JOURNAL OF MATERIALS SCIENCE: MATERIALS IN MEDICINE 9 (1998) 589–596

Interdiffusion in short-fibre reinforced hydroxyapatite ceramics

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Sintering in air and hot isostatic pressing are production methods regarded as being capable of producing fibre-reinforced hydroxyapatite ceramics for biomedical applications. These composites may have the advantage of improved mechanical properties and be suitable for applications in areas where there are significant levels of load on the material. The use of pure hydroxyapatite is restricted to those free of dynamical load. Obtaining improved mechanical strength is a question of the bond between the matrix phase and the fibre-reinforcement phase. However, a chemical bond between both phases, indicated by large diffusion zones, might lead to the dehydration of the hydroxyapatite leading to undesired tricalcium phosphate in the matrix resulting in a weakening of the mechanical and biological stability of the composites. Composites with three fibre types, alumina, 316L-stainless steel and titanium were prepared and sintered in air or hot isostatically pressed. A reaction zone was noted around the titanium and stainless steel fibres, but not around the alumina fibres. The reaction zone was larger for stainless steel than titanium. Hot isostatic pressing also reduced the reaction zone markedly compared to sintering in air.

1. Introduction

Hydroxyapatite (HAp) is the main mineral component of natural bone. The well-known bioactivity of HAp leads to a high bone ingrowth capability which gives HAp the potential of being one of the most desired bone-replacement materials. At present, applications for synthetic HAp are restricted to areas free of dynamic load bearing, because synthetic HAp is known for its weakness and brittleness, revealed by its low fracture toughness value of 1.1–1.2 $MN\,m^{-3/2}$ [1]. The only exception where HAp is applied in dynamically loaded situations is the use of HAp as a coating material [2–6].

The use of solid HAp requires a suitable method of material toughening. A common method of improving the fracture toughness of ceramic materials is toughening the ceramic matrix by the addition of short fibres as a second phase (Fig. 1). Manufacturing techniques such as sintering or hot isostatic pressing (HIP) seem to be suitable for processing reinforced HAp ceramics. The results of preliminary studies showed that HIP fibre-reinforced HAp allows the fracture toughness to be improved up to a range comparable to that of bone (K_{IC} = 2–12 $MN\,m^{-3/2}$ [7]). For 316L fibre-reinforced HAp ceramics of 96% density, fracture toughness values of K_{IC} = 11 $MN\,m^{-3/2}$ could be observed [8].

However, in applying these high-temperature/high-pressure processes, the sensitivity of the materials to thermal treatment has also to be taken into account. High temperatures, in conjunction with impurities, accelerate the formation of tricalcium phosphate and tetracalcium phosphate [9]. This chemical reaction is of a non-reversible nature. Impurities may even decrease the temperature at which the process begins. This fact is of interest, as fibres have to be regarded as desired impurities. Fig. 2 illustrates the decomposition behaviour of hydroxyapatite.

The chemical reaction may take place within the HAp matrix itself, and also in the vicinity of the fibres embedded in the matrix phase (Fig. 3). Even though a chemical reaction in the matrix–fibre interface would possibly enhance the interfacial bond mechanically, the formation of phases different from HAp would be supported. Thus the biocompatibility of the materials could be jeopardized.

The structural properties of the fibre-reinforced HAp are affected by the complete manufacturing process. So each manufacturing stage (powder production, greed-body production, sintering) is crucially important for the performance of the material.

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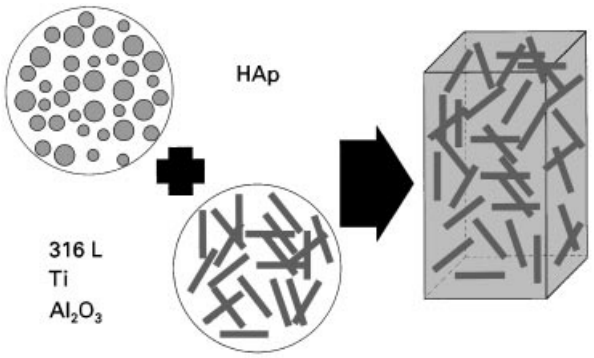


Figure 1 Hydroxyapatite composites: components.

