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Abrasive wear behaviour of bio-active glass ceramics containing apatite

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Abstract. In this study, abrasive wear behaviour of bio-active glass ceramic materials produced with two different processes is studied. Hot pressing process and conventional casting and controlled crystallization process were used to produce bio-active ceramics. Fracture toughness of studied material was calculated by fracture toughness equations using experimental hardness results of the bio-active glass ceramic material. Two fracture toughness equations in the literature were used to identify the wear behaviour of studied ceramics. Wear resistance results that identified with both of the equations were similar. The results showed that the abrasive wear resistance of the bio-active glass ceramics produced with hot pressing process was found to be higher than that of the ceramics produced by conventional casting and controlled crystallization process.

Keywords. Wear; abrasive wear; bio-active glass ceramic; glass; ceramic.

1. Introduction

Bio-active glass bonds chemically to both hard and soft tissues by development of a biologically active apatite layer (Hench 1998). Combination of bio-active glass in porous composite encourages bonding to bone and may affect calcification in the artificial soft tissue (Loty *et al* 1997). Mechanical properties of porous polymer/bioactive glass composites are a concern due to the porous structure and the potentially weak interface between polymer and ceramic phase (Rich *et al* 2002). Mechanical properties can be improved by modification of the polymer phase and/or ceramic phase (Marcolongo *et al* 1997; Wang *et al* 1998; Roether *et al* 2002). Bio-active materials have chemical or structural similarities to the inorganic mineral in bone. The obvious production route of bio-active glass ceramics is to sinter hydroxyapatite powder. The problems with this method are the thermal instability of hydroxyapatite and poor mechanical properties of the sintered product. Bioactivity of glasses is due to a hydroxyapatite layer, which is formed as a result of a reaction between the glass and body environment. The Young's modulus of bioactive glasses is about 35 GPa, hence implants from these materials are stiffer than cortical bone (15–25 GPa). Main disadvantages of the bio-active glasses are their poor mechanical properties. The fracture toughness of bio-active glass ceramics (1·2–2·25 $MN/m^{3/2}$) is lower than that of cortical bone (2·2–5·7 $MN/m^{3/2}$) and therefore, this property of bio-active glass ceramics must be improved for load bearing implant applications. These properties are not adequate for bio-active glasses to be used for highly stressed implants (Alanyali 1992). The main reason for development of bio-active glass–ceramics is the desire to produce implant materials with superior mechanical properties to those of the glasses. Mechanical properties of bio-active glass ceramics are given in table 1. Bio-active glass ceramics are produced using the conventional route of casting followed by a crystallization heat treatment and by compacting of a powder of the parent phase followed by sintering and crystallization (Alanyali 1992). Apatite is a major crystalline phase of bio-active glass ceramics that crystallizes evenly throughout the material. Dependent on the composition the apatite may be hydroxyapatite or fluoroapatite which has the same crystal structure and similar lattice parameters. The constituents of most bio-active glass ceramics are the same as those for bio-active glasses but with the P_2O_5 slightly higher and the Na_2O less (Loty *et al* 1997; Hench 1998). P_2O_5 is a nucleating agent and in these materials it is also an important constituent of the crystalline phase apatite. Fracture due to micro-cracks is commonly seen in brittle materials that have low fracture toughness, e.g. ceramics (Srawley 1976; Ponton and Rawlings 1989). When a sharp tip indents the surface of brittle material, during loading and unloading stages, main cracks and near-tip micro-cracks occur, respectively beneath the surface of material (Lawn and Swain 1975; Evans and Charles 1976; Lawn 1993). Micro-crack mechanism occurring during loading and releasing stages of force is schematically illustrated in figure 1.

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Table 1. Mechanical properties of bio-active glass ceramics (Alanyali 1992).

