Metal fibre reinforced hydroxy-apatite ceramics

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The reinforcement of hydroxy-apatite ceramics with metal fibres is discussed. Hastelloy X and FeCralloy fibres were dispersed in hydroxy-apatite powder slurry. The fibre–powder slurries were dried and sieved over a wide aperture sieve. The resulting granules were used for die-pressing. Volume fractions used were 10, 20 and 30%. The compacts obtained in this way were isostatically repressed at 4 k bar. These compacts showed considerable strength and toughness. Hot-pressing of the compacts was done at about 1000° C and a pressure between 0.2 and 1.0 k bar for 15 min. The resulting materials were characterized by fractography and strength, fracture toughness, Young's modulus and hardness measurements. Both strength and fracture toughness increased while Young's modulus and hardness decreased with increasing volume fraction of fibres. The strength and fracture toughness of composites containing 20 vol % metal fibres showed an increase of the strength and fracture toughness by a factor of about 2 and 6, respectively, as compared with the strength of about 100 MPa and a toughness of $1.0 \, \mathrm{MPa \, m^{1/2}}$ for the sintered, pure matrix materials. The results obtained are also promising for other metal fibre–ceramic matrix composites.

1. Introduction

Hydroxy-apatite [$Ca_5(PO_4)_3 \cdot OH$, OH-Ap] is the main mineral constituent of bones and teeth. Quite a few attempts have been made to use a ceramic based on this composition as an implant material as, besides tricalcium phosphate [$Ca_3(PO_4)_2$], it is the only fully biocompatible material [1, 2]. The use of porous ceramics for esthetical surgery is successful since this ceramic is fully absorbed by the body and "reformed" as natural bone [2]. The application of high density phosphate ceramics as a load bearing implant is, however, retarded primarily due to its low strength and fracture toughness and considerable subcritical crack growth [3–14]. Consequently the mechanical properties of the material need improvement. Various reinforcement mechanisms are known. Transformation toughening by ZrO_2 particles is one proposition. Some attempts to produce ZrO_2 toughened OH-Ap ceramics revealed, however, that the ZrO_2 particles become fully stabilized by the sintering process, probably due to the presence of calcium in the material [15]. Another possibility to obtain a better strength and fracture toughness is the introduction of fibres in the OH-Ap ceramics. Because the OH-Ap ceramic has a thermal expansion coefficient of about $15 \times 10^{-6} \, K^{-1}$ [14, this work], the choice of potentially useful fibres is limited. Fibres of, e.g. Al_2O_3, SiC and carbon are available in sufficiently large quantities but all have a low thermal expansion coefficient. This combination results in tensile stresses in the matrix. Therefore primarily metal fibres with a high(er) thermal expansion coefficient and some ductility remain. Attempts to incorporate metal fibres in OH-Ap ceramics are reported in this paper.

2. Experimental procedure

The powder used for the preparation of the fibre composite was a commercially available OH-Ap powder (Merck A. G., Darmstadt, Germany), used also in earlier investigations dealing with pure OH-Ap ceramics [12, 13]. Characteristics are given in Table I. The fibres chosen are also commercially available. Al_2O_3 (Dupont FP, diameter 20 μm), titanium Inconel 601, stainless steel, Hastelloy X and FeCralloy fibres were tried. All metal fibres were purchased from N.V. Bekaert S.A. (Zwevegem, Belgium). The Hastelloy X and FeCralloy fibres were the most successful and are further denoted by fibre H and F, respectively. Compositions and further characteristics of these fibres are given in Table I. The metal fibres were delivered chopped at 1 mm length in polyvinylalcohol binder. The as-received fibres were intensively washed with water to remove the binder. In this washing process cold-welded bundles of fibres, present as a result of the chopping process, were removed as well.

