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# Influence of fluorine content on the crystallization behavior of apatite-wollastonite glass-ceramics

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In 1982 Kokubo *et al.* [1] found that the heat treatment of glass powder compacts in the system CaO-MgO-$SiO_2$-$P_2O_5$-$CaF_2$ resulted in a dense, homogeneous glass-ceramic composed of apatite and $\beta$-wollastonite crystals (AW glass ceramics). The commercially available material is based on a $SiO_2$-$P_2O_5$-CaO-MgO-$CaF_2$ glass of the composition expressed in weight percent 34.0%$SiO_2$, 16.2%$P_2O_5$, 44.7%CaO, 4.6%MgO and 0.5%$CaF_2$. This composition labelled AW1 is given in mole percent in Table I.

Favorable properties of the glass-ceramic included; good mechanical strength [2, 3] and an ability to chemically bond with bone [1, 4, 5]. As a result, the AW glass-ceramic has been used clinically in bone fillers and as a structural material in prosthetic applications [1, 6, 7]. Analysis of a bulk crystallized sample of AW glass-ceramic revealed that the surface nucleation and rapid growth of wollastonite crystals caused internal cracks. A similar analysis of heat-treated powder compacts revealed that sintering and full densification occurs at a temperature much lower than that of the first crystallization temperature ($\sim$800 °C) [3]. Cast AW components exhibited poor mechanical properties due to cracks at crystal boundaries. However, sintered AW components are difficult and expensive to machine, as a result of the hardness of the material. The apatite phase present is thought to be a mixed fluorapatite/oxyapatite/hydroxyapatite. However, since it is impossible to distinguish between these three forms of apatite easily by conventional XRD the exact nature of the apatite phase is unclear. A preliminary examination of the AW glass composition expressed in mole percent is enlightening. The Ca:P:F ratio is 7.03:1:0.05, thus the composition is calcium rich with respect to the apatite stoichiometry (Ca:P = 1.67) and highly fluorine deficient with regard to the fluorapatite (FAP) $Ca_5(PO_4)_3F$ stoichiometry (P:F = 3:1). Only about one sixth of the phosphorus present in the AW composition can be converted to FAP. Given that fluorine is frequently included in low dielectric loss glass compositions to drive out hydroxyl groups, the idea of FAP and hydroxyapatite (HA) or a mixed hydroxy/fluorapatite crystals being formed in the heat treated AW glass-ceramic can be discounted. It is more likely, that the apatite present is FAP and oxyapatite (OA) or a solid solution of these two phases. It must be noted however that OA converts to HA in the presence of water and this may occur at the surface by reaction with atmospheric water prior to X-ray powder diffraction being carried out.

Hill *et al.* [8–10] developed a castable glass-ceramic from the $SiO_2$-$Al_2O_3$-$P_2O_5$-CaO-$CaF_2$ system that bulk nucleated, via prior amorphous phase separation, and crystallized to FAP and mullite. The needle-like apatite crystals give these glass ceramics high fracture toughness and high strength [8, 11]. However, the system contains aluminum, which may have a detrimental effect, *in vivo*, if released [12]. A study of the effect of fluorine in this system revealed that both nucleation and crystallization behavior are strongly influenced by fluorine content. In the absence of fluorine, these glass compositions crystallized to $\beta$-wollastonite, rather than FAP. Furthermore, fluorine dramatically reduced the glass transition temperature ($T_g$), reduced the FAP crystallization temperature and promoted bulk nucleation of the apatite phase [10] .

Hoeland *et al.* [13, 14] have found similar results to Hill *et al.* Carpenter *et al.* [15] have found an apatite to form in $SiO_2$-$P_2O_5$-CaO-MgO glasses without fluorine and in this case, the apatite is thought to be HA. In the AW glass studied by Kokubo *et al.* [3] and those studied by Carpenter *et al.* [15], the apatite forms with a spherulitic morphology. In contrast, in the fluorapatite glass-ceramics studied by Hill *et al.* [8–10] and Hoeland *et al.* [13, 14], the apatite forms as elongated needle like crystals with the long axis perpendicular to the *c*-axis. The fluorapatite crystals are thought to grow by a screw dislocation mechanism of crystal growth and this view is supported by the fact, that on etching such crystals, circular holes are formed at the center of the hexagonal face and presumably run in the direction of the *c*-axis. The elongated nature of the FAP crystals is thought to contribute to the strength and toughness of the final glass-ceramics [8, 11]. FAP is chemically and thermodynamically more stable than either HA or OA [16]. Incorporation of fluorine into a $SiO_2$-$P_2O_5$-CaO melt is therefore likely to promote FAP nucleation. However, despite this, the influence of fluorine content on the nucleation and crystallization behavior of $SiO_2$-$P_2O_5$-CaO-MgO glass compositions, has not been investigated. Fluorine would be expected to promote apatite nucleation. It might be expected that FAP forms first and subsequent crystallization of OA then takes place on the surface of the FAP. Increasing the fluorine content of the glass may increase the proportion of the apatite phase formed.

