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Fatigue and life-time of bioactive glass–ceramic A–W containing apatite and wollastonite

T. KOKUBO, S. ITO, M. SHIGEMATSU, S. SAKKA
Institute for Chemical Research, Kyoto University, Uji, Kyoto-Fu 611, Japan
T. YAMAMURO
Faculty of Medicine, Kyoto University, Kyoto 606, Japan

High-strength bioactive glass–ceramic A–W containing apatite and wollastonite shows the least dynamic fatigue among glass and glass–ceramics of the same composition and of different structure in a simulated body fluid at 36.5° C. An average life-time estimated from the fatigue of glass–ceramic A–W is 10 years under continuous loading of bending stress of 65 MPa in the simulated body fluid, whereas that of a sintered dense hydroxyapatite ceramic is only 1 min. Articles of the glass–ceramic which withstand the stress of 215 MPa in an inert atmosphere are guaranteed for 10 years life-time in the body environment. The glass–ceramic shows an increase in strength, without having an appreciable change in fatigue, when placed in the simulated body fluid without being loaded. Its practical life-time can therefore be expected to be much longer than that estimated above.

1. Introduction

Heat-treatment of a glass powder compact in the system $CaO–MgO–SiO_2–P_2O_5–CaF_2$ at an appropriate temperature produces dense and homogeneous glass–ceramic A–W which contains fine-grained oxyfluoroapatite and β-wollastonite [1–4]. This glass–ceramic shows a high bending strength of 215 MPa in a dry environment and a high fracture toughness of 2.0 MPa $m^{1/2}$ [5]. It is easily machined into various shapes. In addition, this glass–ceramic forms tight chemical bonds with living bone in a short period when it is implanted into a bone defect [2, 6, 7]. Animal and clinical experiments for application of this glass–ceramic to artificial bones and tooth root are now being conducted [8]. In these applications, fatigue and life-time of the glass–ceramic in a body environment are very important problems. In this study, these problems were investigated in a simulated body fluid.

2. Experimental technique

Four kinds of glass and glass–ceramics including glass–ceramic A–W were used in the experiments. They have the same composition of MgO 4.6, CaO 44.7, SiO_2 34.0, P_2O_5 16.2 and CaF_2 0.5 wt %, but are composed of different phases as shown in Table I. G is a glass, and A is a glass–ceramic containing only oxyfluoroapatite [$Ca_{10}(PO_4)_6(O, F_2)$] as the crystalline phase. A–W is a glass–ceramic containing the apatite and the β-wollastonite ($CaO \cdot SiO_2$), as mentioned above. A–W–CP is also a glass–ceramic containing whitlockite (β-$3CaO \cdot P_2O_5$) besides the apatite and the wollastonite. Methods for preparing these glasses and glass–ceramics are described elsewhere [4, 5].

A sintered dense hydroxyapatite ceramic, which was kindly supplied by Mitsubishi Mining and Cement Co. (Yokose, Chichibu, Saitama Prefecture 368, Japan) was also subjected to the experiments for reference. The ceramic had been sintered at 1200° C and had a relative density of 98.5%. All the samples described above had been previously confirmed to form tight chemical bonds with living bone by *in vivo* experiments [9].

Dynamic fatigue of the samples was examined by the following method. Rectangular specimens $20 \times 5 \times 5\,mm^3$ which were sawed from blocks of the samples were abraded with No. 2000 alumina powders and their edges were very lightly bevelled with emery paper to minimize the effect of edge flaws. Fracture strength of the specimens was measured in a simulated body fluid by a three point bending method at five different loading rates from 0.005 to 2.0 mm min^{-1}. The span length was 16 mm. The simulated body fluid was prepared by dissolving reagent grade chemicals of NaCl, $NaHCO_3$, KCl, $K_2HPO_4 \cdot 3H_2O$, $MgCl_2 \cdot 6H_2O$ and $CaCl_2$ into a pure water so that ion concentrations of the fluid were almost equal to those in the human blood plasma [10]. The ion concentrations are shown in Table II. The fluid was buffered at a pH of 7.25 with 50 mM trishydroxyaminomethane [$(CH_2OH)_3CNH_2$] and 45 mM hydrochloric acid (HCl). The temperature was maintained at 36.5 ± 0.5° C. Some specimens were soaked in the fluid for one month before the measurement. At least six measurements were made to obtain one data point.