Mixing of the powder and fibres appeared to be highly critical for obtaining useful compacts. Volume fractions of fibres used in the starting mixture were 10, 20 and 30%. In each case the appropriate amounts of powder and fibres were wet-mixed in a high shear rate mixer (IKA Universalmühle M-20) for about 5 sec. After that the larger lumps were removed and the remainder was mixed for another 5 sec. The resulting slurry was, after drying, dispersed by sieving through a wide aperture nylon sieve. The powder–fibre mixture so obtained had a relative density of about 15% and was used to fill perspex dies. The filling was done piecewise in a number of layers each of about 0.5 cm thickness. After pressing at 100 to 500 bar, depending

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TABLE I Material characteristics and processing conditions

Material	vol %	T (°C)	P (k bar)	q (%)	Material
OH-Ap	0	950	0.2	93	Ca/P ratio 1.62 specific surface area 65 m^2 g^{-1}
H	10	1000	0.5	95.6	Hastelloy X
H	20	1000	0.7	93.8	comp. Ni 51, Cr 22, Mo 9, Fe 18
H	30	1000	1.0	100	diameter 8 μm $E = 221$ GPa $H_K = 2.0$ GPa
F	10	1000	0.7	99.7	FeCralloy
F	20	1000	0.7	99.2	comp. Fe 79, Cr 16, Al 5
F	30	1000	0.7	99.8	diameter 22 μm $E = 207$ GPa $H_K = 2.1$ GPa

OH-Ap: Pure OH-Ap ceramic
H: Hastelloy X containing composite
F: FeCralloy containing composite
E: Young's modulus
H_K: Knoop hardness (2 N load, 15 sec)
Compositions in wt %.

q: relative density
P: hot-pressing pressure
T: hot-pressing temperature

on the size of the die, shaped preforms typically with a relative density of 25% resulted. These preforms were isostatically repressed at 4 k bar resulting in a relative density of about 60%. The compacts so obtained showed considerable strength and are easily handled. Therefore the values of the strength and fracture toughness were measured on dry sawn specimens in the same way as for the hot-pressed material (see below). In each case three specimens were used resulting in a sample standard deviation of 9%. The stiffness of the compact was calculated from the deflection of a three-point bend specimen during strength testing.

Uni-axial hot-pressing was done at temperatures around 1000° C for 15 min and pressures ranging from 0.2 to 1 k bar. The atmosphere was flowing N_2 except for the pure OH-Ap ceramic which was hot-pressed in air. A heating and cooling rate of 200° C h^{-1} was used for the composites while 60° C h^{-1} was used for the pure OH-Ap ceramic. The density, q, of the material so obtained was determined from the weight and size of machined rectangular blocks. Relative densities near 100% were obtained (Table I). The microstructure of the composites was revealed, after grinding and polishing, by optical (OM) and electron microscopy (SEM).

Blocks of the densified materials were machined into specimens of 3 mm × 9 mm × 45 mm for mechanical testing. Strength, S_f, and fracture toughness, K_{Ic}, were measured in a three-point bend set-up with a span of 36 mm at a crosshead speed of 1 mm min^{-1}. For both measurements the sample standard deviation was about 10%. Typically five to ten specimens were used for each measurement. In case of K_{Ic} measurements a notch was machined in the specimens with a relative depth of about 0.15 and a width of about 100 μm. Precracking was done by putting a Knoop indentation (4 N load) at the notch root at both sides of the specimen. The compliance factor for the three-point bend test was calculated according to Brown and Srawley [17].

The longitudinal wave velocity, V_1, was measured

at 10 MHz using the pulse-echo technique. Due to a too large damping the transverse wave velocity, V_s, could not be measured. Therefore the Young's modulus, E, was calculated with the conventional formulae for isotropic materials using an estimated Poisson's ratio, v, of 0.275. Finally, the hardness, H_K, was determined using a Knoop indenter at 2 N load applied for 15 sec.

The thermal expansion coefficient, a, of the pure OH-Ap ceramics was determined from room temperature up to 600° C using a dual rod dilatometer. Sintered specimens of 95% relative density and a grain size of about 5 μm were used. The procedure to prepare this specimen was as described before [13].

3. Results and discussion

In this section first the results of the exploratory experiments are reported. Next the results of the more systematic experiments on OH-Ap ceramics with fibres H and F are discussed.