Material	Bending strength (MPa)	Three-point bending fracture toughness ($MN/m^{3/2}$)
Sintered hydroxyapatite	196	
Sintered hydroxyapatite	50–115 (N_2)	0,6–1,1 (N_2)
Sintered hydroxyapatite	13–48	
Sintered hydroxyapatite	113	
Sintered glass ceramic (A)	88 (air)–14 (N_2)	1,2 (N_2)
Sintered glass ceramic (A, W)	178 (air)–193 (N_2)	1,2 (N_2)
Sintered glass ceramic (A, W, Cp)	213 (air)–14 (N_2)	1,2 (N_2)

A: apatite, W: wollastonite, Cp: whitlockite.

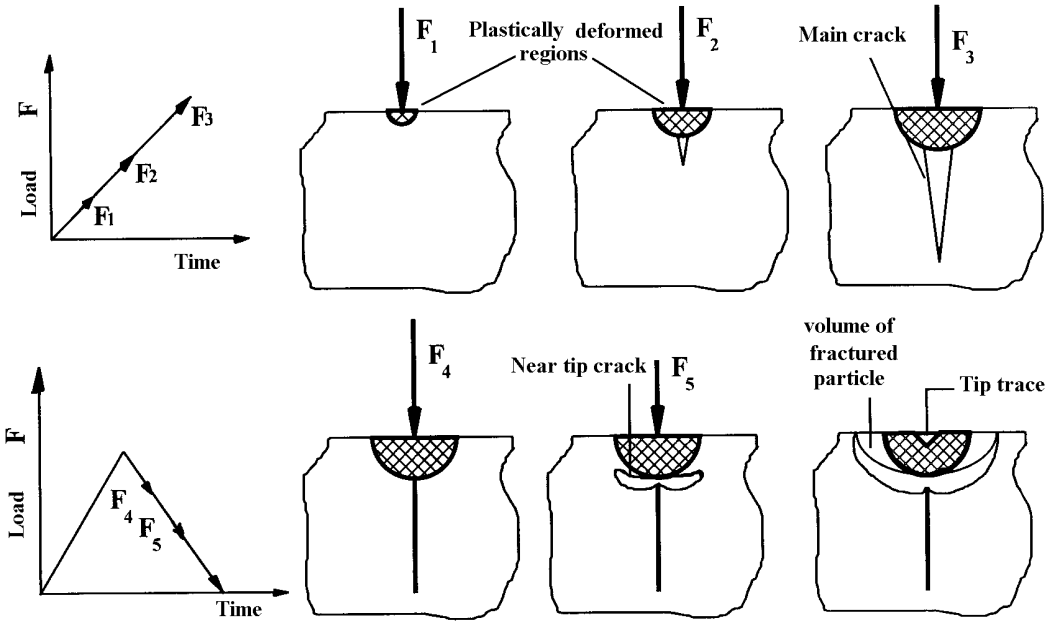

Figure 1. Main crack and near tip cracks after indentation of a sharp rigid tip.

Table 2. Constituents of studied bio-active glass ceramics.

Constituent phase	Amount (%)
Na_2O	4·47
CaO	28·62
Al_2O_3	6·45
SiO_2	50·65
P_2O_5	7·04
CaF_2	2·77

When the tip is applied onto the surface of the brittle material, high stresses occur at the contact point. As a result plastic deformation takes place around the indentation tip. When the load is gradually increased to a critical level (F_2), main crack initiates in the brittle material. If the load is continued to rise up to the level of F_3 the main crack enlarges. At this stage, if the load is lowered to the level of F_4, the main crack closes as seen in figure 1. If the load is decreased below the value of F_5, plastically deformed regions prevent the main crack to be closed and cause near-tip micro-cracks under the surface that advance towards the surface of the brittle material. The cause of occurrence and advance of near-tip micro-cracks in the presence of residual stresses is due to plastic deformation.

The aim of this study is to define abrasive wear resistance of bio-active glass ceramics. In our present study the fracture toughness of bio-active glass ceramics was calculated with two different equations using experimentally measured hardness value of bio-active glass ceramics. After that the fracture toughness values of bio-active glass ceramics were used to identify wear behaviour of studied ceramics.