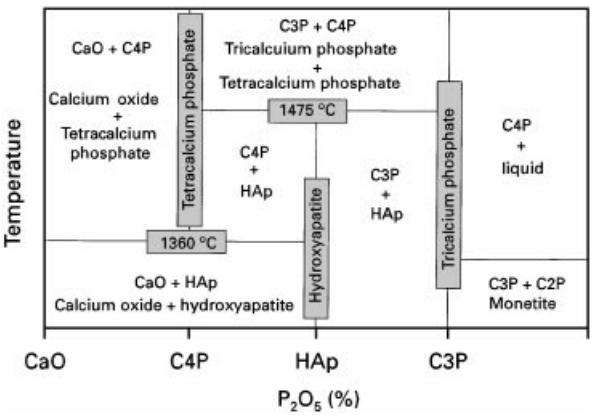


Figure 2 Phase equilibrium diagram of different calcium phosphates.

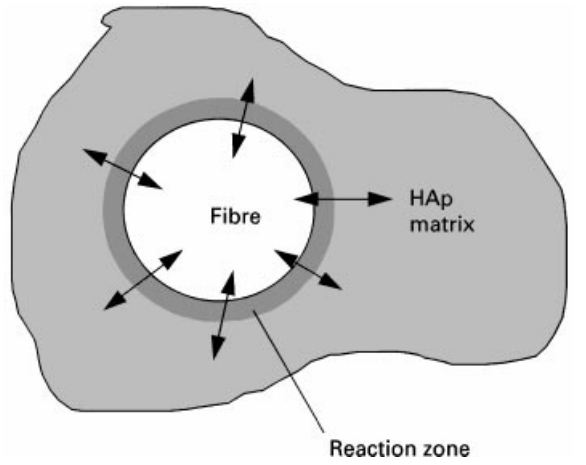


Figure 3 The reaction zone (interdiffusion) between fibre and matrix.

2. Materials and methods

The matrix phase of the composites to be created was formed by a commercially available hydroxyapatite powder, type Merck 2196 (Merck AG, Darmstadt/Germany). The particle size was in the range 2–20 μm.

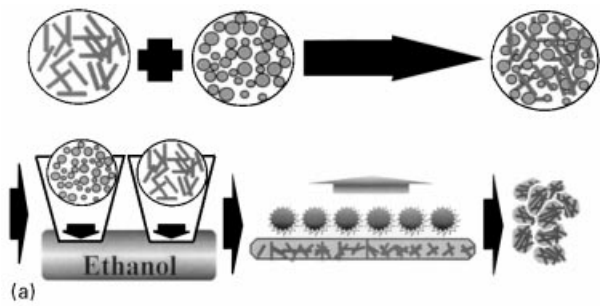
Two types of reinforcement fibres were used. Metallic fibres, 316L-stainless steel fibres (Knight Precision Wires, UK) and titanium fibres (Bekaert Fibre Technologies, Belgium) both of 50 μm diameter and 0.7–1.3 mm length and ceramic fibres, alumina fibres (Mitsuya Boeki, Japan) of 10 μm diameter and 0.3–0.5 mm length, were used (Fig. 2).

All fibre materials selected for the reinforcement phase have a proven record as biomaterials. Among the ceramics used in orthopaedics and orthodontics, alumina is the most chemically inactive. After its early evaluation, alumina was soon regarded as the prototype of so-called bioinert materials [10]. The outstanding biocompatibility of titanium and titanium alloys was recognized by early medical researchers, and pure titanium and TiAlV 64 alloy have become most widely used. The clinical success of titanium alloys is due to their outstanding mechanical properties, corrosion resistance and superior biocompatibility [11]. Iron-based alloys currently form one of the predominant groups of metallic materials for biomedical applications. For implantation in the case of multicomponent weight-bearing situations, type 316L stainless steel ($Fe_{33}Cr_8Ni_6Mo$), an austenitic alloy combining extremely high corrosion resistance with high mechanical strength, is most frequently selected [12].

