JOURNAL OF MATERIALS SCIENCE 16 (1981) 1592–1598

Preparation, microstructure and mechanical properties of dense polycrystalline hydroxy apatite

G. DE WITH, H. J. A. VAN DIJK, N. HATTU, K. PRIJS
Philips Research Laboratories, 5600 MD Eindhoven, The Netherlands

Hydroxy apatite ceramic blocks of varying density have been prepared from a commercial powder. The elastic properties, fracture toughness, strength and sub-critical crack growth of these materials have been investigated. Young's modulus for the nearly fully dense material is 112 GPa while the compressive strength is about 800 MPa. For the same material the strength and fracture toughness under dry conditions are 115 MPa and 1.0 MPa $m^{1/2}$, respectively. Substantial slow crack growth was found under these conditions. Under wet conditions the values for strength and fracture toughness drop to about 75% of their "dry" values. In this case very serious slow crack growth is present.

1. Introduction

Hydroxy apatite ceramics ($Ca_5(PO_4)_3OH$; OHAp) have been used succesfully as a substitute material for defective bone tissue [1, 2]. So far two modifications of the ceramic have been described; a highly porous one and a densely sintered one [3]. Both modifications exhibit excellent bio-compatibility after implantation. The porous ceramics with a porosity of up to 60% are converted completely to natural bone tissue [1]. The applicability of this material, however, is restricted to non-stressed regions of the skeleton. This is due to the inferior tensile strength of the material [4]. It was shown that when the material is sintered to nearly full density its bio-compatibility is preserved, although upon implantation the material no longer converts to natural bone [3].

Little information on the mechanical properties of the highly dense material is available. Some tensile and compressive strength data are reported [5, 6] while one of these papers also deals briefly with slow crack growth. Information on Young's modulus is mainly available for theoretically dense powder compacts [7, 8]. Data on fracture toughness are not available at all. This paper describes the mechanical properties of the dense OHAp ceramics, sintered from a commercially available powder, as a function of the conditions of preparation and testing.

2. Experimental methods

2.1. Material preparation

Commercial powder (Merck A.G., Darmstadt, Germany) was used for the preparation of the dense apatite blocks. This powder has a Ca/P ratio of 1.62 and a specific surface area of 65 $m^2 g^{-1}$, as measured with standard N_2-BET equipment. It contains 1 to 10 ppm Cu and Pb, 10 to 100 ppm Ge and 100 to 1000 ppm Al, Fe, Si, Ti and Mn and more then 1000 ppm Mg and Na.

The powder was mixed with 5% (wt/wt) water and compacted in a perspex die at a moderate pressure (5 MPa). The resulting bodies were vacuum sealed in rubber bags and subsequently pressed isostatically at a pressure of 100 MPa. The compacts with typical dimensions of $8 \times 3 \times 3$ cm^3 and a green density of about 50% were sintered for 6 h at various peak temperatures in a moist oxygen atmosphere. The heating and cooling rates were kept constant for all samples at 60 K h^{-1}.

For the compacts, six different firing temperatures were chosen in order to vary the density of the resulting ceramics. We refer to them as OHAp Types 1 to 6, in order of increasing density. The ceramics show a blue discoloration, probably caused by the impurity content of the starting powder [9].

2.2. Measurement procedure

The microstructure of each type of material was

0022–2461/81/061592–07$02.70/0

revealed, after polishing with diamond paste, by chemical etching in 1% phosphoric acid for about 30 sec. Scanning electron micrographs were taken of each microstructure. Prior to SEM examination the surface was shadowed with gold to eliminate charging effects.

Area distributions of the grains in the SEMs were measured with a digital planimeter*. From these data the volume–grain-size distributions were calculated using the Johnson–Saltikow transformation [10]. The grain sizes were log-normally distributed.