2. Materials and methods

The constituents of the tested bio-active glass ceramics are given in table 2. Two crack equations in the literature were used to calculate the fracture toughness of the studied

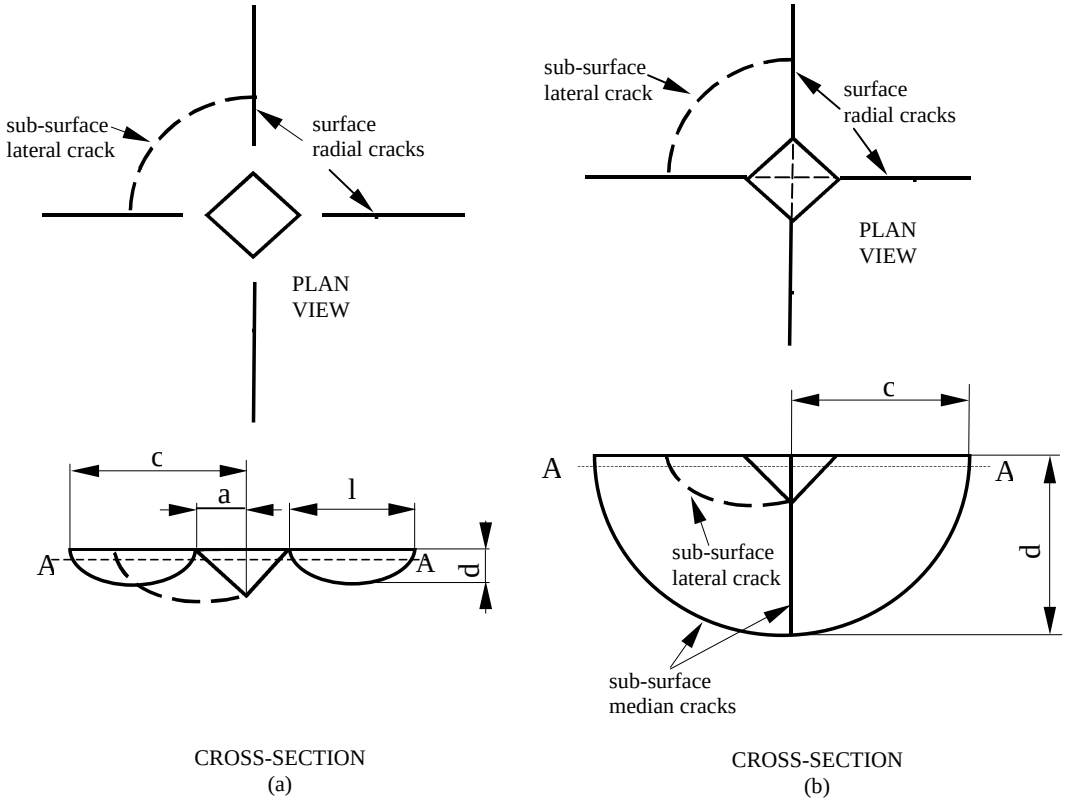

Figure 2. (**a**) Schematic plan and cross-sectional views of an idealized Vickers indent Palmqvist crack system and (**b**) schematic plan and cross-sectional views of an idealized Vickers indent radial-median or half penny crack system.

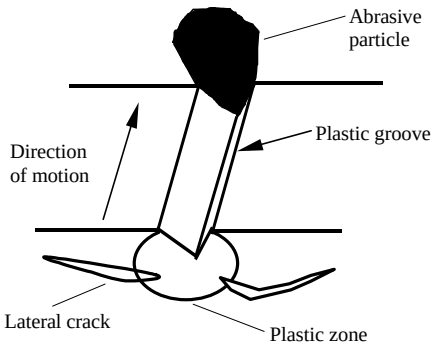

Figure 3. Schematic illustration of material removal in a brittle material by extension of lateral cracks from beneath a plastic groove (Srawley 1976; Ponton and Rawlings 1989; Alanyali 1992).

materials. The Vickers hardness of the studied ceramics was experimentally tested. Idealised Vickers indent radial-median and Vickers indent Palmqvist crack system mechanisms are given in figure 2.

