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# Dense hydroxylapatite: fatigue and fracture strength after various treatments, from diametral tests

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Dense hydroxylapatite was examined with the diametral test at different loading rates, after treatment in different solutions, and under static load. The fatigue tests showed that hydroxylapatite is quite resistant to fatigue as compared with other oxides. The simple Weibull distribution of strengths was not obeyed. Different solution treatments and implanting the hydroxylapatite did not appreciably change its strength.

## 1. Introduction

A sintered hydroxylapatite with density close to theoretical shows promise as a biological implant material [1]. The influence of physiological fluids on the strength of an implant can determine its usefulness, and was studied for dense hydroxylapatite ("Durapatite") in this work.

Fatigue of oxides, both crystalline and glassy, under load is caused by the stress-accelerated reaction of water with the oxide at crack tips. As the reaction proceeds the crack tip becomes sharper, increasing the stress there and the rate of reaction, and so on until failure. In this work the fatigue of Durapatite was studied in static loading (delayed failure) and at different loading rates (dynamic fatigue).

Bend tests are commonly used for measuring strengths of ceramics. However, these tests require bar or rod samples that are hard to make in large numbers, and they also accentuate the influence of surface flaws on strength. The diametral compression test provides an attractive alternative to bend tests; previous work on this test is discussed in [2] and [3]. In this test a right circular cylinder is compressed diametrically between two flat plates. The maximum tensile stress is developed normal to the loading direction across the loading diameter. This maximum tensile stress is, therefore, present across the diameters of both flat surfaces of the cylinder and also across a plane from one end of the cylinder to another. Thus both surface and volume flaws contribute to failure, as has been established experimentally [3].

The diametral test is especially appropriate for materials being considered for dental and other biomedical applications, since the stresses on teeth and some bone implants are similar to those in the diametral test. We, therefore, chose to use this test for Durapatite and also because large numbers of samples could be easily made.

## 2. Experimental methods

Sintered rods of Durapatite 15 mm long and 5 mm diameter were cut into discs 3 mm thick with a slow speed diamond saw. The discs were sonically cleaned in methanol, then in water, and dried.

Twenty discs were incubated in 100 ml human saliva, filtered twice through a 0.45 $\mu$m filter. Twenty more were incubated in 100 ml Hank's balanced salt solution [employed as a pseudo-extracellular fluid (PECF)] and twenty more were incubated in 100 ml distilled water. Potassium penicillin G (10 000 units) and streptomycin (10 000$\gamma$) were added to each flask, which was

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stored at 37° C. The flasks were swirled once a week. After 8 weeks the samples were removed, rinsed three times with 100 ml distilled water and air-dried.

Thirty discs were autoclaved. Ten were air-dried, and twenty were implanted subcutaneously in beagle dogs. After 9 weeks, nineteen of the twenty implanted discs were recovered, removed from their fibrous tissue capsules, rinsed with distilled water and air-dried.

The diametral tests were made in a special compression jig similar to that used by Spriggs *et al.* [4]. The top and bottom plates for bearing surfaces were made of high modulus tool steel, Rockwell hardness $R_c 62$. The tests were carried out in an Instron testing machine at a cross-head speed of 0.05 cm $min^{-1}$, unless otherwise noted. All specimens were soaked 2 min in absolute ethanol before testing. The relative humidity varied from 50% to 65%; all tests were at room temperature, about 22° C.

The maximum tensile stress $S$, which occurs on the diametral plane between loading points, is given by:

$$S = \frac{2P}{Dt}, \quad (1)$$

where $P$ is the load, $D$ the sample diameter (5 mm), and $t$ its thickness (3 mm).

In the diametral test there are high compressive stresses at the loading lines. To reduce these stresses the load is distributed by inserting a pad of soft material between the hard loading plates and the specimen. A successful padding material leads to tensile failures, in which the sample splits into two half-cylinders along the loaded diameter. Often the samples broke in the "triple-cleft" mode, in which the sample splits symmetrically about the loaded diameter into four pieces. A "tongue and groove" in the outer surfaces and smooth central fracture are characteristic of this mode. The triple-cleft fracture results from a second fracture after the first fracture along the diameter. Thus both the simple tensile and triple-cleft modes demonstrate tensile failures, from which tensile strengths can be calculated. Shear failures and shattering of the sample into many pieces are indicative of excessively high stress at the loading lines.