2.1. Materials processing

Composite powders of a volumetric matrix/fibre ratio of 90:10 and 80:20 for HAp–316L, HAp–Al_2O_3 and HAp–Ti composites were prepared. HAp powder was also prepared without the addition of fibres as standard material.

In order to manufacture a solid composite material characterized by an optimal fibre dispersion in the matrix, a dispersion method which avoids fibre clumping and allows dispersion throughout the matrix material was applied [13]. Different composite powders consisting of HAp/fibre mixtures were manufactured. Fig. 4a illustrates the principle of the manufacturing



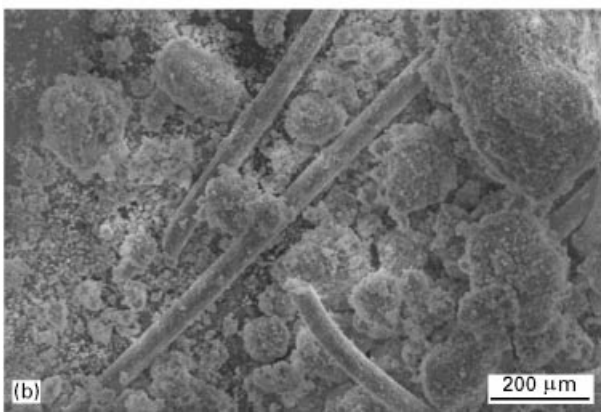


Figure 4(a) The principles of powder production, and (b) the hydroxyapatite/316L 80/20 powder.

process and Fig. 4b shows the composite powder HAp/316L 80/20 ready for further processing.

Green bodies of the composite material were produced by uniaxial pressing, followed by cold isostatic pressing. Green-body pellets were manufactured according to the procedure described earlier by the authors [8]. The green bodies were either treated by sintering in air (Sinter) or hot isostatic pressing (HIP). Fig. 5 illustrates the main features of both processes, sintering and hot isostatic pressing. Sintering was performed in a graphite furnace. Heating and cooling rates were 150 °C h^{-1}, soaking time was 1 h in an air atmosphere and at atmospheric pressure. The soak temperature was 1000 °C.

To achieve a maximum density the pellets were hot isostatically pressed either encapsulated in steel or alternatively in pyrex glass. HIP temperatures were

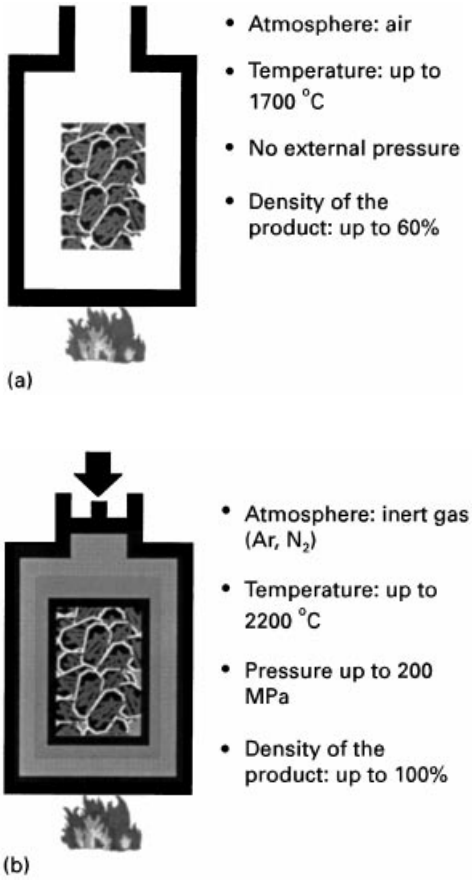


Figure 5 The principles of (a) sintering in air, and (b) hot isostatic pressing.