In order to obtain the failure probability of glass–ceramic A–W, the fracture strength of 30 specimens was measured in a dry N_2 gas atmosphere at a loading rate of 0.5 mm min^{-1}. For reference, the fracture strength of the hydroxyapatite ceramic HAp in the dry N_2 gas atmosphere was also measured at a loading rate of 0.5 mm min^{-1} using six specimens.

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TABLE I Constituent phases of glasses and glass–ceramics

Sample	Phase (wt %)			
	Apatite	Wollastonite	Whitlockite	Glassy phase
G	0	0	0	100
A	35	0	0	65
A–W	35	40	0	25
A–W–CP	20	55	15	10

3. Results and discussion

3.1. Dynamic fatigue

The results of the measurement of fracture strengths of the glass and glass–ceramics in the simulated body fluid are shown in Fig. 1 as a function of stress rate. At the right hand side of Fig. 1, fracture strengths in a dry N_2 gas atmosphere are also shown for comparison. The value for glass–ceramic A–W was obtained in the present study whereas those for other samples were cited from a previous paper [5]. It can be seen from Fig. 1 that the fracture strengths of all the glass and glass–ceramics in the simulated body fluid are lower than those in the dry N_2 gas atmosphere, and decrease with decreasing stress rate. This means that all the glass and glass–ceramics show a dynamic fatigue, which might be due to a subcritical crack growth occurring during the stressing in the simulated body fluid.

The magnitude of the decrease in the fracture strength with decreasing stress rate, however, largely depends upon the type of samples; i.e. the magnitude decreases in the order of G > A > A–W–CP > A–W. This means that glass–ceramic A–W shows the least fatigue among the glass and glass–ceramics of the same composition and of different structure. This would indicate that the subcritical crack growth is suppressed by the apatite and the wollastonite crystals but facilitated by the whitlockite crystal.

Fig. 2 shows the fracture strengths of glass–ceramic A–W in the simulated body fluid in comparison with those of hydroxyapatite ceramic HAp. At the right hand side of Fig. 2, fracture strengths in the dry N_2 gas atmosphere are shown. These values were also obtained in the present study. It can be seen from Fig. 2 that glass–ceramic A–W shows considerably higher strength than hydroxyapatite ceramics HAp at any stress rate in the simulated body fluid as well as in the dry N_2 gas atmosphere. The dependence of the fracture strength upon the stress rate for the former is a little smaller than that for the latter.

Generally, the dependence of fracture strength σ_f upon stress rate $\dot{\sigma}$ of glasses and glass–ceramics in an aqueous environment is given by the following equation [11].

$$\ln \sigma_f = \left(\frac{1}{n+1}\right) \ln \dot{\sigma} + \left(\frac{1}{n+1}\right) \ln [B(n+1)] + \left(\frac{n-2}{n+1}\right) \ln \sigma_{IC} \quad (1)$$

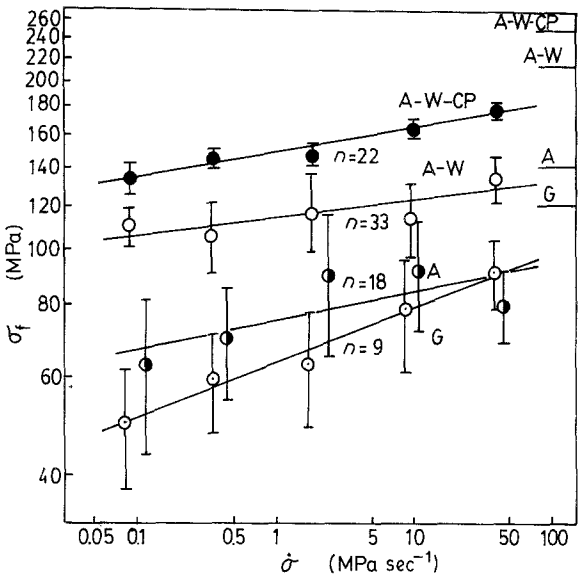

Figure 1 Fracture strength σ_f of glass and glass–ceramics in a simulated body fluid as a function of stress rate $\dot{\sigma}$. Bars at right hand side show the strengths in dry N_2 gas atmosphere.

