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Effect of Fe_2O_3 addition on the sinterability and machinability of glass-ceramics in the system $MgO–CaO–SiO_2–P_2O_5$

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Abstract

The sintering and the crystallisation behaviour of a glass in the $CaO–SiO_2–MgO–P_2O_5$ system were studied by considering Fe_2O_3 as the nucleant agent. The addition of 5.0 wt.% Fe_2O_3 to the glass produces a sinterable glass-ceramic, with high relative density and mechanical strength. The glass-ceramic contains apatite, whitlockite and diopside phases at low temperatures and, in addition, wollastonite at high temperatures. The above-mentioned glass-ceramic has moderate machinability without onset of fracture.

Keywords: Glass ceramics; Machinability; Sintering; Mechanical properties; Nucleating agent

1. Introduction

There are a limited number of compositions of glasses, glass-ceramics, and other polycrystalline materials that bond to bone and, are therefore, considered to be bioactive materials. Glass-ceramics show an ability to form strong chemical bonds with living bone as well as to achieve high mechanical strength. These glass-ceramics should be useful for prosthetic applications in a number of load-bearing situations.[1] Kokubo et al.[2,3] found that some glass-ceramics in the system $MgO–CaO–SiO_2–P_2O_5$ (A–W glass-ceramics) can form a tight chemical bond with bones and have a fairly high mechanical strength. Shyu and Wu[4–6] have studied the crystallisation of one such glass-ceramic, that being based on the eutectic in the system $MgO–CaO–SiO_2–P_2O_5$. Liu and Chou[7] studied another composition in the same system, but with a composition different from that of the A–W glass-ceramic. This had a superior strength and fracture toughness when compared to the A–W material. The crystallisation of TiO_2-doped glass-ceramics in the same system has also been investigated by some authors.[1,8]

In the present work, the sinterability and crystallisation of Fe_2O_3-doped glass-ceramics in the system $MgO–CaO–SiO_2–P_2O_5$ was investigated by differential thermal analysis (DTA), X-ray diffraction (XRD), and measurement of linear shrinkage. The machinability of these glass-ceramics was evaluated by naked eye observation after material removal.

2. Experimental procedure

2.1. Glass preparation

Glasses were prepared by fusing reagent-grade chemicals in a platinum crucible. The glasses were melted and maintained at 1430 °C in an electric furnace for 1 h. The molten glasses were then quenched in cold distilled water. The chemical composition of the glasses are displayed in Table 1.

2.2. Methods of analysis

The frits obtained were ground in an electric hard porcelain mortar for 3 h and then ball-milled for 5 h, in aqueous media. The particle size measurements of the powdered glasses were carried out by a laser particle size analyser (Fritsch, Analysette 22). The crystallisation temperature of the glasses was determined by simultaneous thermal analysis (STA) (Polymer Laboratories, model 1640) using 6 mg of glass powders in a platinum crucible in an air atmosphere

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Table 1
Chemical composition (wt.%) of glasses

Glass	CaO	SiO_2	MgO	P_2O_5	Fe_2O_3
1	47.50	30.50	4.50	17.00	0.50
2	46.79	30.04	4.43	16.74	2.00
3	46.07	29.58	4.36	16.49	3.50
4	45.35	29.12	4.30	16.23	5.00

Table 2
The first crystallisation peak temperatures of glasses

Glass	T_p (°C)
1	875
2	883
3	885
4	912

with a heating rate of 20 °C min^{-1}. The glass powders were mixed with 7 wt.% methyl cellulose and cold-pressed using a laboratory uniaxial hydraulic press into 10 mm × 2 mm disks at pressure of 65 MPa.

The sinterability of the glasses was investigated by sintering them for 240 min at the 700, 775, 850, 925, 1000, 1075 and 1130 °C with a heating rate of 20 °C min^{-1} in an electric furnace. The crystalline phases precipitated during sintering were identified by XRD (Siemens, model D-500). The bulk density of the sintered glass-ceramics was determined by the Archimedes method. The powder density of the glass-ceramics was measured by gas pycnometer (Micromeritics, model AccuPyc 1330).