From blocks of the various materials, small specimens (of dimensions $1 \times 3 \times 15\,\mathrm{mm}^3$) and large specimens (of dimensions $3 \times 9 \times 45\,\mathrm{mm}^3$) were sawn. The density ρ (as a percentage of the theoretical density) of each type of material was determined from the weight and dimensions of the large specimens, assuming the theoretical density to be $3.156\,\mathrm{g\,cm}^{-3}$. For the more dense specimens the density was also determined by Archimedes method. Good agreement was found.

The longitudinal wave velocity, v_l, and the shear wave velocity, v_s, were determined at 10 MHz and 20 MHz, respectively, using the pulse-echo technique† [11] on the large specimens. Young's modulus, E, and Poisson's ratio, ν, were calculated from ρ, v_l and v_s using the conventional formulae for isotropic materials [11]. No correction was made for attenuation since $\tan\delta$ was at most 0.05. Excellent agreement with the literature was found for several other materials by means of this method.

The strength, σ_f, of the small specimens was measured in a three-point bending set-up using a span of 12 mm. The cross-head speed of the universal testing machine‡ was $1.75\,\mu\mathrm{m\,sec}^{-1}$.

The measurement of the fracture toughness, K_IC, of the small specimens was done in the same way. The fracture toughness of the large specimens was also measured in a three-point bend test with span 36 mm and again a cross-head speed of $1.75\,\mu\mathrm{m\,sec}^{-1}$. In each fracture toughness specimen a notch of width $\sim 100\,\mu\mathrm{m}$ and relative depth ~ 0.15 was sawn. Pre-cracking was done by means of a Vickers hardness indentation (1 N load) just below the notch root on both sides of the specimens. The value of the compliance factor Y was calculated according to Brown and Srawley [12].

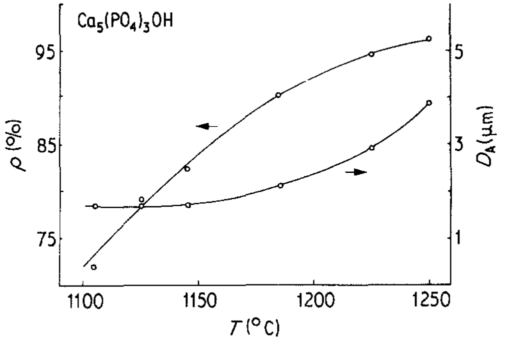

Figure 1 Mean grain size, D_A, and density, ρ, of the OHAp ceramics.

Strength as well as fracture toughness measurements were carried out in a dry N_2 gas atmosphere in order to prevent sub-critical crack growth. Most of the experiments were also carried out in distilled water in order to check the influence of a wet environment. For the fracture toughness and strength measurements, on average 7 and 10 specimens, respectively, were used. The estimated standard deviations in a single measurement were 12% and 18%, respectively.

SEMs were taken of a fracture surface for each type of material, again after covering the surface with a thin gold layer.

Compressive strength measurements were carried out with small cylinders, diameter approximately 5 mm and length approximately 15 mm. No special precautions were taken, except for steps to ensure high planparallelism.

Double torsion experiments were carried out on plates of OHAp Type 5. The dimensions of these plates were $2 \times 24 \times 75\,\mathrm{mm}^3$. A pregroove with semi-circular cross-section and of depth 1 mm was cut in the plates in order to guide the crack.

3. Results and disccusion

3.1. Grain size, density and microstructure

Fig. 1 shows the grain size, D_A, and the density, ρ, against firing temperature. A regular increase of both quantities with temperature is observed. Since the density is a main variable in many calculations, all further results are expressed as a function of density. We refer to the different materials as OHAp Type 1 to 6 in order of increasing density.

An estimate of the activation energy for

---

*Kontron-MOP-AM-03.

†Panametrics 5223.

‡Tinius Olsen Electomatic.