Soft materials such as cardboard or wood have been used as pads; in this work we found metals to be more satisfactory, as did Marion and Johnstone [5] for samples of minerals and glass. Rectangular pads of cold-rolled steel (CRS20), brass, aluminium, and copper of different hardness and thickness were tested as padding material. The harder materials gave a low value of fracture strength and many shear or shattering fractures. Soft aluminium gave too large a contact area, resulting in a high calculated fracture stress. A medium soft copper, 1 mm thick, was the best pad for hydroxylapatite; it usually gave tensile or triple-cleft fractures, and was used in all tests unless otherwise mentioned. Shear and shattered failures were not used.

Static fatigue tests were made in a special three-station apparatus for applying heavy loads with a high lever ratio. When the sample failed, a microswitch turned off a 24 h clock.

## 3. Experimental results and discussion

The results of strength measurements at different loading rates are shown in Table I. They were examined statistically with the Kruskal and Wallis rank test [6, 7], in which unmatched random groups of measurements are examined to see whether or not they belong to a common pool of measurements. The strength values were found to differ significantly at different loading rates with $P = 0.33\%$.

If the rate of reaction $v$ of water with an oxide depends on the stress $\sigma$ at a crack tip by the relation

$$v = K_1 \sigma^n \quad (2)$$

where $K_1$ and $n$ are constants, Charles [8] found that the loading rate $\beta$ is related to the fracture stress $S_f$ by the equation:

$$\frac{1}{\beta^{n+1}} = K_2 S_f \quad (3)$$

where $K_2$ is a constant. Thus the slope of a plot of $\log \beta$ against $\log S_f$ is $1/(n+1)$. From a least squares line for such a plot for the data of Table I, $n$ is found to be 80. Since a high value of $n$ demonstrates low fatigue, and $n$ for silicate glasses

TABLE I Influence of loading on strength of dense hydroxylapatite

| Cross-head speed (cm $min^{-1}$) | No. of samples | Average strength | | Coeff. of variation |
|---|---|---|---|---|
| | | (MN $m^{-2}$) | ($10^3$ psi) | |
| 0.0005 | 17 | 109 | 15.8 | 0.06 |
| 0.005 | 16 | 112 | 16.3 | 0.07 |
| 0.05 | 32 | 117 | 16.9 | 0.10 |
| 0.25 | 15 | 112 | 16.2 | 0.07 |
| 1.25 | 17 | 121 | 17.5 | 0.09 |

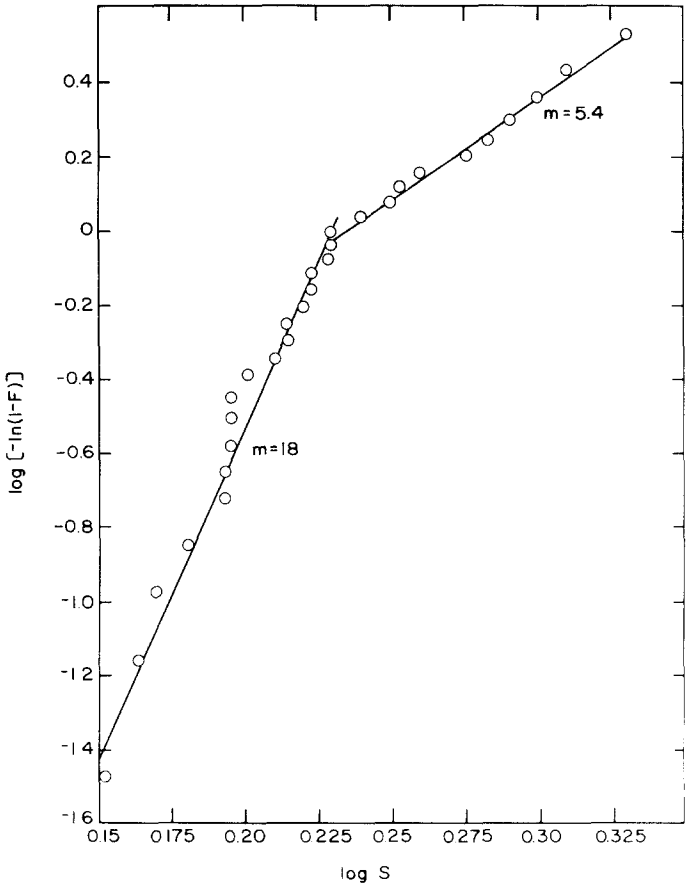


*Figure 1* Weibull failure plot of log [ln $(1-F)$] against log load for untreated hydroxylapatite discs in diametral loading; cross-head speed 0.05 cm $min^{-1}$.