3.1. Exploratory experiments

The measurement of the thermal expansion coefficient of the pure OH-Ap ceramics yielded a strongly temperature dependent a-value. The thermal expansion coefficient can be represented by $a = (12.4 + 0.0103T) \times 10^{-6}$ K^{-1} where T is given in centigrades. The average value of a from room temperature to 550° C is 15.1 × 10^{-6} K^{-1}. This value is in approximate agreement with the value of 15.9 × 10^{-6} K^{-1} that can be calculated for the same temperature interval from the data as measured by X-ray diffraction [16]. The high value of the expansion coefficient is thus confirmed.

In spite of this high value of a, we nevertheless tried to incorporate Al_2O_3 fibres (with an a-value of about 8 × 10^{-6} K^{-1}) in an OH-Ap matrix. This was done since we expected for this combination very little or no reaction between the two components. This expectation turned out indeed to be true, but due to the unfavourable difference of a-values, the material showed a textbook case cracked matrix (Fig. 1). No further experiments were done with this combination.
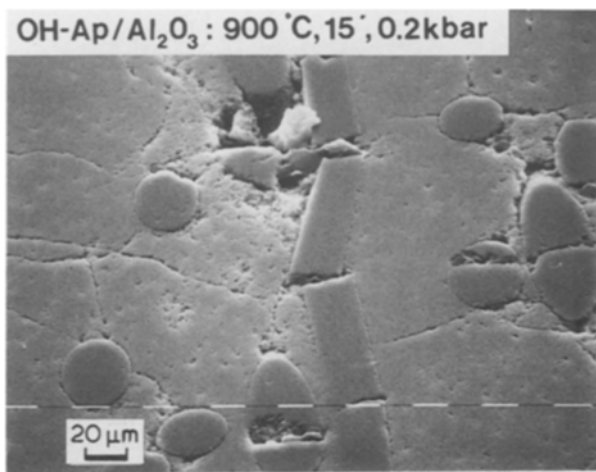
OH-Ap/Al₂O₃ : 900 °C, 15′, 0.2kbar

20 μm

Figure 1 SEM micrograph of a 10 vol % Al₂O₃ fibre containing OH-Ap composite. Note the extensive cracking of the matrix but no reaction layer at the fibre–matrix interface.

The next type of fibre material tried was titanium (with an a-value of about 8.5×10^{-6} K^{-1}). This metal has essentially the same problem as Al₂O₃, but is somewhat less brittle. In this case also the OH-Ap matrix was heavily cracked and no further experiments were done. Next we tried stainless steel fibres with the expectation that the ductility of this metal would be sufficient to avoid matrix cracking. Indeed this was true but there appeared to be an extensive reaction between the metal and the matrix even when hot-pressed in N₂. Inconel 601 fibres reacted somewhat less dramatically than the stainless steel fibres, but still were considered too reactive. From these experiments it became clear that we needed some ductility but also a limited reaction between the components at the hot-pressing temperature. Furthermore, the fibres should be available in sufficiently large quantities. The number of metal fibres fulfilling these requirements is limited. We have chosen here the Hastelloy X and FeCralloy fibres denoted by H and F, respectively. Finally, it should be noted that examination of micrographs of the composites indicated no or only very little preferential orientation of the fibres.

3.2. Experiments with Hastelloy X and FeCralloy fibres

The hot-pressing conditions and resulting densities of the materials produced with the H and F fibres are listed in Table I. Micrographs of two typical materials are shown in Figs 2 and 3. From these micrographs it is clear that the H fibres show a reaction layer of about 5 μm thickness while the F fibres show a reaction layer of about 2 μm thickness. For the H fibre composite, energy dispersive analysis of X-rays (EDAX) showed that the reaction layer between OH-Ap and the Hastelloy X was enriched with chromium as compared with the fibres. In Table II the properties of the various materials are listed. For comparison the properties of pure OH-Ap ceramics [12, 13] are given as well. For both materials the fracture toughness increases rapidly using 10 or 20 vol % fibres, but only slightly when increasing the volume fraction fibres to 30%. Young's modulus, E, also increases because the E-value of the metal is higher than that of the OH-Ap matrix. For the nearly fully dense F fibre composites the rule of mixtures is obeyed well. The Knoop hardness, on the other hand, decreases because the hardness of the metals is lower than that of the matrix. For this parameter the rule of mixtures is not obeyed at all.