where n is a constant related to the velocity of subcritical crack growth, B is a constant related to n and fracture toughness, and σ_{IC} is the fracture strength in an inert environment. The term $(1/(n+1))$ corresponds to the slope of the line representing the relation between $\ln \sigma_f$ and $\ln \dot{\sigma}$. The smaller the dependence of the strength upon stress rate is, the larger n is. Applying Equation 1 to the relations shown in Figs 1 and 2, and substituting the fracture strength σ_{N_2} in the dry N_2 gas atmosphere for σ_{IC}, we obtain the n and $\ln B$ values given in Table III for the respective samples. In Table III, σ_{N_2} values used for the calculations are also shown. The value of n, 33, of glass–ceramic A–W is almost equal to that (36) of fused silica in pure water [11], and a little smaller than that (44) of a dense pure alumina ceramic in Ringer's solution [12]. The value of n (27) obtained for hydroxyapatite ceramic in the present study is considerably larger than that (12) reported by de With *et al.* [13] for a hydroxyapatite ceramic in distilled water.

3.2. Life-time

Generally, the life-time t_f, i.e. time to failure, of glasses and glass–ceramics loaded with a stress σ_a in an aqueous environment is given by the following equation [11].

$$\ln t_f = \ln B + (n-2) \ln \sigma_{IC} - n \ln \sigma_a \quad (2)$$

Substituting n, $\ln B$ and σ_{N_2} values given in Table III for n, $\ln B$ and σ_{IC} in Equation 2, we obtain the life-time t_f given in Fig. 3 as a function of applied stress for the respective samples. It can be seen from Fig. 3 that life-times of glass–ceramics A–W and A–W–CP are much longer than those of glass G and glass–ceramic A as well as hydroxyapatite ceramic

TABLE II Ion concentrations (mM) in the simulated body fluid and human blood plasma

	Na^+	K^+	Mg^{2+}	Ca^{2+}	Cl^-	HCO_3^-	HPO_4^{2-}
Simulated fluid	142.0	5.0	1.5	2.5	148.8	4.2	1.0
Human plasma	142.0	5.0	1.5	2.5	103.0	13.5	1.0

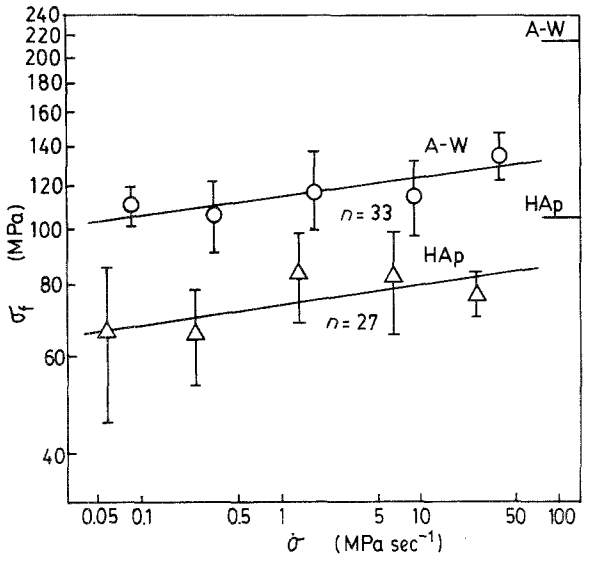

Figure 2 Fracture strengths σ_f of glass–ceramic A–W in the simulated body fluid as a function of stress rate $\dot{\sigma}$, in comparison with those of a sintered hydroxyapatite ceramic HAp.