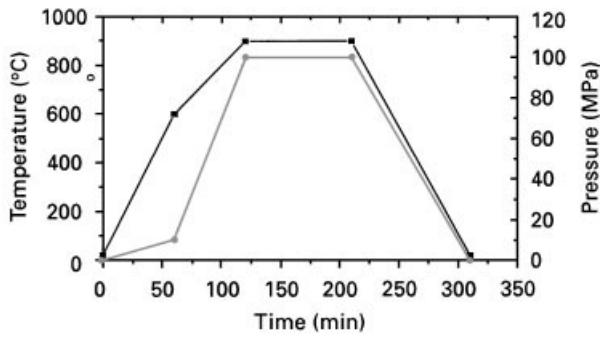


Figure 6 Pressure–time–temperature diagram of the HIP process. (■) Temperature, (●) pressure.

900 and 1000 °C applying a gas pressure of 100 MPa. Fig. 6 shows the pressure–time diagram of the applied HIP process.

2.2. Microstructural investigations and decomposing behaviour

For the microstructural analyses of the interfaces, matrix/fibre segments of each cycle were embedded in epoxy under vacuum. After hardening, the samples were prepared by grinding and polishing. SEM investigations using a Cambridge S360 (Cambridge Instruments, UK) scanning electron microscope were conducted to evaluate the microstructure of the composite bodies.

During the SEM investigations elemental analysis was performed by energy dispersive spectroscopy (EDS) in conjunction with the SEM. Particular attention was paid to reactions in the matrix/fibre interface as microdiffusion. After a suitable discrete fibre was located, a photograph was taken and points were chosen at 0.5 μm intervals to analyse the content of the chemical elements present.

3. Results and discussion

3.1. Microstructure of the composites

The conducted SEM studies reveal that the density of the green bodies is highly dependent on the sintering method applied. Fig. 7 compares micrographs of cross-sections of hydroxyapatite/stainless steel 80/20 after three production steps: as the green body (uniaxially pressed and cold isostatically pressed), processed by sintering, or processed by HIP. The sample processed by sintering shows high porosity (dark areas in between the matrix represent pores infiltrated by epoxy). Apparently the hydroxyapatite matrix is stabilized by the 316L-mesh, preventing the matrix from collapsing. In contrast, the sample produced by HIP shows a high density close to 100%.

Fig. 8 compares micrographs of cross-sections of hydroxyapatite/titanium 80/20 samples after the three processing steps. The morphology is similar to that of the HAp/316L samples. High density can be observed in the HIPed samples, whereas the sintered samples are, again, characterized by high porosity.

For both metallic fibre types ($d = 50$ μm, $l = 0.7$–1.3 mm) it appears that the density has decreased in the sintered body taking the untreated green body as baseline. However, density measurements indicated that the composite density actually increased. The fact that the degree of shrinkage within the matrix phase is higher than the shrinkage of the whole composite, leads to cross-sections suggesting exactly the opposite.

Fig. 9 compares micrographs of cross-sections of hydroxyapatite/alumina samples. Owing to the much smaller fibre types ($d = 10$ μm, $l = 0.3$–0.5 mm), the shrinkage after the processing steps seems to be more uniform. The morphology is relatively homogeneous compared to the metallic fibres, and is free of pores.

SEM microstructural investigation revealed that the microstructure of HAp–fibre composites depends