The strength was measured only for the F fibre composite. The strength of the F fibre composites increases also upon increasing the volume fraction fibres, but not as rapidly as the K_{Ic}. This indicates that the critical flaw size has increased considerably from the value for the pure OH-Ap ceramics. An estimate of the defect size, a_c, can be made by applying the fracture mechanics formula

$$K_{Ic} = Y S_f a_c^{1/2} \tag{1}$$

Using the experimental value for K_{Ic} and S_f, together with $Y = 1.26$, the appropriate value for semicircular surface defects [18], yields for the pure OH-Ap ceramics an a_c-value of about 60 μm while for the composites an a_c-value of about 600 μm results. This estimate shows that the processing procedure can be improved considerably.

OH-Ap/20 vol % Hastelloy X

50 μm

(a)

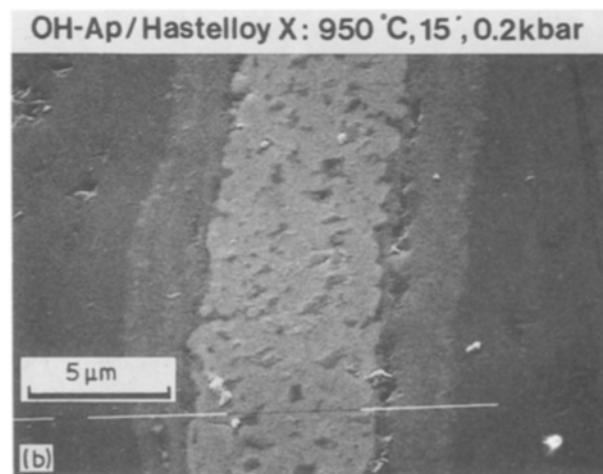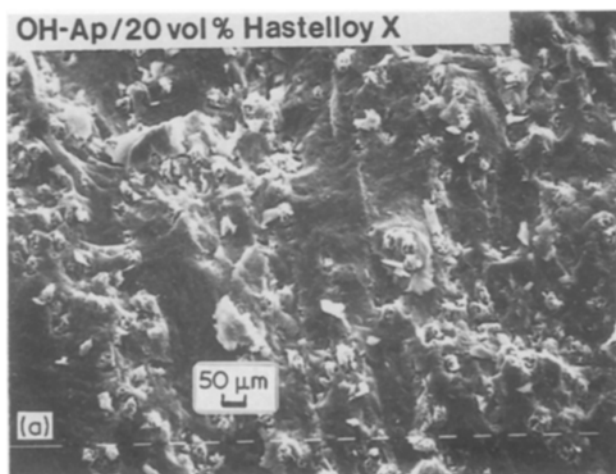

OH-Ap/Hastelloy X: 950 °C, 15′, 0.2kbar

5 μm

(b)