For bending strength tests, rectangular bars with dimensions of 4.9 mm × 4.5 mm × 60 mm were cold-pressed.

Bending strength values were determined by three point loading method, using an Instron universal testing machine, model 1196. For each sample, six measurements were made in the air.

3. Results and discussion

The effect of glass powder particle size on the sintering behaviour of various glasses and glass-ceramics have been investigated.[9,10] While there are many reports which refer to the effect of glass particle size on its sinterability, Eftekhari Yekta and Marghussian[11] described that there is also a threshold mean particle size (∼7 μm) for the glass powders above which the sinterability decreased rapidly. Therefore, the mean particle size of nearly all glass powders at the present work, was adapted about 2 μm. Fig. 1 depicts the particle size distribution of glass 1 powder.

Fig. 2 shows the DTA traces of the above-mentioned glasses containing different amounts of Fe_2O_3 as nucleating agent, their first crystallisation peak temperatures have been summarised in Table 2. It can then be elucidated that the gradual addition of Fe_2O_3 to the base glass, up to 3.5 wt.%, shifts the crystallisation peak to lower temperature but more addition of Fe_2O_3 shifts it to higher temperature. This behaviour indicates that the nucleation ability of crystalline phases improve by addition of Fe_2O_3. Fig. 3 depicts the variation of linear shrinkage of compacted glass powder with temperature. It can be seen that addition of Fe_2O_3 up to 3.5 wt.%, as respected, leads to reduction of sinterability, may be due to decreasing of viscous flow of glass. However, by more addition of Fe_2O_3, i.e. 5 wt.%, the densification trend changes adversely and the sinterability improves. It seems that small amount of Fe_2O_3 acts as a nucleant agent in glass but its more addition will act as a flux.

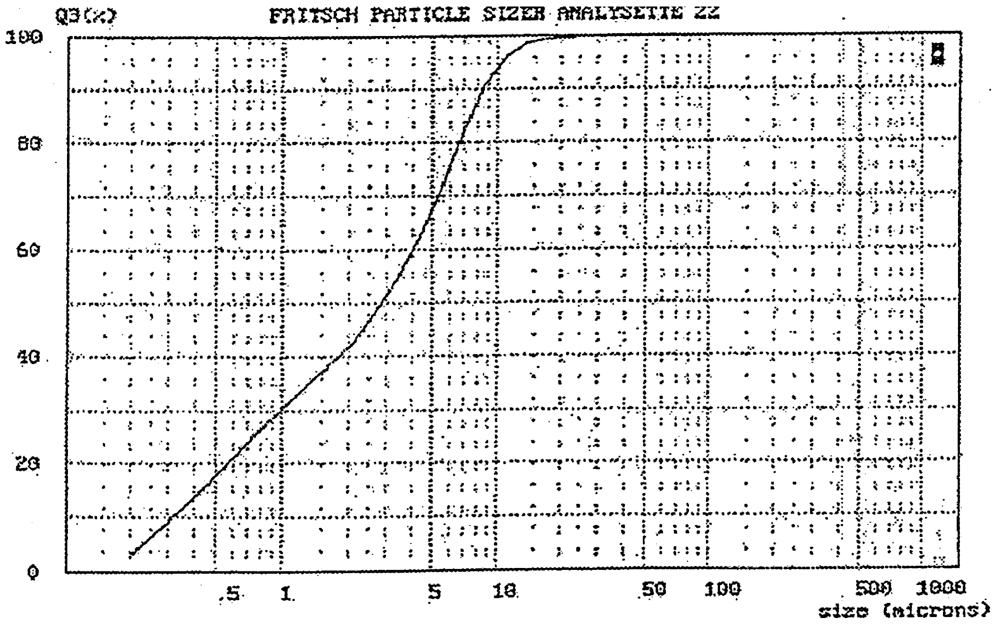

Fig. 1. Particle size distribution of glass powder number 1.