The present letter describes the influence of substituting fluorine for oxygen in the AW glass composition on the crystallization behavior followed by differential

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TABLE I Glass compositions studied in mole percent

| Component/name | MgO | CaO | $SiO_2$ | $P_2O_5$ | $CaF_2$ |
|---|---|---|---|---|---|
| AWK0 | 7.11 | 50.28 | 35.46 | 7.15 | 0 |
| AWK1 | 7.11 | 49.88 | 35.46 | 7.15 | 0.4 |
| AWK2 | 7.11 | 45.51 | 35.46 | 7.15 | 4.77 |

TABLE II Summary of thermal analysis data obtained by DTA

| Glass | $T_g$ (°C) | Tp1 (°C) (Powder) | Tp1 (°C) (Frit) | Tp2 (°C) (Powder) | Tp2 (°C) (Frit) |
|---|---|---|---|---|---|
| AWK0 | 750 | 911 | 960 | 965 | 1030 |
| AWK1 | 735 | 887 | 887 | 927 | 1025 |
| AWK2 | 695 | 798 | 798 | 892 | 972 |

thermal analysis and X-ray diffraction. The glass compositions are given in Table I. AW1 is the original AW composition studied by Kokubo *et al.* [3]. AW0 is the original AW glass composition with the $CaF_2$ replaced by CaO on a molar basis. AW2 is a glass with increased fluorine and sufficient fluorine to convert all the phosphorus to FAP. The glasses were produced by a high temperature melt quench route using a platinum crucible and electric melting in a similar fashion to that carried out by Kokubo *et al.* [3].

The glass frit produced was ground to give particles <90 $\mu$m. Frit particles and particles <90 $\mu$m were characterized by differential thermal analysis using a Stanton Redcroft DTA/TGA 1600 (Rheometric Scientific, Epsom, UK) with a flowing dry nitrogen atmosphere and a heating rate of 10 °C $min^{-1}$.

Fig. 1 shows the DTA traces for the three glasses. The glass transition temperature, $T_g$, reduced significantly with increasing fluorine content falling from 750 °C for the fluorine free composition to 695 °C for the highest 4.8 mole percent calcium fluoride content glass (Table II and Fig. 2).

Previous studies have shown the glass transition temperature to reduce significantly with fluorine content of calcium fluoro-alumino-silicate glasses [11, 17]. The DTA trace for the AW1 glass (Fig. 1) is similar to that found by Kokubo *et al.* [3]. Two distinct crystallization exotherms are observed. The first crystallization peak (Tp1) is thought to correspond to that of apatite, while the second (Tp2) to apatite and wollastonite. X-ray powder diffraction showed that, for all of the glass-ceramics studied, Tp1 corresponds to the formation of apatite and Tp2 corresponds to the formation of $\beta$-wollastonite plus apatite (Fig. 3).

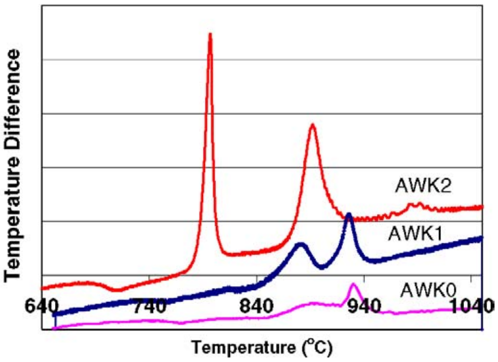

*Figure 1* DTA traces for the AK0, AK1 and AK2 glasses. Note the shift of the glass transition and peak crystallization temperatures to lower values with increasing fluorine content.

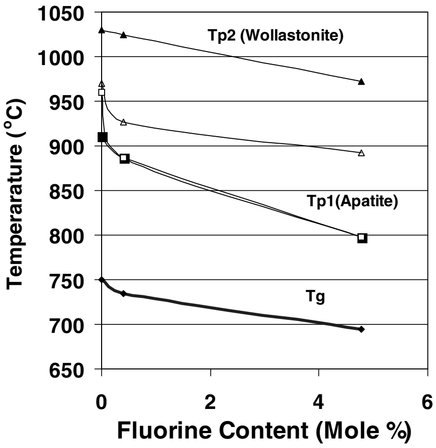

*Figure 2* $T_g$, Tp1 and Tp2 plotted against the fluorine content of the glass: ■ = Tp1 <90 $\mu$m, □ = Tp1 frit, ▲ = Tp2 <90 $\mu$m and △ = Tp2 frit.