Figure 2 SEM micrographs of a 20 vol % Hastelloy X fibre containing OH-Ap composite. (a) fracture surface showing very limited pull-out. (b) polished surface showing a reaction layer of about 5 μm thickness between the fibres and the matrix.
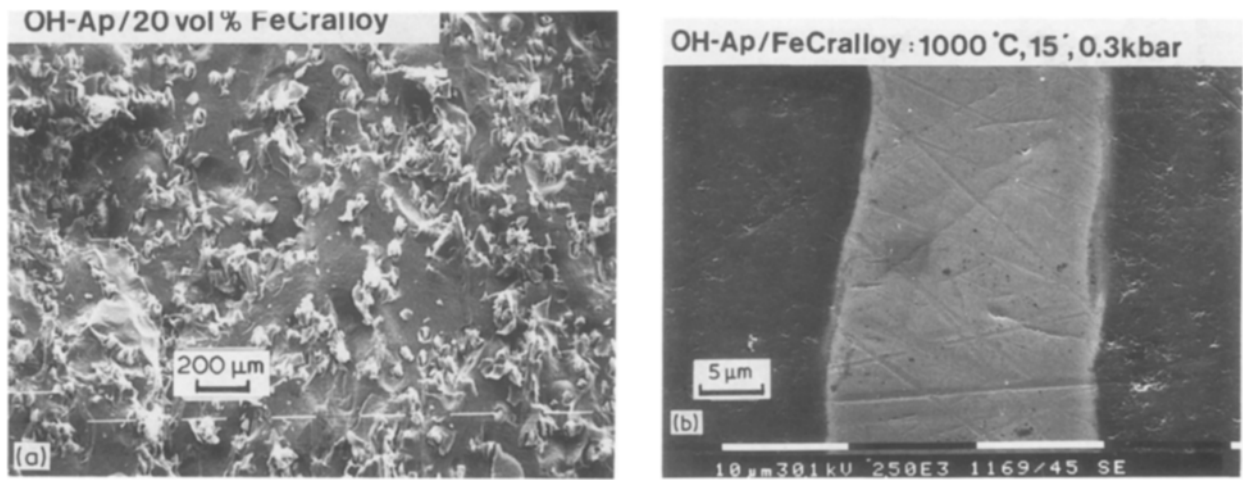
Figure 3 SEM micrograph of a 20 vol % FeCralloy fibre containing OH-Ap composite. (a) Fracture surface showing limited pull-out. (b) Polished surface showing a reaction layer of about 2 μm thickness between the matrix and the fibres.

Contrary to the F fibre composites, for H fibre composites the toughness specimens did not split into two halves after testing but remained connected. Examination of the fracture surfaces (Figs 2a and 3a), however, revealed very limited pull-out of the fibres in both cases. Because no fibre pull-out whatsoever is observed, a contribution of this mechanism to the fracture energy can be neglected. A simple first estimate of the fracture energy is then provided by the rule of mixtures

$$J_c = (1 - V_f)J_m + V_f J_f \qquad (2)$$

where $J_c(J_m, J_f)$ is the fracture energy of the composite (matrix, fibre) and V_f the volume fraction of the fibres. The fracture energies for the metals involved are typically about $2000 \, J \, m^{-2}$. The exact value is dependent on microstructure and heat treatment. Attempts to measure the fracture energy of the metals were not done. For the Hastelloy X and FeCralloy a Knoop hardness (2 N load, 15 sec) of 2.0 and 2.1 GPa respectively was measured corresponding to yield strength of

about 0.7 GPa. This implies a considerable specimen size necessary for proper toughness testing. We take for both metals a value for J_f of about $600 \, J \, m^{-2}$. The value for J_f is low as compared with order of magnitude quoted but such a low value can be expected in view of the unfavourable heat treatment for the metals due to the hot-pressing procedure. The value for J_m is taken $11 \, J \, m^{-2}$, the value appropriate for hot-pressed OH-Ap ceramics (Table II). Using these values together with the experimental values of the Young's moduli results in the estimates for $K_{Ic} = (2J_c E)^{1/2}$ as given in Table II. Comparing the experimental and calculated values it is obvious that the trend and order of magnitude are correctly predicted.

Finally, during processing it was noticed that the powder compacts repressed at 4 k bar showed considerable strength, stiffness and toughness. Therefore the Young's modulus, strength and fracture toughness were measured (Table II). This table shows that the value of these parameters is already a considerable fraction of those of the hot-pressed materials.