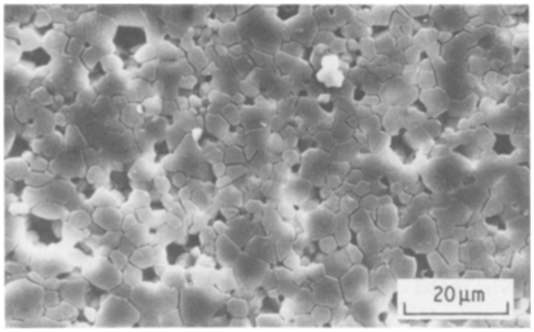

Figure 2 SEM of the OHAp ceramic, Type 5.

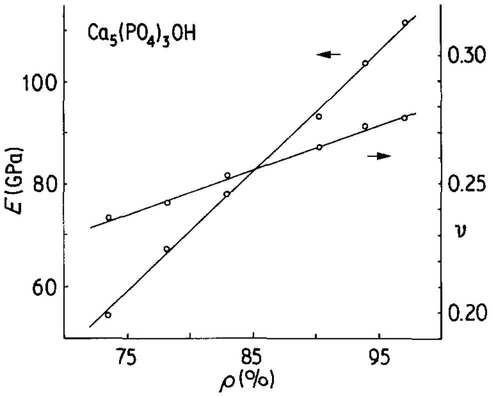

Figure 3 Young's modulus, E, and Poisson's ratio, ν, of the OHAp ceramics.

grain growth can be made from the grain size-temperature data. The grain size D can be described by

$$D = B(t)\exp(-\Delta H/RT),$$

where $B(t)$ is a function of time t, ΔH is the activation energy, T is the absolute temperature and R is the gas constant. A value of $\Delta H = 34\,\text{kcal mol}^{-1}$ results from a least-squares fit of $\ln D$ against $1/T$. The data from Fig. 1 were used, except those for material Type 1 and 2 since these were considered to be less reliable. The activation energy as determined by Jarcho *et al.* [5] was $\Delta H = 56\,\text{kcal mol}^{-1}$. From the grain size data as given by Kijima and Tsutsumi [13] a value of $57\,\text{kcal mol}^{-1}$ can be calculated. The lower value resulting from the Merck OHAp data is probably due to the somewhat higher impurity content of this material or the relative low Ca/P ratio.

In Fig. 2 the microstructure of OHAp (Type 5) is given. It shows a regular grain distribution. The X-ray diffraction pattern of the powder showed only OHAp peaks. If sintering was carried out at a temperature below 1150° C no other phases could be identified. At 1150° C the formation of β-Ca-orthophosphate is observed whereas at about 1250° C peaks of α-Ca-orthophosphate appear. The temperature at which these phases appear are lower than those reported earlier [14]. The moist sintering atmosphere, meant to suppress the formation of these second phases, is apparently more effective with porous materials than with the dense ones.

3.2. Elastic properties

The elastic constants of a bio-material are important parameters in its mechanical behaviour. For OHAp both Young's modulus, E, and Poisson's ratio, ν, show a linear dependence on density (Fig. 3). A least-squares fit of the data was made with $A = A_0(1 - \alpha_A P)$, where A denotes either E or ν, A_0 denotes E or ν at zero porosity, P is the fractional porosity and α_A is the "porosity factor". The resulting equations are $E = 117\,(1-2.01P)$ GPa and $\nu = 0.281\,(1-0.60P)$. The correlation coefficients of these fits were 0.998 and 0.993, respectively.

Various other experimental investigations on the elastic constants of OHAp are known. For theoretically dense powder compacts, E has been measured several times [7, 8]. For a sintered compact only one value is known [5]. Reasonable agreement between the different experimental values, averaging to $E = 113$ GPa, is found (Table

TABLE I Comparison of the different determinations of the elastic constants for dense OHAp

E (GPa)	ν	Method	References
115	0.261	Single-crystal constant averaging	This work using data from [19]
108	–	Ultrasonic interferometry on synthetic OHAp powder compact	[7]
117	0.27	Ultrasonic interferometry on synthetic OHAp powder compact	[8]
114	0.28	Ultrasonic interferometry on mineral OHAp powder compact	[8]
34.5	–	Sintered OHAp, no method given	[5]
117	0.281	Sintered OHAp, pulse echo technique	This work