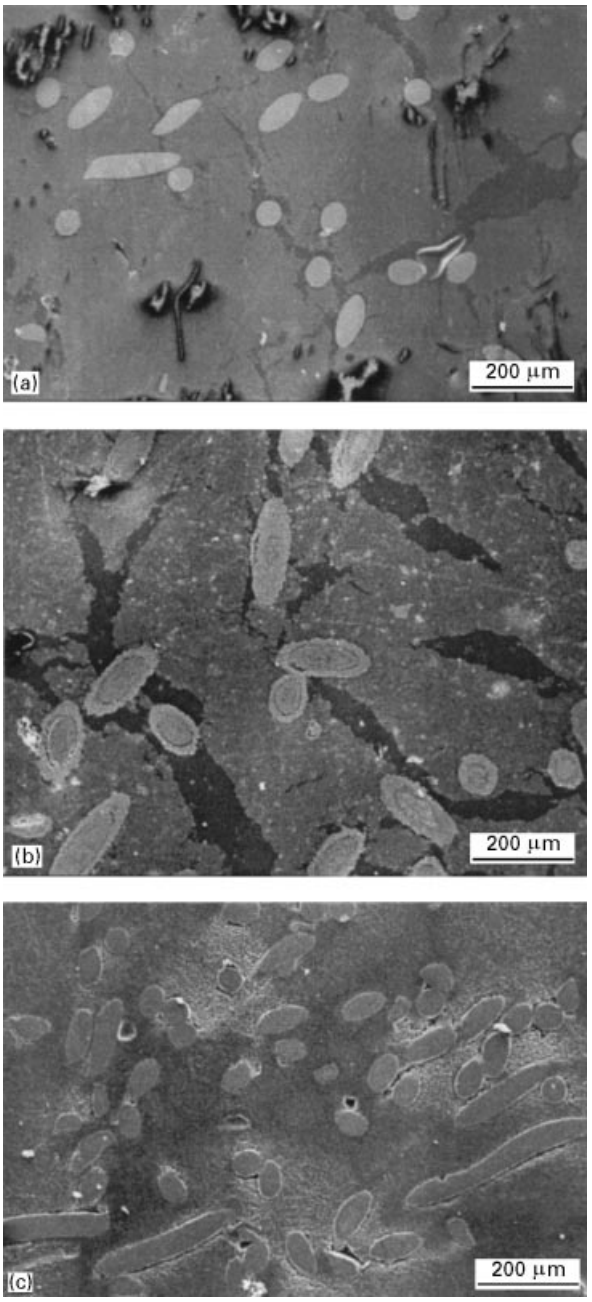


Figure 7 HAp/316L 80/20 in different stages: (a) green body, unprocessed; (b) sintered; (c) hot isostatically pressed.

