a temperature of 1040 °C yielded

a material of smaller and uniform particle distribution and the density of ca. 2.35 g/cm^3 (96% of the theoretical density).

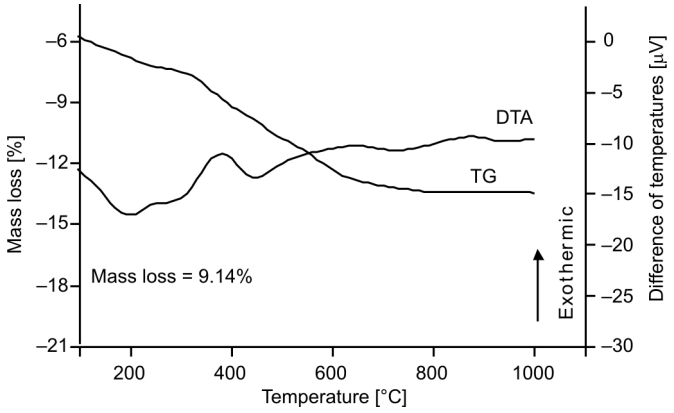

Fig. 1. TG/DTA curves for ceramic powder of magnesium aluminum silicate glass (specimen MAS-5)

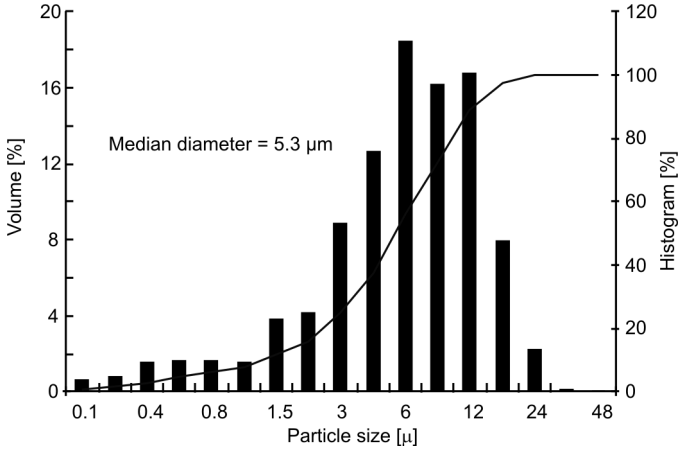

Fig. 2. Particle size distribution of ceramic powder of magnesium aluminum silicate glass (specimen MAS-5)

During pressing it was observed that if the initial charge was not pulverized for a sufficiently long time after calcination, the sintered briquette had a lot of open pores on the surface. Thus, in order to minimize the porosity in the sintered product, quite a long period was used for pulverization: finally 72 h duration was selected. The sintering parameters, along with the green and sintered densities of samples MAS-1 to MAS-5, are given in Table 2. The data for samples MAS-4 and MAS-5 sintered at other temperatures are also given in Table 2. A insignificant increase in density was observed in the sintering temperature range 1040–1060 °C, the duration being in the range 2–4 h. It was observed that as the sintering temperature was increased beyond

1060 °C, excessive thermal energy leads to some rearrangement among the grains as well as some isotropic crystal growth. In addition, decomposition of fluorophlogopite phase, formed at lower temperature, takes place, leading to the development of internal line cracks/voids [9] in the material. As a result of this, the material appears swelled and its density decreases at higher sintering temperatures.

Table 2. Sintering parameters, green and sintered densities

Specimen	Sintering conditions (Temperature [°C]/time [h])	Green density [g/cm^3]	Sintered density [g/cm^3]
MAS-1	1040/3	1.79	2.18
MAS-2	1040/3	1.74	2.12
MAS-3	1040/3	1.91	2.29
MAS-4	1040/3	1.68	2.15
MAS-4a	1040/2	1.65	2.12
MAS-4b	1050/2	1.72	2.14
MAS-4c	1060/2	1.64	2.14
MAS-5	1040/3	1.79	2.35
MAS-5a	1060/2	1.86	2.34
MAS-5b	1080/2	1.74	2.35

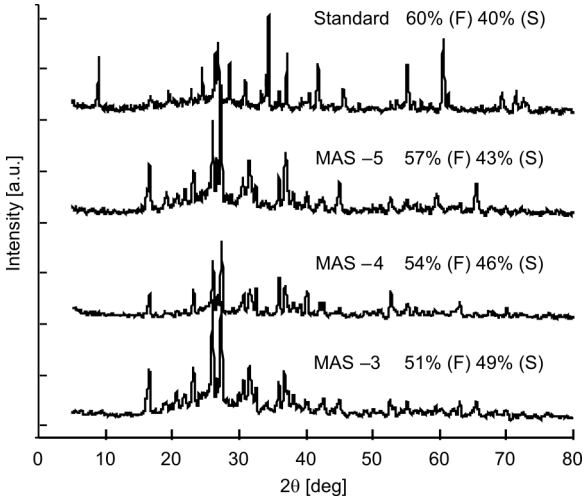

Fig. 3. XRD patterns of magnesium aluminum silicate glass ceramic, specimens MAS-3-5 (F – fluorophlogopite, S – sillimanite phase)

The XRD patterns of specimens MAS-1 to MAS-5, sintered at 1040 °C for 3 h, are presented in Fig. 3. The XRD peaks were indexed. The predominant phases in the synthesized MAS specimens were identified as fluorophlogopite (F), sillimanite (S) and lausite (L). The percentage of these phases in each specimen is given in Table 3. The specimen MAS-5 shows the predominant fluorophlogopite phase. Figure 4 shows

radiographic data for the estimation of porosity. The specimen MAS-5 after sintering is shown in Fig. 4a. Radiography of specimen MAS-5 was conducted in order to evaluate the porosity. The radiographic image, as indicated in Fig. 4b, does not show any sign of porosity.

