

Effect of microstructure on the tribological properties of apatite-wollastonite glass ceramic

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A relationship between microstructure and the tribological properties of Apatite-Wollastonite glass ceramics (A-W GC), fabricated by different techniques of melt casting and powder packing processing, was studied. The surface crystallization of wollastonite caused a unique surface strengthening in an A-W GC prepared by the melt casting process. The wear rate did not vary between the free surface and interior in an A-W GC made by the powder packing process, whereas an increase of the wear rate with an increase in the distance from the free surface was detected in an A-W GC fabricated by the melt casting process. However, the melt casting process resulted in a higher wear resistance in an A-W glass ceramics for prosthetic applications.

Key words: Tribology, Apatite-Wollastonite, Glass ceramic, Melt casting, Powder packing.

Introduction

Glass-ceramics in the MgO-CaO-SiO₂-P₂O₅ system, containing apatite and wollastonite phases, have shown good mechanical properties, chemical durability, high resistance to slow crack growth, and an ability of forming strong chemical bonding with living bone [1-3]. Owing to such desirable properties, Apatite-Wollastonite (A-W GC) glass-ceramics have drawn a great deal of attention as biomaterials either in powder form as a bone filler or in bulk material for prosthetic applications [4-6]. The replacement of natural bone attributed to bioactivity and enhanced mechanical properties has progressed.

The microstructure and properties of the A-W GC can vary depending on the fabrication process. Kokubo and colleagues [1-4] claimed that the powder packing process produced mechanically strong A-W GC for bone replacement usage. They suggested that wollastonite crystals occurred homogeneously in each grain boundary and inhibited crack propagation. Recently, Park and Öztürk [7] fabricated an A-W GC by a melt casting process and showed an A-W glass-ceramics with higher hardness and better wear resistance compared with commercial dental glass ceramics.

In this study, MgO-CaO-SiO₂-P₂O₅-F based A-W glass-ceramics were fabricated through two different methods of melt casting and powder packing processes, and their hardness and tribological properties were compared.

Experimental Procedure

Glass of the nominal composition of MgO 4.6, CaO 45.0, SiO₂ 34.0, P₂O₅ 16.2 and F₂ 0.2 wt% was prepared from reagent grade powders of MgO, CaCO₃, SiO₂, CaHPO₄·2H₂O, and CaF₂. Batches of ~15 g were melted at 1500 °C for 1 h in an electric furnace. Melting took place in a platinum crucible, under normal laboratory conditions without controlling the atmosphere. The melt was poured onto a stainless steel plate to make disk-shaped bulk glass. This method was termed melt casting. On the other hand, for the powder packing process, the bulk glass was ground down to 325 mesh and mixed with isopropyl alcohol at a weight ratio of 1 : 1. A small amount of n-butyl was used as a binder. The dried glass powder was pressed into a disk 40 mm in diameter and 7 mm in thickness at a load of 40 kN. The same heat treatment was applied to both glasses at 780 °C for 1 h and then at 900 °C for 0.5 h with a heating rate of 5K minute⁻¹.

The crystal morphology of the crystallized samples was examined by a Scanning Electron Microscope (SEM, Jeol 6400). For SEM examination, the sample was mounted in an epoxy resin and ground by 240, 400, 800 and 1200 grit abrasive papers, and polished consecutively with 3 and 1 μm diamond pastes, and then etched with 0.05 N hydrochloric acid for 1 minute. The free surface, and the sub-surfaces obtained at depths of 0.1, 0.3, and 0.5 mm from the free surface were examined in the bulk glass-ceramic and pressed glass-ceramic. Each one of the sub-surfaces was achieved by removing the free surface of the glass-ceramic through the grinding and polishing procedure described above. The crystalline phases

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formed in the free surface, and in the sub-surfaces were identified by X-Ray Diffraction (XRD, Rigaku Geigerflex-DMAK/B) using copper $K\alpha$ radiation.

The tribological tests on the free surface and sub-surfaces were performed at a load of 10 N, a rotating speed of 0.25 cm/s and a sliding distance of 50 m. Lubrication was not applied to avoid the complication of tribo-chemical effects. The wear track diameter was 1 cm. A pin-on-disk tribometer (CSEM Instruments) was used to conduct tribological tests in accordance with ASTM G99-95A standard [8].