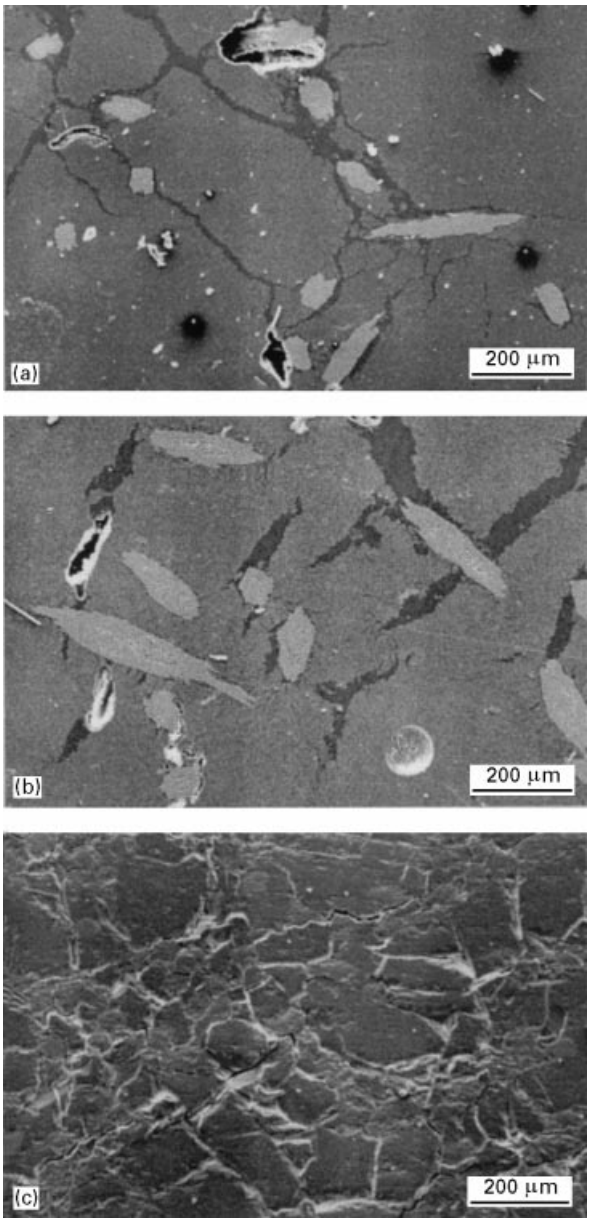


Figure 8 HAp/Ti 80/20 in different stages: (a) green body, unprocessed; (b) sintered; (c) hot isostatically pressed.

on the process. The highest density can be achieved by applying the HIP-technology. Sintering leads to composites of low density. However, uniform shrinkage and a homogeneous microstructure is less a question of the fibre material, than a question of the fibres' geometry. The smaller the fibres the more uniform is the material shrinkage and the closer to full density achievable by sintering in air.

3.2. Interdiffusion between matrix and fibre

3.2.1. HAp–316L System

Sintering in air of HAp–316L fibre-reinforced composites at 1000 °C leads to the formation of a diffusion zone surrounding the fibres. The vicinity of the fibres is characterized by elements originating from the fibres and nickel, chromium and iron could be detected by EDS. The diffusion zone is a ring 12.5 μm wide. The EDS analysis reveals that sintering in air at 1000 °C leads to a massive diffusion from the fibres to the matrix (Fig. 10). The diffusion zone seems to be coated around each fibre which even stays after pulling out of the fibres from the matrix, shown by the fracture surface in Fig. 11.

In contrast, the diffusion within the hot isostatically pressed samples of the HAp–316L system is very small. Elements from the matrix (calcium, phosphorus) appear to have diffused inside a narrow ring (2 μm) of each fibre. No elements diffusing from the fibre towards the matrix could be observed, as Fig. 12 illustrates.

3.2.2. HAp–Ti System

After sintering in air, a diffusion zone of about 5 μm thickness could be detected. The diffusion is a two-way diffusion. Elements from the matrix move