One model for the abrasive wear of brittle materials is based on the removal of material by lateral cracking. As a sharp particle slides over the surface forming a plastic groove, lateral cracks grow upwards to the free surface from the base of the subsurface deformed region as seen in figure 3. Abrasive wear caused by micro cracking formation is observed in materials such as ceramics which have lower fracture toughness. The volume of worn material on the ceramic is more than the groove that formed by abrasive particle. The formation of cracks around the groove reaches to the surface of the worn material and cause the detachment of large material particles from the structure of material as shown schematically in figure 3. Fracture toughness of studied bio-active glass ceramics was experimentally determined by Alanyali (1992) in his work with three-point bending test. Schematic diagram of three-point bending test is given in figure 4. Single edge notched beam (SENB) technique was used in three-point bending tests by Alanyali. Three-point bending test was performed on 5 specimens produced from studied bio-active glass ceramics. The dimensions of specimens, which were used in three-point bending tests, are given in table 3. For three-point bending test, the samples were cut to approximately equal size, placed on fine silicon carbide paper, then polished on one side using diamond polishing wheels. The fracture toughness samples were then notched across the centre of the polished side using a diamond-cutting wheel. The following equations in the

literature (Sevim *et al* 2005) were used to calculate the fracture toughness of the specimens

$$K_c = 0{\cdot}4636\left[\frac{P}{a^{3/2}}\right]\left[\frac{E}{H}\right]^{2/5}[10^F], \quad (1)$$

$$K_c = 0{\cdot}0363\left[\frac{P}{a^{1{\cdot}5}}\right]\left[\frac{E}{H}\right]^{2/5}\left[\frac{a}{c}\right]^{1{\cdot}56}, \quad (2)$$

where P is the applied indenter load, E the Young's modulus, K_c the critical stress intensity factor for indentation fracture, a the indentation half diagonal length and H the mean contact or indentation pressure exerted by the Vickers indenter ($P/2a^2$) and $F = -1{,}59 - 0{,}34B - 2{,}02B^2 + 11{,}23B^3 - 24{,}97B^4 + 16{,}32B^5$.

The data required for crack equations (1) and (2) were obtained experimentally using micro-hardness test results. For micro-hardness tests the bio-active glass ceramic specimens in dimension of $50 \times 20 \times 2$ mm were produced with conventional casting (CP31) and compacting (CP1) processes. Crystallizing process at 800°C for 24 h was applied to the CP31 specimens, which were produced with conventional casting technique. The CP1 specimens were produced using hot pressing technique at 1000°C for 1 h. The surfaces of the bio-active glass ceramic specimens were polished using 1 μm diamond paste. Polished specimens were etched in HCl for 5 s and then specimens were placed into an aluminium plate. To ensure conductivity the edges of the specimens were coated with a mixture of silver and alcohol. Specimen preparing stage was finalized by coating the entire surface of the specimens with gold for 2 min by using vacuum sputter in order to obtain net views of the surfaces. Vickers micro-hardness tests were carried out on prepared bio-active glass ceramic. Richester Steilmayer mark, Briviskop BVR 250 H model tester was used for micro hardness tests. 9·80665N indent load was used in hardness tests. 10 indentations (6 for CP1 and 4 for CP31) were used to calculate mean crack length. Experimentally measured crack lengths and micro hardness of specimens are given in table 4.

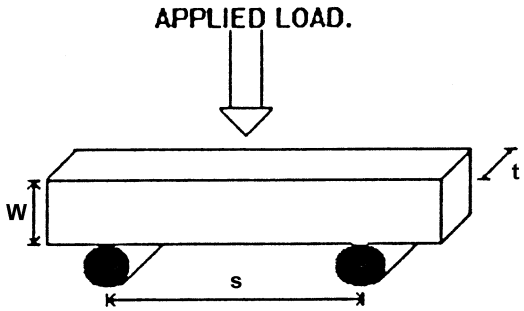

Figure 4. Schematic diagram of the three-point bending test.