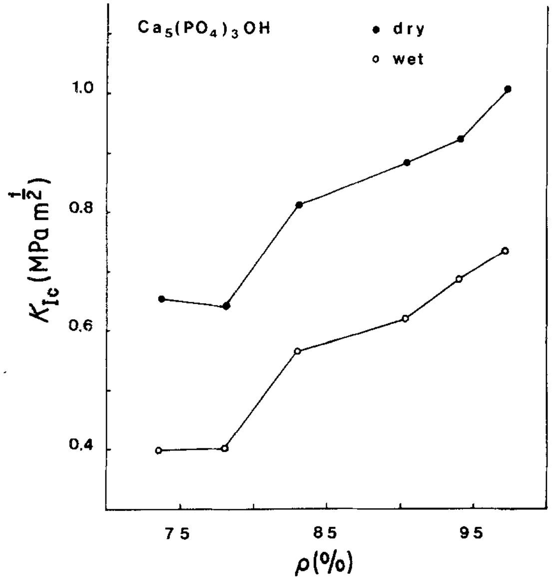

Figure 4 Fracture toughness, K_{IC}, of the OHAp ceramics as measured with small specimens under dry and wet conditions.

I) aside from one exception. For highly dense sintered OHAp, Jarcho *et al.* [5] determined E to be 34.5 GPa without mentioning the method of determination. This value seems low. The value sometimes quoted for apatite in the literature (see e.g. [15]), $E = 109$ GPa, refers to an average of the single-crystal constants for fluorapatite as determined by Bhimasenacher [16] in 1945.

Values of E_0 and ν_0 can, in principle, also be calculated from single-crystal elastic constants using the Voigt–Reuss–Hill average scheme [17]. The elastic constants for single-crystal OHAp have been determined by Tan [18] from diffuse X-ray reflection intensities. The resulting values for E and ν are shown in Table I. Good agreement with experimental values is found for E as well as ν. It should be borne in mind, however, for both the comparison between the different experimental values and the theoretical one that the OHAp Types 4, 5 and 6 as used in this work contained a certain amount of second phase.

3.3. Fracture toughness

Fig. 4 shows the fracture toughness of the OHAp samples, as measured with the small specimens, both for the dry and wet conditions. A steady increase with density is observed. The same trend is observed for the fracture toughness as measured with the large specimens (Fig. 5) under dry conditions. For the toughest OHAp, Type 6, the value

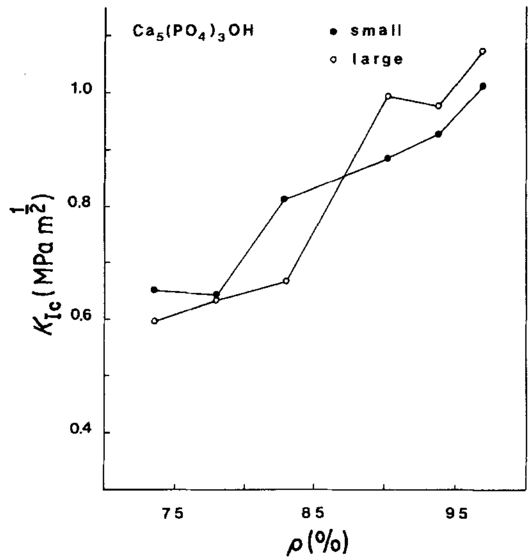

Figure 5 Fracture toughness, K_{IC}, of the OHAp ceramics as measured with small and large specimens under dry conditions.

of K_{IC} is 1 MPa m$^{1/2}$. Under wet conditions the fracture toughness is roughly 0.25 MPa m$^{1/2}$ lower in all cases (Fig. 4). A serious influence of the environment is thus observed for the OHAp.