[8] is about 13, and even for polycrystalline alumina [9] $n$ is 31, dense hydroxylapatite is exceptionally resistant to fatigue for an oxide.

Static fatigue results on glasses are not consistent with Equation 2; a better relation is:

$$v = v_\infty e^{-\alpha/\sigma} \tag{4}$$

where $\alpha$ and $v_\infty$ are constants [10, 11]. Thus an analogous relation between $\beta$ and $S_f$ is:

$$-\ln \beta = \frac{\alpha/\sigma_t}{S_f/S_N} + K_3 \tag{5}$$

where $\sigma_t$ is the theoretical cohesive strength of the material and $S_N$ is the fracture strength at $-196^\circ$ C, where there is no fatigue. The data in Table I are not taken over a wide enough strength range to distinguish between Equations 3 and 5. A least-squares fit to Equation 5 gives $\alpha/\sigma_t = 75$ for hydroxylapatite. This value can be compared with $\alpha/\sigma_t \approx 7$ for silicate glasses and 21 for alumina [11]; the larger $\alpha/\sigma_t$ the less sensitive the material is to fatigue, and the good fatigue resistance of hydroxylapatite is confirmed.

The distribution of strengths can be described by the Weibull equation:

$$-\ln (1-F) = (S/S_0)^m \tag{6}$$

where $F$ is the fraction of samples that break below stress $S$, $S_0$ is a scaling parameter, and $m$ is a measure of the spread of the distribution. If Equation 6 is obeyed a plot of log [$-\ln (1-F)$] against log $S$ should be a straight line. Such a plot is shown in Fig. 1 for untreated samples broken at a cross-head speed of 0.05 cm $min^{-1}$. The simple Weibull function of Equation 6 is not obeyed; the plot shows two linear portions. Strengths for abraded soda-lime, silica, and borosilicate glasses also show two straight lines on a Weibull plot [12]. In the present case one might guess that the two linear portions represented two separate populations of flaws, one on the sample surface and one in the interior, since the diametral test is sensitive to both types of flaws. There is no independent evidence for this possibility, and it seems more likely that both surface and volume flaws have a complex distribution.

Table II shows the strengths of hydroxylapatite samples treated in various solutions before testing.

TABLE II Influence of pretreatment of strength of dense hydroxylapatite

| Treatment | No. of samples | Average strength | | Coeff. of variation |
|---|---|---|---|---|
| | | ($MN m^{-2}$) | ($10^3$ psi) | |
| None | 32 | 117 | 16.9 | 0.10 |
| Water | 19 | 108 | 15.6 | 0.12 |
| Saliva | 15 | 110 | 16.0 | 0.07 |
| PECF | 15 | 116 | 16.8 | 0.07 |
| Implanted | 16 | 111 | 16.1 | 0.11 |
| Autoclaved | 8 | 112 | 16.2 | 0.10 |

The samples incubated in saliva, PCEF and autoclave appeared to be unchanged after treatment at 37° C. The samples incubated in water had a thin, soft, opaque coating, perhaps because the antibiotics gave a slightly acid solution; the saliva and PCEF probably have enough buffering capacity to minimize the pH change. The data in Table II were examined by the Kruskal and Wallis rank test [6, 7], and the differences between the different samples were found not statistically significant ($P > 10\%$). Thus the treatments had little or no influence on hydroxylapatite strength.

Some preliminary static fatigue measurements were made on untreated hydroxylapatite samples. Three discs were held at a stress of $100 MN m^{-2}$ using steel pads, which is about 80% of the liquid nitrogen breaking strength with these pads. The average failure time was about 7000 min, which is much longer than other ceramics such as alumina can endure at this fraction of inert strength [13].

All these results demonstrate the relatively strong fatigue resistance of hydroxylapatite as compared to other oxides.

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