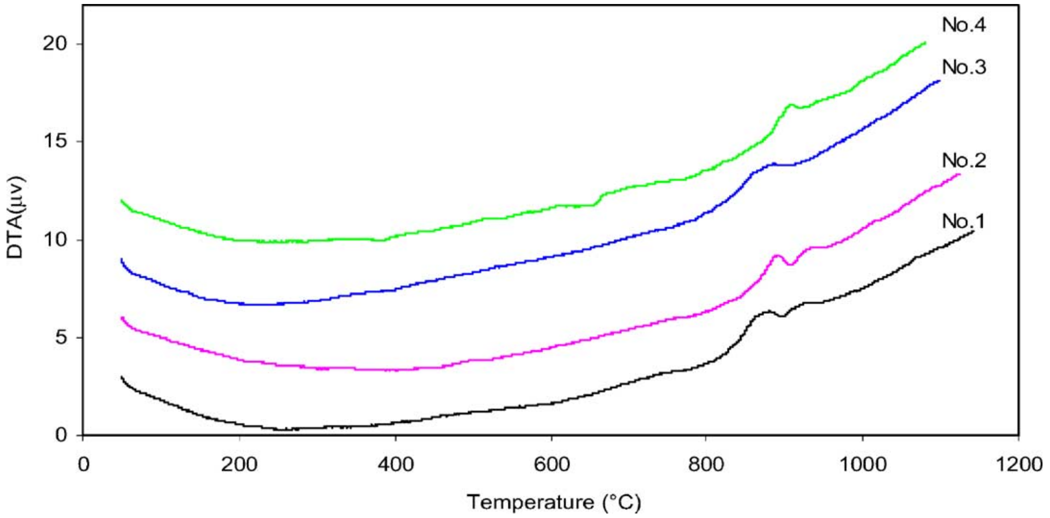

Fig. 2. DTA traces of glasses (heating rate, 20 °C min^{-1}).

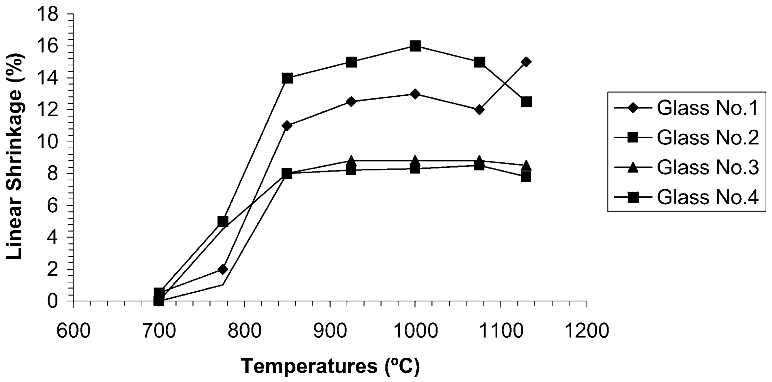

Fig. 3. Variation of linear shrinkage of glasses with firing temperature.

With comparison of sintering results and crystallisation peak temperature of each glass, it can be concluded that the maximum temperature, which leads to full density, is always more than crystallisation peak temperature of the glasses. This indicates that complete densification occurred through viscous flow of the residual glass and crystallisation is proceeded to viscous flow of glass.

As discussed before hand, the most sinterability was observed in glass containing 5 wt.% Fe_2O_3, which its relative density variation with temperature has been shown in