3.4. Strength

The strength of the materials, as measured with small specimens under dry and wet conditions, is shown in Fig. 6. Here too an increase of strength with density is observed. For the strongest OHAp,

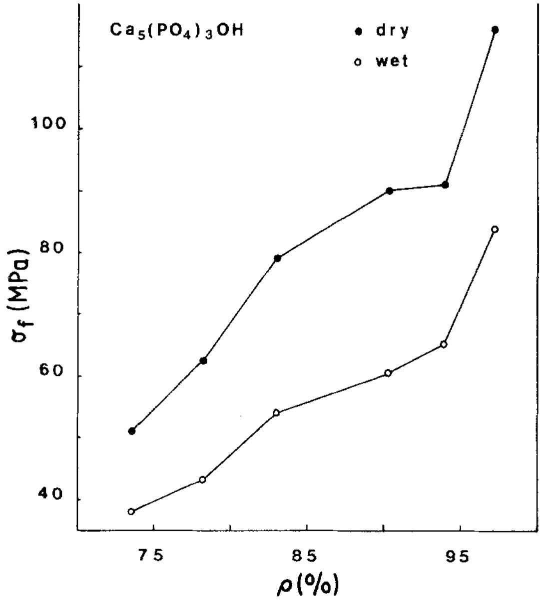

Figure 6 Strength, σ_f, of the OHAp ceramics as measured with small specimens under dry and wet conditions.

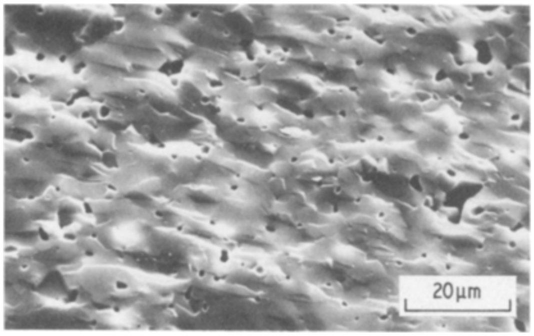

Figure 7 SEM of the fracture surface of the OHAp ceramics Type 5.

Type 6, the value of σ_f is 115 MPa. Also, a quite large difference in strength as measured under dry and wet conditions is observed. On average the strength under wet conditions is 24 MPa lower than under dry conditions. A typical fracture surface for OHAp Type 5 is shown in Fig. 7.

From the strength, σ_f, and fracture toughness, K_{IC}, the average maximum flaw size in the material can be calculated from

$$a_c = K_{IC}^2/Y^2\sigma_f^2.$$

Here it was assumed that $Y = 1.26$, which is appropriate for semi-circular surface cracks [19]. The resulting crack length is approximately constant for all grades. Also, the crack lengths as calculated from the measurements under dry and wet conditions are very nearly equal. An average crack length of 68 μm results. Together with the 0.25 MPa m$^{1/2}$ difference in fracture toughness this results in a strength reduction, upon changing from dry to wet conditions, of 24 MPa as calculated from

$$\Delta\sigma_f = \Delta K_{IC}/Y\sqrt{a_c}.$$

Hence, strength and fracture toughness measurements are highly consistent, recalling that the experimental value of $\Delta\sigma_f$ is 24 MPa.

Polishing generally increases the strength. A number of specimens of OHAp type were polished on one side down to 1 μm diamond paste. The strength was measured again under dry and wet conditions. No significant influence of polishing was found, however. A possible explanation is as follows. Upon polishing the height of the specimens diminished on average by 2 μm. The size of the zone that contains the machining flaws is assumed to be equal to the calculated flaw size, 68 μm. Hence upon polishing, the maximum crack length available does not decrease significantly and accordingly no strength increase is found.

Two other strength determinations are reported in the literature. One, using the conventional bending test [9], results in $\sigma_f = 100$ MPa for the as-cut samples of nearly theoretically dense OHAp, containing no second phase. (Compare $\sigma_f = 115$ MPa as measured in this work.) In this case a strength increase of about a factor of 2 was found upon polishing the specimens. The other [22] uses the diametral test and results in $\sigma_f = 109$ to 121 MPa depending on loading rate. In the diametral test no uniaxial conditions are present and hence a fair comparison is difficult to make.