Table 3. Percentage of phases in magnesium aluminum silicate glass ceramic observed by X-ray diffraction

Specimen	Fluorophlogopite (F) [%]	Lausite (L) or sillimanite (S) [%]
MAS-1	28	71
MAS-2	30	69
MAS-3	51	49
MAS-4	54	46
MAS-5	57	43

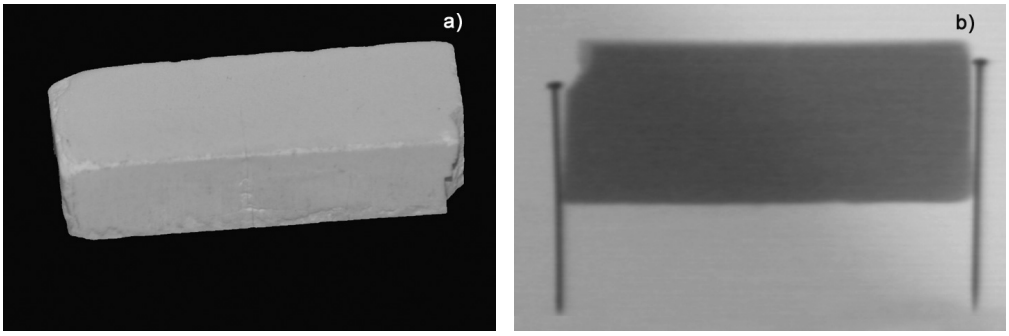

Fig. 4. Sintered specimen (MAS-5) of magnesium aluminum silicate glass ceramics (a) and a radiographic (RG) image of MAS-5 (b)

This means that the specimen MAS-5 has a through porosity. However, some surface porosity was observed in specimen MAS-5 by SEM. Figure 5 shows a SEM image of a sintered specimen of MAS-5.

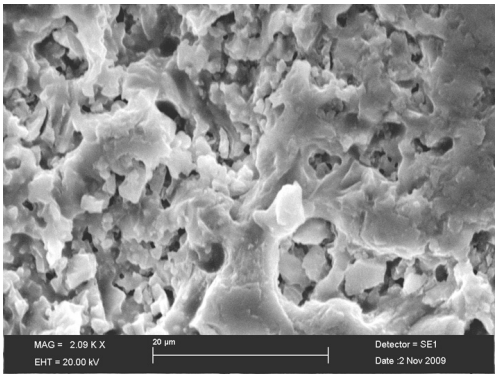

Fig. 5. SEM image of magnesium aluminum silicate glass ceramic (Specimen MAS-5)

Table 4. Effect of acids and bases on magnesium aluminum silicate glass ceramic

Specimen	Resistance to acid weight loss per unit area				Resistance to base weight loss per unit area			
	Temperature [°C]	Time [h]	HCl (5%) [mg/cm^2]	HF (5%) [mg/cm^2]	Temperature [°C]	Time [h]	NaOH (5%) [mg/cm^2]	Na_2CO_3 (5%) [mg/cm^2]
MAS-4	95	24	67	17.51	95	6	10.62	Nil
MAS-4a	95	24	87	156	95	6	9.52	2.13
MAS-5	95	24	48	6	95	6	11.82	1.35

The sintered specimens were tested for resistance to acids and bases when subjected to 5% hydrochloric acid, hydrofluoric acid at 95 °C for 24 h for acids and 6 h for sodium hydroxide and sodium carbonate bases (Table 4). The chemical resistance, i.e. weight loss per unit area (mg/cm^2) of MAS-4a either acids or base was found significant and the values were similar to those of Wawrziniak et al. [11].

4. Conclusions

Magnesium aluminum silicate glass (MAS) ceramic was prepared successfully by a sintering route. The chemical composition of specimen MAS-5 was found appropriate as compared to other four compositions, i.e. MAS-1-4. TG-DTA analysis showed that specimen MAS-5 was thermally stable at temperatures above 900 °C, and that it experienced a 9.14% weight loss after heating up to 900 °C.

MAS-5 sintered 1040 °C yielded a smaller and uniform particle size distribution, which was 96% of the theoretical density. Three various phases: fluorophlogopite (F), sillimanite (S) and lausite (L) were identified in the synthesized magnesium aluminum silicate glass ceramics, however the MAS-5 specimen predominantly consists of fluorophlogopite phase with a uniform particle size distribution. Radiographic tests show at least (3–4%) through porosity, whereas the SEM image indicates some surface porosity.

Acknowledgements

The authors wish to acknowledge the contributions of Dr. A. H. Qureshi for helpful discussions and for his assistance with the preparation of the manuscript. We are also grateful to Mr. M.M.R. Baig for assistance during the preparation of sintered specimens and the measurement of density using an ultra pycnometer 1000 (Quantachrome).

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Received 30 March 2009
Revised 13 November 2009