A zirconia ball 5 mm in diameter was chosen as the counterface material due to its higher hardness and lower specific wear rate than the materials studied. Zirconia is often used as a material for ceramic cups that mate with the metallic stem or ceramic head in total hip replacement surgery [9]. After each individual tribological test, the surface profile of the sample was measured using a stylus profilometer (Surtronic 3+) to determine the wear track depth and wear area. The cross-sectional area of the wear track was calculated by averaging the wear area of four points of maximum mutual distance (90° spacing) on the wear track of the disk. Wear volume was then calculated by multiplying the cross-sectional area of the wear track by the circumference of the track.

The hardness of the specimens was measured using a Knoop Hardness tester. At least five measurements were taken at different locations loading with 500 g for 15 s.

Results and Discussion

The micrographs taken from the cross-section of the A-W GC made by melt casting and powder packing processes are shown in Fig. 1. The cast glass-ceramic exhibited a heterogeneous microstructure consisting of apatite and wollastonite crystals randomly distributed throughout a glass matrix [7]. A significant difference in microstructure between the free surface and interior

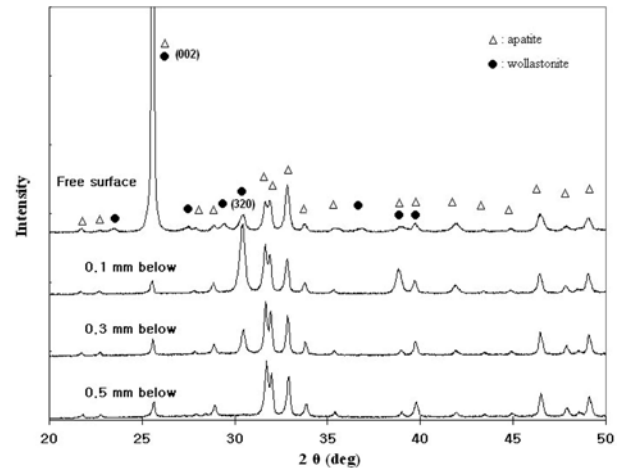


Fig. 2. XRD patterns of the A-W GC fabricated by a melt casting process showing the higher content of wollastonite nearer to the free surface. XRD taken from 0.5 mm depth from free surface only shows the apatite crystals.

is presented in Fig. 1(a) whereas from Fig. 1(b), the pressed glass-ceramic showed a consistent microstructure, irrespective of the depth from free surface.

The crystallization mechanism of Apatite differs from that of wollastonite. The apatite phase is precipitated on a bulk scale due to the three-dimensional bulk crystallization mechanism, whereas wollastonite crystallized by a two-dimensional surface crystallization mechanism and preferred to precipitate from the free surface [7, 10]. Typical growing pattern of these crystals should be growth vertical to the surface without adding any additives or surface treatments [11]. This surface crystallization process affects the properties of the surface and the interior. Thus, a depth-dependent variation in properties is anticipated.

Figure 2 shows XRD patterns obtained from the free surface, and at distances of 0.1, 0.3, and 0.5 mm from the free surface in the cast glass ceramic. A preferred orientation with the (002) plane of the wollastonite crystal

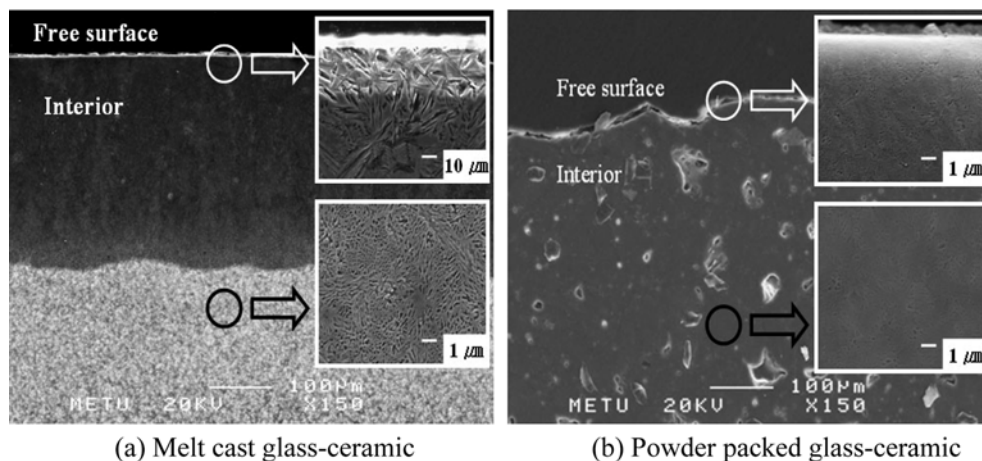


Fig. 1. SEM micrographs taken from the cross sectional area of the A-W GC showing (a) typical elongated needle-shaped microstructure of wollastonite at the free surface and apatite crystals in the interior in the melt cast glass ceramics, (b) homogeneous microstructure in the pressed glass ceramic.