Table 3. The dimensions of the specimens, which were used in three-point bending tests (samples 1 and 2: CP1, hot pressed, 3–5: CP31, conventional casting).

Sample	t (mm)	W (mm)	L (mm)	a (mm)	Y	K_{1c} (M Nm$^{-3/2}$)
1	2·875	5·930	32·0	1·089	1·7474	1·506
2	2·950	6·150	32·0	1·089	1·7467	1·573
3	2·240	4·810	29·0	0·660	1·7558	1·777
4	2·270	3·810	27·0	0·630	1·7471	1·987
5	2·390	5·150	31·0	0·900	1·7467	2·104

An abrasive particle causes main cracks beneath the surface of the brittle material and sub-cracks as the load decreases. The following equation in the literature (Sevim 1989) was used to identify abrasive wear resistance of studied materials

$$W_V = a \cdot \frac{F^{5/4}}{K_c^{3/4} \cdot H^{1/2}}, \quad (3)$$

where a is an index independent from material.

3. Results and discussion

Theoretical fracture toughness values calculated with crack equations (1) and (2) and experimental fracture toughness that identified with three-point bending tests of studied bio-active glass ceramic materials are given in figure 5. Coefficients of correlation (R) is given in figure 5. Required data for equations were obtained from Vickers micro-hardness tests experimentally. The Young's modulus values of the studied bio-active glass ceramics were determined by Alanyali (1992) as 86·2 GPa for CP1 and 82·2 GPa for CP31 specimens. Average experimental c values were used as c_{ave} in the crack equations instead of c term. The fracture toughness results of (2) was in agreement with three-point bending test results. Correlation coefficient of fracture toughness equations which represents the relationship between determined fracture toughness values is $R = 0{\cdot}98$ for equations and experimental bending test as seen in figure 5. Micro hardness value of bio-active glass ceramics (minimum, 7894 MPa and maximum, 9120 MPa) produced with hot pressing process is higher than that produced with conventional casting and controlled crystallization process (minimum, 6374 MPa and maximum, 7061 MPa).

Volumetric abrasive wear behaviour of studied bio-active glass ceramics and cortical bone are identified using (3). Fracture toughness value (K_c) required for abrasive wear (3) was derived from (1) and (2). Abrasive wear resistance of bio-active glass ceramics and cortical bone are given in figures 6 and 7. No significant difference was found in the abrasive wear resistance calculated with (1) and (2). Abrasive wear resistance of bio-active glass cera-

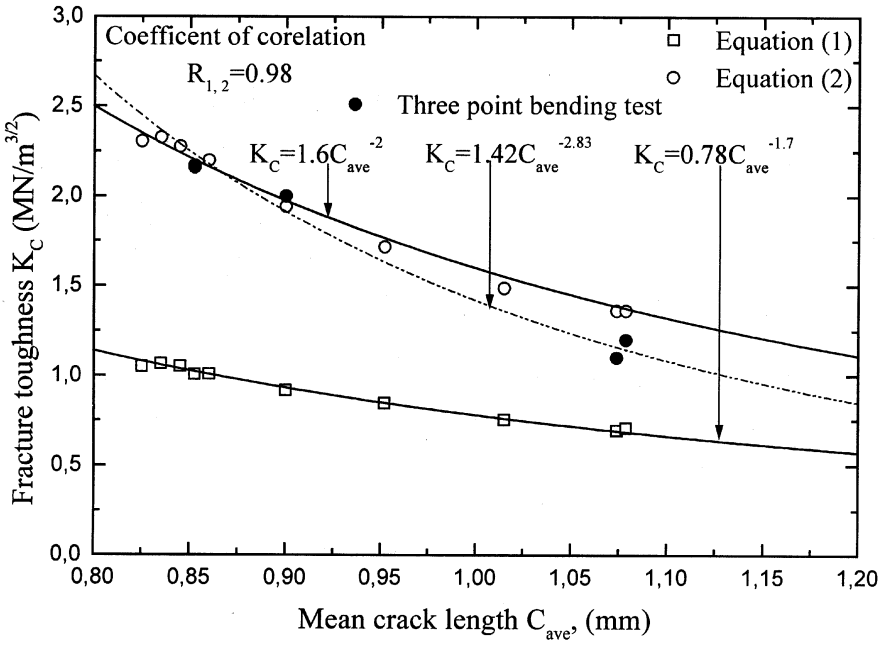

Figure 5. Theoretical and experimental fracture toughness of studied material vs mean crack length.