Both papers mentioned previously [5, 6] report strength values for different environments.

For an OHAp ceramic containing only 87 wt% apatite, Jarcho *et al.* [5] report a strength value as measured in air of 79 MPa and in liquid N_2 of 101 MPa. A strength difference of 22 MPa is thus found. This difference compares favourably with the 24 MPa as determined in our case. However, the material is somewhat different and the test conditions not comparable.

Thomas *et al.* [6] treated their OHAp for 3 weeks with water at 37° C containing several types of biologically active components. According to the Kruskal and Willis rank test, at the 10% significance level the strength after the treatment did not differ significantly from the strength as measured on the untreated material, about 112 MPa. They conclude that no environmental (water) influence on the strength is present. However, the actual strength measurements were carried out in air after drying. For nearly 100% dense materials no influence is thus expected since at the time of the test itself, water (responsible for the strength decrease) is not readily available.

The compressive strength was measured for grade 6 only. The resulting value is 798 MPa with a sample standard deviation of 56 MPa using eight specimens. This value is reasonably high and corresponds favourably with the compressive strength of 917 MPa (standard deviation 138 MPa) as reported by Jarcho *et al.* [5] also for nearly fully dense OHAp.

3.5. Slow crack growth

Apart from the instantaneous strength, the long time duration strength is important especially in biomedical applications. The decrease of strength

TABLE II Strain-rate dependence of strength for the OHAp ceramic, Type 5

$v(\mu m\ sec^{-1})$*	Dry		Wet	
	σ_f (MPa)	m†	σ_f (MPa)	m†
1.97×10^{-1}	96	9.3	66	4.8
1.75	94	4.4	69	4.9
2.04×10^{1}	101	5.1	82	5.8
1.80×10^{2}	124	7.1	115	9.4

*Cross-head speed.
†Weibull modulus based on 14 specimens.

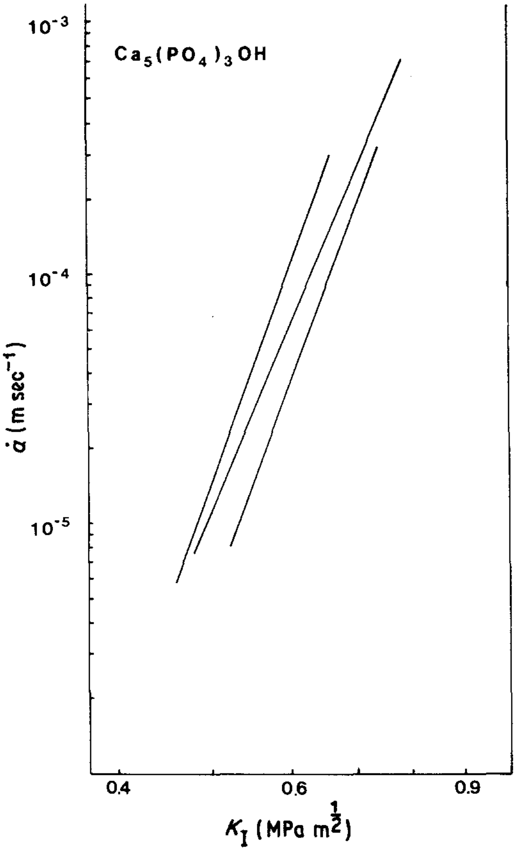

Figure 8 $K_I - \dot{a}$ diagram for the OHAp ceramic, Type 5.

of brittle oxidic materials is caused by the slow (or subcritical) crack growth. Assuming that the crack velocity $\dot{a}$ is related to the stress intensity K_I by $\dot{a} = AK_I^n$, the exponent n can be estimated from the strain-rate dependence of strength [20] using the relation: $\ln \bar{\sigma}_f = 1/(n+1)\{\ln v + B\}$ where $\bar{\sigma}_f$ is the mean strength at a certain cross-head speed, v, of the testing machine.