(JSPD #10-489) along with the apatite crystal (JSPD card #9-432) can be observed on the free surface. The preferred orientation of the wollastonite crystals with the texture of the (320) plane was detected at a distance of 0.1 mm below the free surface, and at a distance of 0.3 mm the texture no more existed. Apatite was the only phase at a distance of 0.5 mm from the free surface. A typical characteristic of surface crystallization, in which crystals grow from the free surface towards the interior, is apparent. The thickness of the layer at which the wollastonite phase with a preferred orientation together with the apatite phase is approximately 350 μm as shown in Fig. 1(a).

Figure 3 shows XRD patterns obtained from the free surface and the depths of 0.1, 0.3, and 0.5 mm from the free surface in the pressed glass ceramic. There was no preferred orientation of the wollastonite crystal (JSPD card #10-489). The ratio of the wollastonite and apatite crystal (JSPD card #9-432) did not vary depending on the depth from the free surface. This could be due to each grain boundary playing the role of free surfaces for the growth wollastonite crystals.

The values for the Knoop hardness (KH) and wear rate for the free surface and the sub-surfaces are presented in Table 1. For the glass ceramics formed by melt casting, the KH value of the free surface was about $650 \pm 12 \text{ H}_V$, but decreased gradually with increasing distance from free surface up to a value of $520 \pm 8 \text{ H}_V$

at a distance of 0.5 mm below the free surface. However, the pressed glass ceramics showed a KH value of about 550 ± 10 at the free surface and nearly the same value of 535 ± 10 at a distance of 0.5 mm below the free surface. The variation of KH value is in accordance with the microstructure. No variation of hardness in the homogeneous crystalline distribution, but a significant decrease of hardness in the heterogeneous microstructure.

The variation of wear rate with the depth from the free surface depending on the fabrication method is shown in Fig. 4. The wear rate of the A-W GC fabricated by the melt casting process increased from 0.7 ± 0.05 to 2.9 ± 0.15 with an increase in the depth from the free surface.

Figure 5 shows the wear tracks at the free surfaces. The glass-ceramic made by melt casting exhibited a weak and narrow wear track compared to the one made by powder packing. This difference could be due to the difference in crystallization mechanism between wollastonite and apatite. The presence and proportion of the wollastonite phase as well as its orientation could effect significantly the microhardness of the A-W glass-ceramics. The wollastonite phase, which has elongated needle-shaped grains, is known to show a higher wear resistance than the apatite phase, which crystallized in the form of dendrites as shown in Fig. 1(a). However, in the A-W GC that was produced by the powder packing process, there is no significant change in wear rate depending on the depth.

Kokubo [2] suggested that the powder packing process is preferable in fabricating biological A-W glass

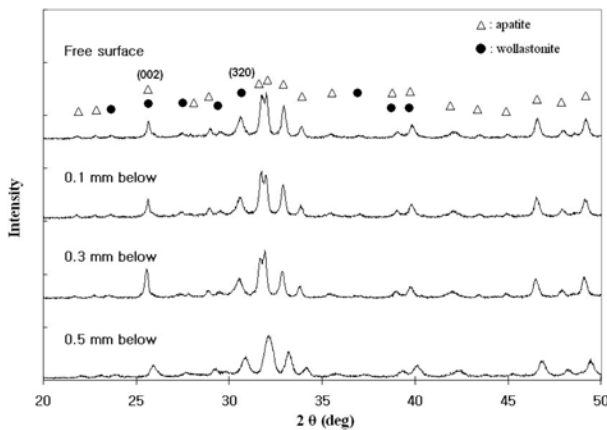


Fig. 3. XRD patterns of the A-W GC by the powder packing process showing no significant variation of peaks depending on the depth from the free surface, and consistent proportions of wollastonite and apatite.

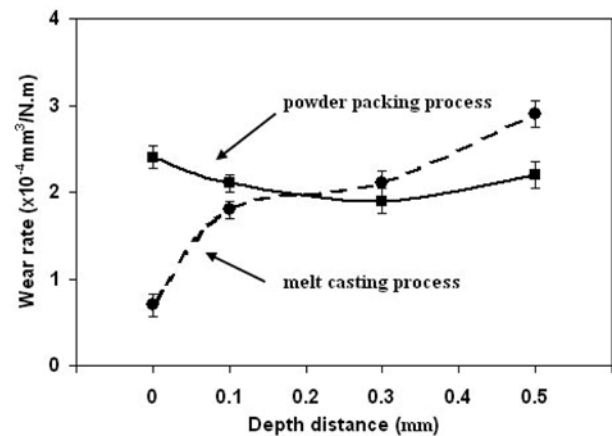


Fig. 4. Variation of wear rate of A-W GC depending on the depth from the free surface and fabrication method. The cast sample showed a lower wear rate compared to the pressed sample.