TABLE II Properties of the Hastelloy and FeCralloy composites

Material	vol %	q (%)	E (GPa)	H_K (GPa)	K_{Ic} (MPa m$^{1/2}$) exp	calc	S_f (MPa)
OH-Ap	0	93	77	4.4	1.3	–	77
OH-Ap	0	97	117	5.4	1.0	–	115*
H-p	10	60	11.6	–	1.6	–	34
H-p	20	60	14.5	–	2.6	–	57
H	10	95.6	120	4.5	4.3	4.2	–
H	20	93.8	107	4.5	6.0	5.3	–
H	30	100	141	4.2	6.1	7.4	–
F-p	10	60	14.1	–	1.8	–	35
F-p	20	60	18.2	–	2.6	–	35
F	10	99.7	126	3.9	3.7	4.3	96
F	20	99.2	135	3.4	7.0	6.0	175
F	30	99.8	142	3.4	7.4	7.4	224

OH-Ap: Pure OH-Ap ceramic
H-p: Hastelloy X containing powder compact
H: Hastelloy X containing hot-pressed composite
F-p: FeCralloy containing powder compact
F: FeCralloy containing hot-pressed composite
q: relative density.
*Data taken from [13] apart from the hardness which was measured by Knoop indentation (2 N load, 15 sec).

4. Final remarks

In this paper it has been shown that the fracture toughness and strength of OH-Ap ceramic matrix materials can be improved by a factor of 6 and 2, respectively, by introducing 20 to 30 vol % metal fibre in the ceramic matrix. Although this is a considerable improvement, the strength can be improved further since the critical defect size has increased as compared with the pure OH-Ap ceramics. It can be expected that other properties like thermal conductivity and fatigue strength are improved as well. It seems also likely that similar improvements in mechanical properties can be realized in other metal fibre–ceramics matrix composites. Low or preferably no reactivity at all, between the ceramic and the metal are a prerequisite, however.

Acknowledgement

References

1. K. DE GROOT, in "Biocompatibility of Clinical Implant Materials", Vol. 1, edited by D. F. Williams, (CRC Press, Boca Raton, 1981) p. 199.
2. *Idem*, in "Ceramics in Surgery", edited by P. Vincenzini, (Elsevier, Amsterdam, 1983) p. 79.
3. M. JARCHO, R. L. SALSBURY, M. B. THOMAS and R. H. DOREMUS, *J. Mater. Sci.* **14** (1979) 142.
4. M. AKAO, H. AOKI, K. KATO and A. SATO, *ibid.* **17** (1982) 343.
5. M. JARCHO, C. H. BOLEN, M. B. THOMAS, J. BOBICK, J. F. KAY and R. H. DOREMUS, *ibid.* **11** (1976) 2027.
6. R. H. DOREMUS, M. B. THOMAS, I. YASUI and M. JARCHO, in "Ceramic Microstructures 76", edited by R. M. Fulrath and J. A. Pask, (Westview Press, Boulder, Colorado, 1977) p. 379.
7. T. KIJIMA and M. TSUTSUMI, *J. Amer. Ceram. Soc.* **62** (1979) 455.
8. J. G. J. PEELEN, B. V. REJDA and K. DE GROOT, *Ceramurgia Int.* **4** (1978) 71.
9. M. B. THOMAS, R. H. DOREMUS, M. JARCH and R. L. SALSBURY, *J. Mater. Sci.* **15** (1980) 891.
10. M. B. THOMAS and R. H. DOREMUS, *Bull. Amer. Ceram. Sci.* **60** (1981) 258.
11. M. AKAO, H. AOKI and K. KATO, *J. Mater. Sci.* **16** (1981) 809.
12. G. DE WITH, H. J. A. VAN DIJK and N. HATTU, *Proc. Brit. Ceram. Soc.* **31** (1981) 181.
13. G. DE WITH, H. J. A. VAN DIJK, N. HATTU and K. PRIJS, *J. Mater. Sci.* **16** (1981) 1592.
14. M. AKAO, N. MIURA and H. AOKI, *Yogyo-Kyokai-shi* **92** (1984) 78.
15. H. J. A. VAN DIJK and G. DE WITH, unpublished work, 1981.
16. G. R. FISCHER, P. BARDHAN and J. E. GEIGER, *J. Mater. Sci. Lett.* **2** (1983) 577.
17. W. F. BROWN and J. E. SRAWLEY, (ASTM-STP-410, ASTM, Philadelphia, 1966).
18. G. K. BANSAL, *J. Amer. Ceram. Soc.* **59** (1976) 87.