HAp. For example, when a bending stress of 65 MPa was continuously applied in the simulated body fluid, glass–ceramic A–W and A–W–CP can withstand the stress over 10 years whereas other samples fail in only 1 min. The bending stress of 65 MPa for an artificial bone corresponds to that of 200 MPa or larger for the natural bone, because a load-bearing cross-sectional area of the former is three times that of the latter or larger, if the former takes a solid rod form as usual, instead of a hollow cylindrical form of the latter. The stress of 200 MPa is almost equal to the maximum stress that the human cortical bone can withstand without failure [14].

3.3. Survival probability

The life-time estimated above is an average one. Failure probability measured in the dry N_2 gas atmosphere for 30 specimens of glass–ceramic A–W is plotted in Fig. 4 against failure stress. In this plot, the failure probability F was taken as

$$F = \frac{i}{N + 1} \tag{3}$$

where i is the rank of failure stress and N is the total number of specimens. The relation between the failure probability F and the failure stress σ_f' in Fig. 4 is well fitted to Weibull's function given by the following equation [11].

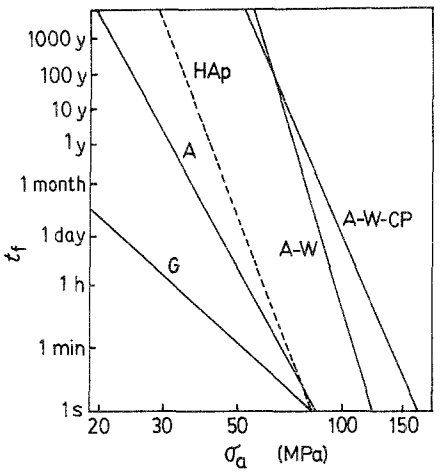

Figure 3 Life-time t_f of samples in the simulated body fluid as a function of applied stress σ_a.

$$\ln\left(\frac{1}{1 - F}\right) = m \ln \sigma_f' + C \tag{4}$$

where the Weibull modulus, m is 9.03 and C is -48.97.

Substituting σ_f' in Equation 4 for σ_{IC} in Equation 2, we obtain the life-time applied stress relations shown by solid lines in Fig. 5 for various failure probabilities. It can be seen from Fig. 5 that the probability of failure of glass–ceramic A–W in 10 years in the simulated body fluid under 65 MPa stress is 0.46, i.e. the probability of survival after 10 years is 0.54. In order to guarantee the life-time of 10 years to all the specimens, a proof test must be performed.

According to fracture mechanics [11], the specimen which withstands the stress σ_p in an inert environment proves to survive under stress σ_a in an aqueous environment for the time t_f given by the following equation:

$$\ln t_f = \ln B - 2 \ln \sigma_a + (n - 2) \ln\left(\frac{\sigma_p}{\sigma_a}\right) \tag{5}$$

Substituting the n and $\ln B$ values given in Table III for n and $\ln B$ in Equation 5, we obtain the $t_f - \sigma_a$ relations given by chain lines in Fig. 5 for various σ_p/σ_a ratios. It can be seen from Fig. 5 that all the specimens which withstand the stress of 215 MPa (65×3.3) in the dry N_2 gas atmosphere are guaranteed for a life-time of 10 years under a bending stress of 65 MPa in the simulated body fluid.