Table 1. Variations of knoop hardness and wear rate of apatite-wollastonite glass-ceramics depending on the fabrication methods and the depth from free surface

Depth distance (mm)	Melt casting process		Powder packing process	
	Knoop hardness (H_V)	Wear rate ($\times 10^{-4} \text{ mm}^3/\text{N}\cdot\text{m}$)	Knoop hardness (H_V)	Wear rate ($\times 10^{-4} \text{ mm}^3/\text{N}\cdot\text{m}$)
0.0	650 ± 12	0.7 ± 0.05	550 ± 10	2.4 ± 0.10
0.1	601 ± 12	1.8 ± 0.10	558 ± 11	2.1 ± 0.12
0.3	550 ± 10	2.1 ± 0.15	562 ± 09	2.0 ± 0.15
0.5	520 ± 8	2.9 ± 0.15	535 ± 10	2.3 ± 0.09

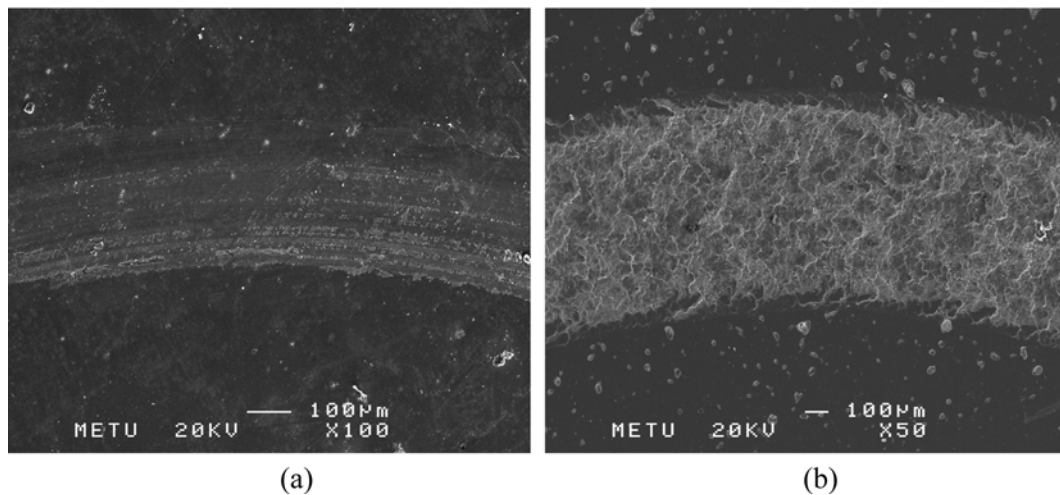


Fig. 5. Wear tracks on the free surfaces for the samples made by (a) the melt casting process and (b) the powder packing process showing a narrower wear track in the cast glass ceramic.

ceramics because it results in a homogeneous distribution of crystals. However, if the crystallization is well controlled, a higher wear resistance and mechanically stronger A-W glass ceramic can be fabricated by the melt casting process. The presence of the wollastonite phase in the free surface could cause the surface strengthening.

Conclusions

Apatite-wollastonite glass ceramics were fabricated either by the melt casting or the powder packing process. The characteristics of each process were examined in terms of microstructure, hardness and wear rate.

1. For the cast glass ceramic, wollastonite existed up to about 350 μm from the free surface, but with a higher content of wollastonite nearer to the free surface, whereas a homogeneous microstructure and consistent proportion of wollastonite to apatite were presented, irrespective of depth from free surface in the pressed glass ceramics.

2. For the glass ceramics formed by melt casting, the KH value of the free surface was about $650 \pm 12 \text{ H}_v$, which was higher than 550 ± 10 of the pressed glass ceramics.

3. The wear rate of the A-W GC fabricated by the melt casting process was $0.7 \pm 0.05 \text{ mm}^3/\text{N.m}$ at free surface which was less than the value of 2.4 ± 0.10 for the pressed glass ceramic.

4. The melt casting process can be considered a promising technique for fabricating higher wear resistance A-W glass ceramics.

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