Table 4. Measured micro-hardness and crack lengths of indentations of bio-active glass ceramic materials (*a*: indentation half-diagonal length, $l = C_{ave} - a$).

Specimen	Measured micro-hardness (MPa)	C_1 (mm)	C_2 (mm)	C_3 (mm)	C_4 (mm)	C_{ave} (mm)	a (mm)	l (mm)
CP1	7894	1·090	0·804	0·840	1·075	0·95225	0·34	0·612
CP1	8434	0·850	0·940	0·860	1·200	0·900	0·30	0·6
CP1	9120	0·992	1·12	0·984	0·992	1·074	0·33	0·744
CP1	8041	0·870	0·925	0·800	0·845	0·860	0·28	0·58
CP1	8336	0·950	1·105	1·110	1·150	1·07875	0·35	0·72875
CP1	8767	1·025	0·985	1·026	1·024	1·015	0·34	0·675
CP31	6374	0·785	0·845	0·915	0·835	0·845	0·32	0·525
CP31	7061	0·800	0·850	0·820	0·830	0·825	0·31	0·515
CP31	6864	0·895	0·850	0·690	0·905	0·835	0·30	0·535
CP31	6669	0·912	0·848	0·810	0·840	0·8525	0·33	0·5225

CP1: Specimens produced with hot pressing technique at 1000°C for 1 h; CP31: specimens produced with conventional casting and controlled crystallization process.

Table 5. Fracture toughness and abrasive wear resistance of bio-active glass ceramic materials.

Specimen	Fracture toughness calculated with (1), (K_c) (M Nm$^{-3/2}$)	Fracture toughness calculated with (2), (K_c) (M Nm$^{-3/2}$)	Abrasive wear resistance calculated with the data of (1)	Abrasive wear resistance calculated with the data of (2)
CP1	2,10767	2,33533	8·9559	9·672
CP1	2,28865	2,246513	9·8468	10·411
CP1	1,72968	1,82382	8·3	8·636
CP1	2,51252	2,68607	10·312	10·842
CP1	1,76435	1,8843	8·054	8·461
CP1	1,87887	2,0272	8·6587	9·166
CP31	1,39107	1,46678	5·893	6·132
CP31	2,02076	2,160024	8·207	8·627
CP31	1,41896	1,51543	6·207	6·52
CP31	1,51106	1,63035	6·413	6·789

CP1: Specimens produced with hot pressing technique at 1000°C for 1 h; CP31: specimens produced with conventional casting and controlled crystallization process.