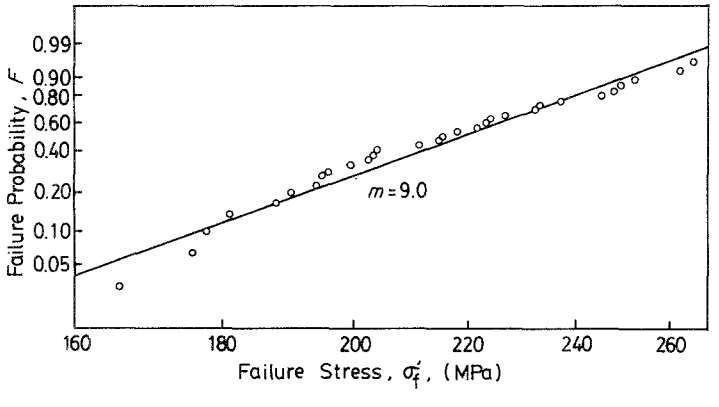

Figure 4 Failure probability F of 30 specimens of glass–ceramic A–W in dry N_2 gas atmosphere as a function of failure stress σ_f'.

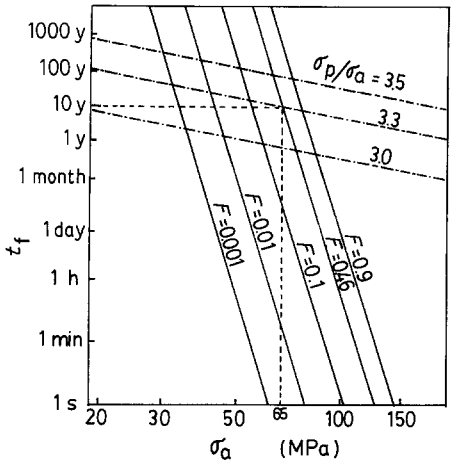

Figure 5 Life-time t_f and applied stress σ_a relations of glass–ceramic A–W for various failure probabilities F, and proof stress σ_p/applied stress σ_a ratios.

3.4. Effect of soaking

The life-time estimated above is that for glass–ceramic A–W continuously loaded in the simulated body fluid. In fact, an artificial bone is not continuously loaded in the body. Fig. 6 shows fracture strengths of glass–ceramic A–W soaked in the simulated body fluid for one month in comparison with those of the glass–ceramic which was not subjected to the soaking. Both strengths were measured in the fluid. It can be seen from Fig. 6 that glass–ceramic A–W shows an increase in the strength at any stress rate, when it is soaked in the simulated body fluid without loading. The magnitude of the dependence of the strength upon the stress rate, i.e. fatigue, is little affected by the soaking. This result indicates that practical life-time of glass–ceramic A–W will be much more prolonged than that estimated above.

The increase in the strength with soaking might be attributed to crack blunting at the surface of the glass–ceramic. The crack blunting might be caused by an apatite deposition on the glass–ceramic in the simulated body fluid [15]. The mechanism of the apatite deposition has been discussed elsewhere [16].

The results described above indicate that glass–ceramic A–W is a promising material for artificial bone which can be successfully used even under load-bearing conditions.

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TABLE III σ_{N_2}, n and ln B of samples

Sample	σ_{N_2}	n	ln B
G	120 ± 20 MPa	9	−5.74
A	141 ± 26	18	−0.063
A–W	215 ± 26	33	−8.53
A–W–CP	243 ± 18	22	2.09
HAp	105 ± 22	27	0.85

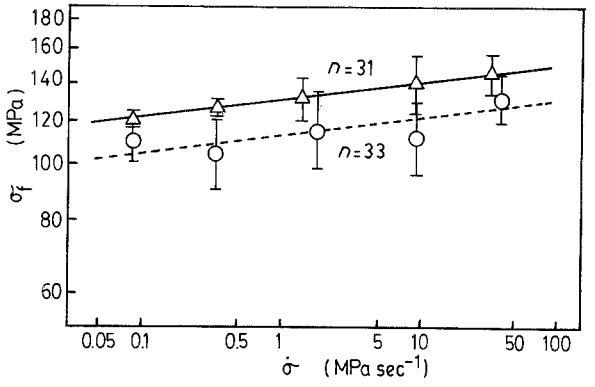

Figure 6 Fracture strength σ_f of glass–ceramic A–W soaked in the simulated body fluid for one month as a function of stressing rate $\dot{\sigma}$, in comparison with those of the glass–ceramic before soaking. △, After soaking for 1 month; ○, not soaked.

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