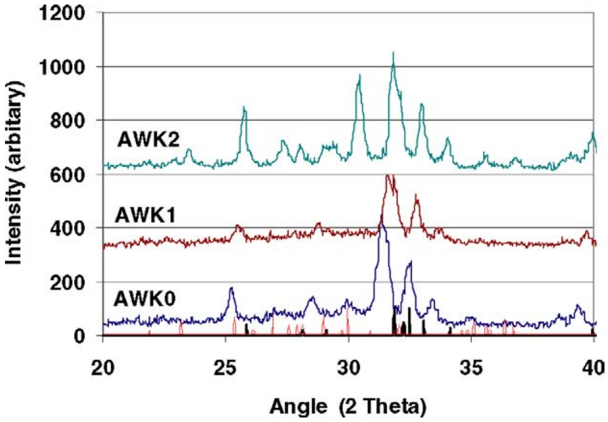

*Figure 3* XRD patterns obtained for all glass-ceramics heated to Tp2. Crystal phases denoted by: | = Wollastonite, | = FAP.

The match to hydroxyapatite and wollastonite was relatively poor for the fluorine free glass AWK0, which may indicate some solid solution behavior, with perhaps some magnesium substituting for calcium in these two phases. Tp1 was independent of glass particle size for AWK1 and AWK2, in contrast Tp2 shifted to higher temperatures on moving from <90 $\mu$m glass particles to frit particles (Figs 2 and 4). In the case of AWK0 the first crystallization peak increased from

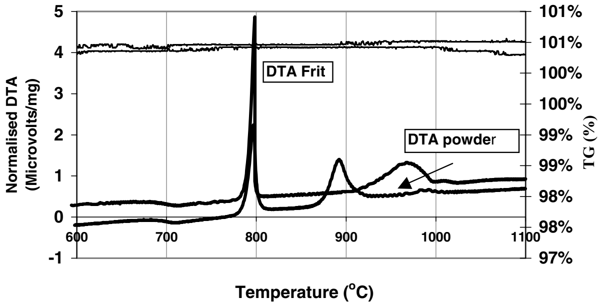

*Figure 4* DTA traces for <90 $\mu$m and frit particle sizes of the AWK2 glass.

911 to 960 °C on going from the <90 μm to frit particles.

An increase in particle size effectively reduces the surface area for nucleation. DTA demonstrates that Tp1 is unaffected by particle size for AWK1 and AWK2 and this infers that the apatite phase originates from bulk nucleation in these compositions. Similarly, the increase in Tp2, along with a decrease in the peak's full-width-half-height ratio as particle size is increased, suggests that wollastonite originates from surface nucleation in all three compositions and apatite, also originates from surface nucleation in AWK0.

Juhasz *et al.* [18] found that for the AWK1 composition, at a critical particle size, apatite nucleated by both surface and bulk processes. In the same study, apatite suppressed the formation of wollastonite. At this critical size, the DTA crystallization peaks were indistinguishable, and in the case of AWK1, this was found to be approximately 18 microns.

The reduction of Tg, Tp1 and Tp2 as fluorine content increases supports the view of Hill *et al.* [17], that fluorine acts to disrupt the glass network, allowing rearrangement of the glass network and crystallization to occur more readily. Tp1 is reduced to a greater extent than Tp2, which suggests that fluorine may not only be acting as a network disruptor. FAP is likely to nucleate more readily than hydroxyapatite/oxyapatite so that the increased availability of fluoride ions may also be promoting the nucleation of FAP.

Increasing fluorine content of the glass also appears to promote the crystallization of the apatite phase. Although no quantitative densification study was carried out, AWK2 was qualitatively found to sinter poorly. Crystallization of apatite would inhibit the ability of the glass to sinter by a viscous flow mechanism. The reduction in the value for Tp1 is much greater than the reduction in $T_g$ on increasing the fluorine content. Consequently, the temperature window (Tp1onset-$T_g$) over which viscous flow sintering occurs is suppressed.

In conclusion, all glasses of the composition 7.11 MgO-$(50.28 - x)$CaO-35.46SiO$_2$-7.15P$_2$O$_5$ $- x$CaF$_2$ where $x = 0, 0.4, 4.77$ crystallize to apatite and wollastonite. Apatite crystallizes at a lower temperature than wollastonite, the former favoring bulk nucleation and the latter surface nucleation. Increasing the fluorine content disrupts the glass network, replacing bridging oxygens with non-bridging fluorines and results in a reduction in $T_g$ and both crystallization temperatures. Fluorine reduces the temperature range over which viscous flow sintering may occur.

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