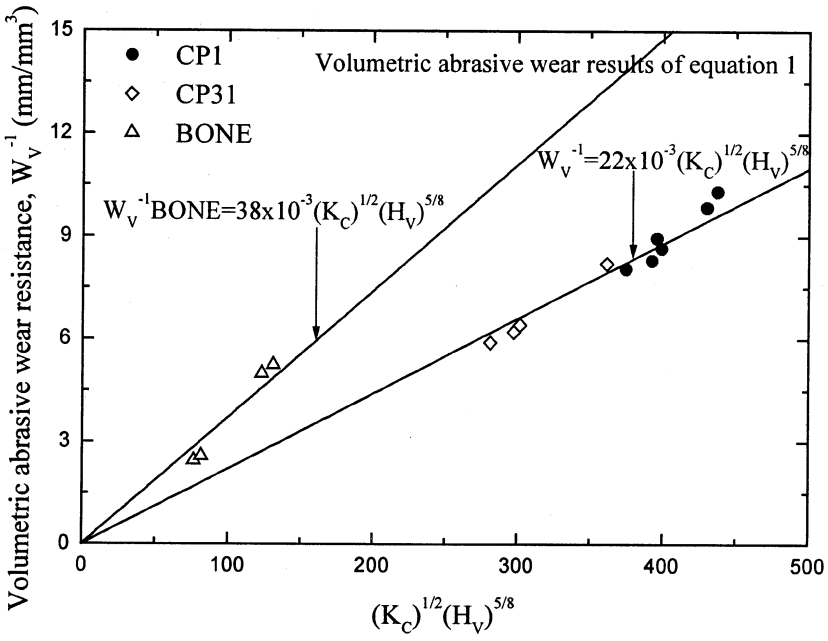

Figure 6. Abrasive wear resistance of bio-active glass ceramics and cortical bone according to K_c obtained from (1).

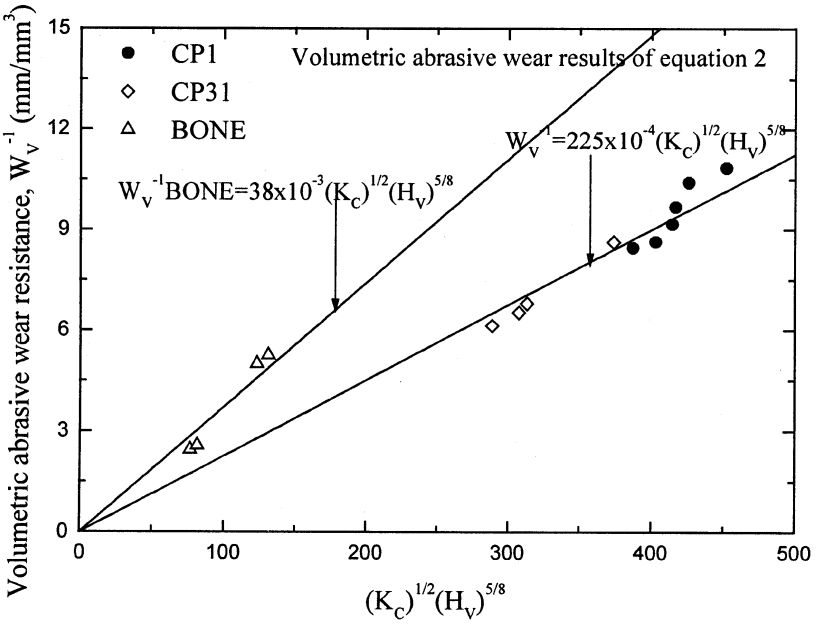

Figure 7. Abrasive wear resistance of bio-active glass ceramics and cortical bone according to K_c obtained from (2).

mics are higher than cortical bone as seen in the figures. Despite cortical bone having higher fracture toughness than bio-active glass ceramics, it has lower abrasive wear resistance as seen in figures 6 and 7. This situation can be explained with lateral cracks as seen in figure 3. More lateral cracks come out in cortical bone, so wear velocity increases as wear resistance decreases (Marcolongo *et al* 1997). Production method of bio-active glass ceramic is effective on the wear resistance property. Higher abrasive wear resistance is obtained for bio-active glass ceramics

produced with hot pressing technique than that of ceramics produced with conventional casting and controlled crystallization process. Abrasive wear resistance difference between ceramics that have same chemical composition can be explained to be due to the irregularities and porosity due to applied production process. Pressing effect results in less porosity in the structure of bio-active glass ceramics and increase the wear resistance.

4. Conclusions

(I) Abrasive wear resistance of bio-active glass ceramics is higher than cortical bone.
(II) Production method of bio-active class material is effective on abrasive wear behaviour property.
(III) Abrasive wear resistance of bio-active glass ceramic materials produced with hot pressing process is higher than that produced with casting and controlled crystallization process.
(IV) Abrasive wear resistance of bio-active glass ceramics is sufficient to be used as implants.
(V) Fracture toughness of bio-active glass ceramics must be improved for implants in human body. These properties of studied material can be developed by producing bio-active glass ceramics as composites containing continuous chord reinforcement.

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