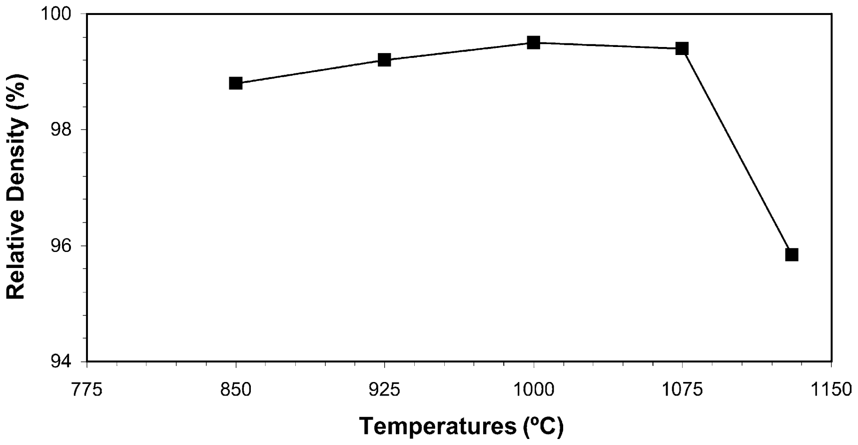

Fig. 4. Variation of relative density of glass number 4 with firing temperature.

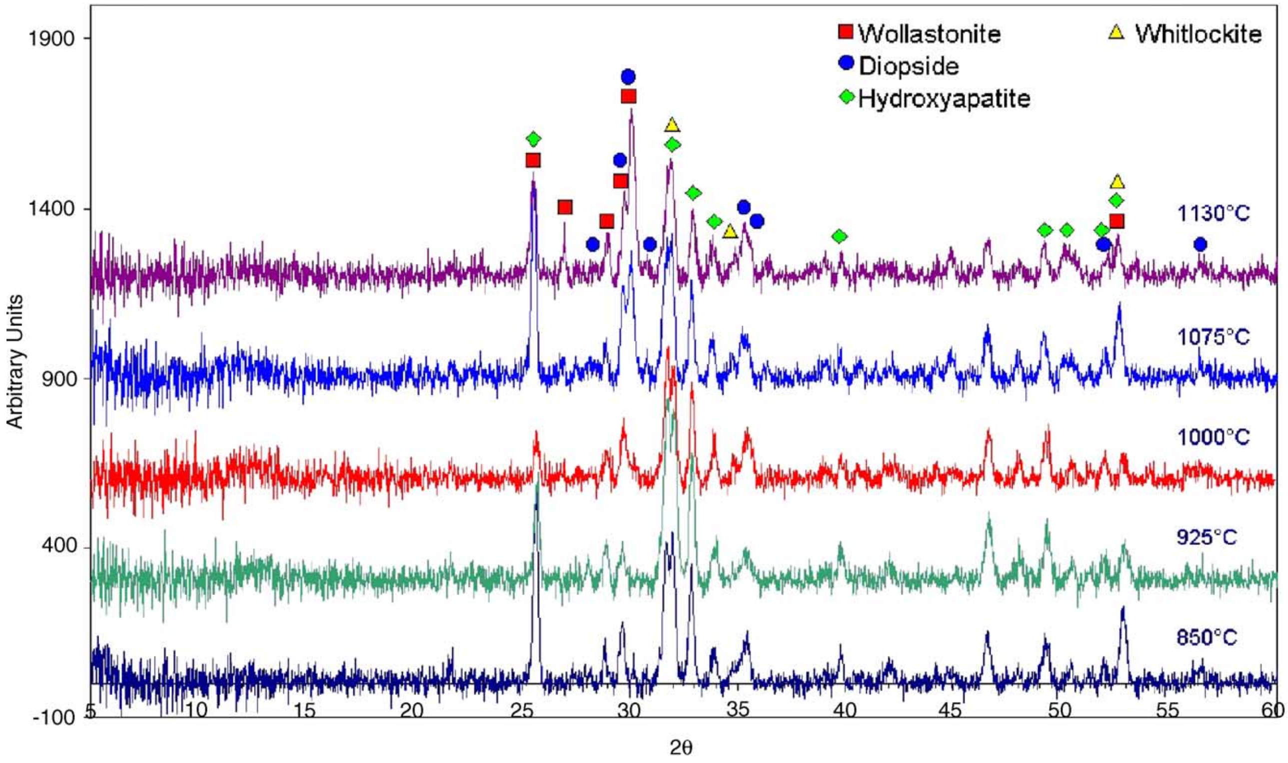

Fig. 5. XRD analysis of glass number 4 heat treated at different temperatures.