For the OHAp Type 5 the strain-rate dependence of the strength under dry and wet conditions was determined using four different cross-head speeds (Table II).

All strength measurements were fitted by a Weibull function. An average Weibull parameter $m \sim 6.4$ resulted (Table II). For dry conditions a least-squares fit plot of $\ln \bar{\sigma}_f$ against $\ln v$ yields a slope of 3.7×10^{-2} (standard deviation $= 1.6 \times 10^{-2}$, correlation coefficient $= 0.85$) while for wet conditions the result is $h = 8.0 \times 10^{-2}$ (standard deviation $= 2.0 \times 10^{-2}$, correlation coefficient $= 0.94$). This corresponds to the fairly low value of $n = 26$ for dry conditions, indicating substantial slow crack growth. Under wet conditions the resulting value for n is 12. This value is very small, indicating very serious crack growth under wet conditions.

Thomas *et al.* [6] also estimated n by the same technique. Although they state n to be 80, a recalculation from their strength and cross-head speed data yields $h = 1.1 \times 10^{-2}$ (standard deviation $= 4.6 \times 10^{-3}$, correlation coefficient $= 0.80$) which results in $n = 92$. This is a very high n value. Their statement that the "dense OHAp is exceptionally resistant to fatigue" (i.e. slow crack growth), however, should be considered with care, since the actual strength measurements were carried out in air only. A serious discrepancy in behaviour between the material as prepared by Thomas *et al.* [6] and our material is thus found.

In order to confirm the strain-rate experiments, double-torsion experiments were carried out, using the load–relaxation technique. For dry conditions three double-torsion plates were fractured. The load–relaxation curves were least-squares fitted by $P = a + b \ln t$ where P is the load and t is the time. Excellent fits were obtained (correlation coefficient ≥ 0.97). The crack velocity, $\dot{a}$, and stress intensity, K_I, were calculated from the (P, t)-fit according to McKinney and Smith [21]. An approximate crack-front shape correction was applied [22]. The resulting $K_I - \dot{a}$ curves were least-squares fitted by $\dot{a} = AK_I^n$ (correlation coefficient ≥ 0.99). An average n value of 10.8 with a sample standard deviation of 0.9 resulted. The average value for $\ln A$ was -4.0 with a sample standard deviation of 0.7, expressing $\dot{a}$ in m sec^{-1} and K_I in MPa m$^{1/2}$. The resulting $K_I - \dot{a}$ plots are shown in Fig. 8.

The crack-growth exponent, n, was also estimated by direct graphical differentiation of the P–t curves and fitting the resulting $K_I - \dot{a}$ curve by $\dot{a} = AK_I^n$. This resulted in $n = 11.4$ with sample standard deviation of 3.8. Hence we conclude that n, as estimated from the double torsion experiments under dry conditions is about 11.

The difference in n value as determined by the strain-rate experiments and by the double-torsion experiments can be at least partly due to the difference in crack geometry: microscopic natural cracks in the strain-rate experiments and a macroscopic-induced crack in the double-torsion experiments.

Under wet conditions it proved to be hardly feasible to perform the experiment. No clear pop-in effect was present and the crack progressed smoothly with even a small load increase.

Hence we conclude that for this type of OHAp substantial crack growth is present even under dry conditions, contrary to the experiments as carried out by Thomas *et al.* [6]. Crack growth becomes very serious under wet conditions.

4. Conclusions

From the discussion, the main points are:

(a) dense calcium hydroxy apatite (OHAp) with small grain size is readily sintered from commercial powder;

(b) Young's modulus for the 100% dense material is about 117 GPa;

(c) the compressive strength is roughly 800 MPa;

(d) the fracture toughness and strength of this material are approximately $1\,\mathrm{MPa\,m^{1/2}}$ and 115 MPa, respectively, under dry conditions. Under wet conditions these values drop to about 75% of their "dry" values. The environment is thus observed to have a serious influence;

(e) substantial subcritical crack growth is present under dry as well as wet conditions. From the strain-rate dependence of strength n is estimated to be 26 and 12, respectively.