Fig. 4. It is observed that the optimum sintering temperature of this specimen was about 1000 °C. It seems that reduction of the linear shrinkage after 1000 °C is somewhat related to the bloating of the glass-ceramic, probably due to reduction of Fe_2O_3 to FeO, and escape of oxygen from the body.

The crystalline phases precipitated with temperature in glass containing 5 wt.% Fe_2O_3, have been shown in Fig. 5. It can be seen that apatite, whitlockite and diopside are precipitated in glasses, fired at low temperatures. However, increasing the firing temperature causes the reduction of apatite and whitlockite phases, and enhancement of wollastonite and diopside.

Fig. 6 shows the variation of bending strength of the glass-ceramic contains 5 wt.% Fe_2O_3, with firing temperature. The bending strength of specimen increases continuously even beyond to the optimum sintering temperature, i.e. 1000 °C, which is compatible with the positive effect of

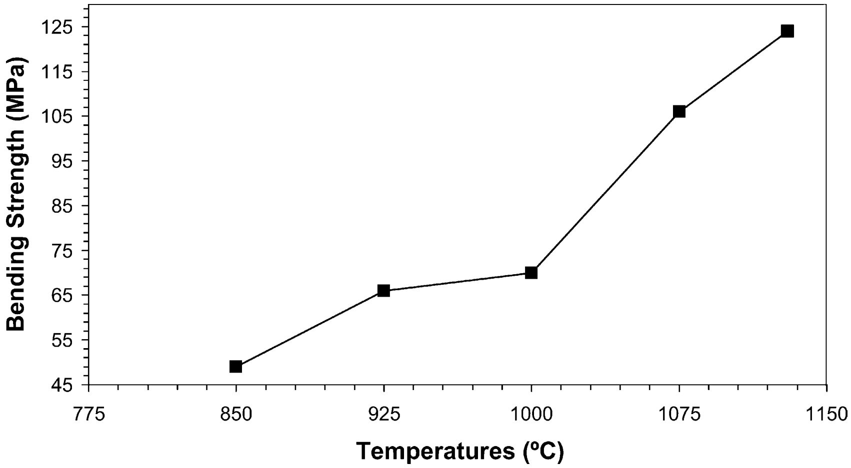

Fig. 6. Variation of bending strength of glasses number 4 with firing temperature.

wollastonite and diopside phases on mechanical strength of glass-ceramics.[12]

The machinability of the glass-ceramics sintered at 1000 and 1130 °C, was examined by a conventional 2 mm drill at a specified drilling rate. Although the machinability of the two specimens were satisfactory, it seems that the machinability of the specimen sintered at 1000 °C, inspite of its less porosity, was more convenient than another one. This different behaviour of specimens could arise from their microhardness differences.

The mean micro-hardness of samples fired at 1000 and 1130 °C were 366 and 573 $\mathrm{kg\,N\,mm^{-2}}$, respectively. The higher hardness of specimens which fired at 1130 °C, is attributed to substitution of apatite and whitlockite by harder diopside and wollastonite phases.[13]

4. Conclusions

1. The bending strength of the sintered glass-ceramics increases with temperature by increasing of wollastonite and diopside amounts.
2. Addition of Fe_2O_3 as nucleant agent showed different behaviour. Up to 3.5 wt.% Fe_2O_3 the crystallisation peak shifts to lower temperature and reduced the sinterability, while utilisation of 5 wt.% Fe_2O_3 shifts the crystallisation peak to higher temperature and improves the sinterability.
3. The machinability of glass-ceramics sintered at 1000 °C was more convenient than sintering at 1130 °C. This was attributed to substitution of apatite and whitlockite by harder phases, i.e. diopside and wollastonite.

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