In conclusion, the following picture can be sketched for this material. Dense OHAp ceramics are readily made from a commercial powder. They show excellent bio-compatilibity. The mechanical properties of these ceramics are probably sufficiently good for loads of short duration. However, serious subcritical crack growth takes place, especially in wet environments. This makes the degradation of strength with time significant. Hence, from the mechanical point of view the subcritical crack growth makes the OHAp in its present form a doubtful candidate for bone replacement in loaded places of the skeleton. If any crack-stopping mechanism would be activated (e.g. fibre reinforcement) or if the material could be used in another form (e.g. metal encapsulated with OHAp) it is possible that the bio-compatibility would be preserved while the mechanical properties are improved.

Acknowledgements

Many thanks are due to Mr S. M. Clark and Mr. P. C. Spurdens, both from Imperial College (London) for their assistance with the experimental work.

References

1. B. V. REJDA, J. G. J. PEELEN and K. DE GROOT, *J. Bioeng.* **1** (1977) 93.
2. E. B. NERY, K. L. LYNCH, W. M. HIRTHE and K. H. MUELLER, *J. Periodontal.* **46** (1975) 328.
3. H. W. DENISSEN, K. DE GROOT and P. J. KLOPPER, *Sci. Ceram.*, to be published.
4. J. G. J. PEELEN, B. V. REJDA and K. DE GROOT, *Philips Tech. Rev.* **37** (1977) 234.
5. M. JARCHO, C. H. BOLEN, M. B. THOMAS, J. BOBICK, J. F. KAY and R. H. DOREMUS, *J. Mater. Sci.* **11** (1976) 2027.
6. M. B. THOMAS, R. H. DOREMUS, J. JARCHO and R. L. SALSBURY, *ibid.* **15** (1980) 391.
7. H. RAO, W. A. THOMPSON, J. L. KATZ and R. A. HARPER, *J. Dent. Res.* **55** (1976) 708.
8. D. E. GRENOBLE, J. L. KATZ, K. L. DUNN, R. S. GILMORE and K. LINGA MURTY, *J. Biomed. Mat. Res.* **6** (1972) 221.
9. P. D. JOHNSON, J. S. PRENNER and J. D. KINGSLEY, *Science* **141** (1963) 1179.
10. E. E. UNDERWOOD, in "Quantitative Microscopy", edited by R. T. DeHoff and F. N. Rhines, (McGraw-Hill, New York, 1968) Ch. 6.
11. H. F. POLLARD, "Sound Waves in Solids", (Pion, London, 1970).
12. W. F. BROWN and J. E. SRAWLEY, ASTM-STP 410, (ASTM, Philadelphia, 1966).
13. T. KIJIMA and M. TSUTSUMI, *J. Amer. Ceram. Soc.* **62** (1979) 455.
14. J. G. J. PEELEN, B. V. REJDA and K. DE GROOT, *Ceramurgia Int.* **4** (1978) 71.
15. K. PIEKARSKI, *Int. J. Eng. Sci.* **11** (1973) 557.
16. J. BHIMASENACHER, *Proc. Indian Acad. Sci.* **22A** (1945) 209.
17. R. HILL, *Proc. Phys. Soc. London* **A65** (1952) 349.
18. S. K. TAN, *Diss. Abstr. Int.* **B34** (1973) 2862.
19. G. R. IRWIN, *J. Appl. Mech.* **29** (1962) 651.
20. J. E. RITTER, in "Fracture Mechanics of Ceramics IV", edited by R. C. Bradt, D. P. H. Hasselman and F. F. Lange (Plenum Press, New York, 1978) p. 667.
21. K. R. McKINNEY and H. L. SMITH, *J. Amer. Ceram. Soc.* **56** (1973) 30.
22. A. G. EVANS, *J. Mater. Sci.* **7** (1972) 1137.

Received 2 October and accepted 14 November 1980.