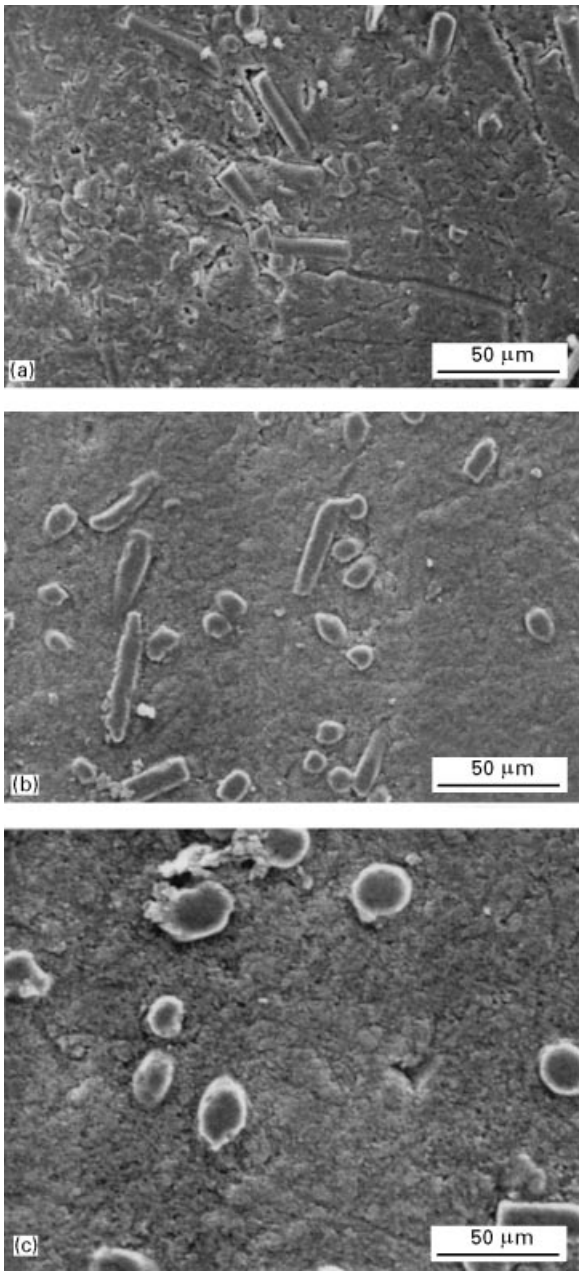


Figure 9 HAp/Al_2O_3 80/20 in different stages: (a) green body, unprocessed; (b) sintered; (c) hot isostatically pressed.

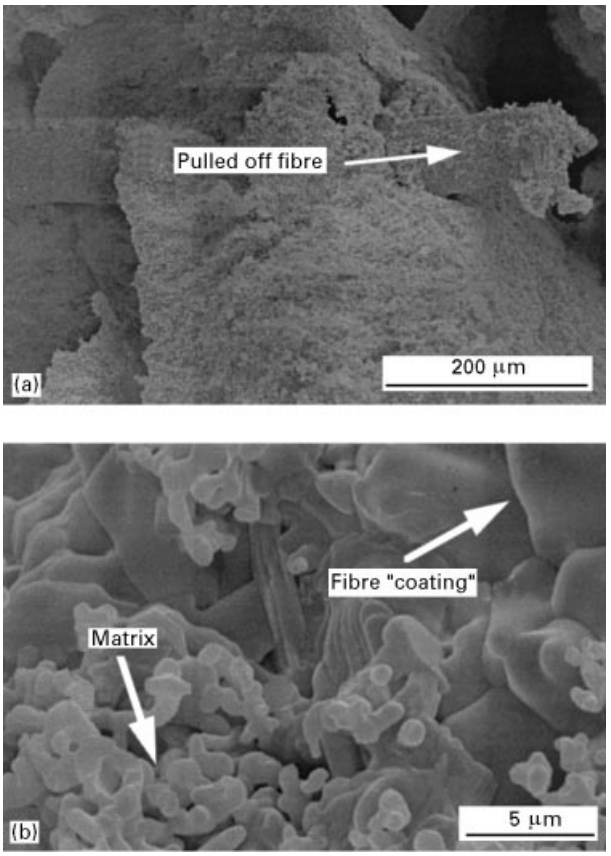
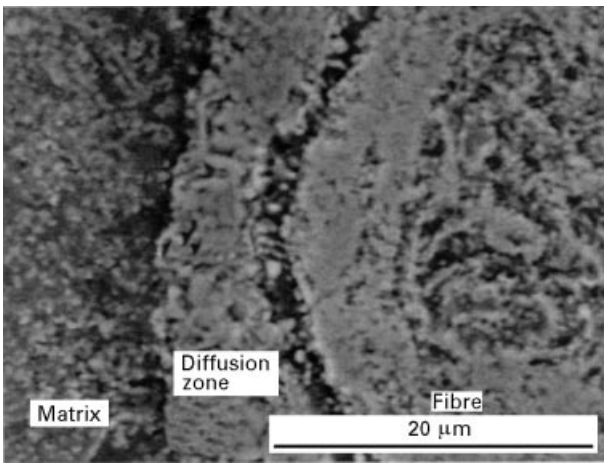


Figure 11 (a,b) The diffusion zone around the fibre.

towards the fibres and elements from the fibres move towards the matrix, which may indicate a likely formation of interfacial reaction products such as calcium–titanium phosphates (Fig. 13).

Hot isostatic pressing reduces the diffusion zone to 2 μm. Again it's a two-way diffusion, but it appears that most of the diffusion is going towards the fibres. EDS analysis indicates a diffusion zone of 1.5 μm towards the fibres, whereas the area of diffusion inside the matrix is only 0.5 μm wide (Fig. 14).



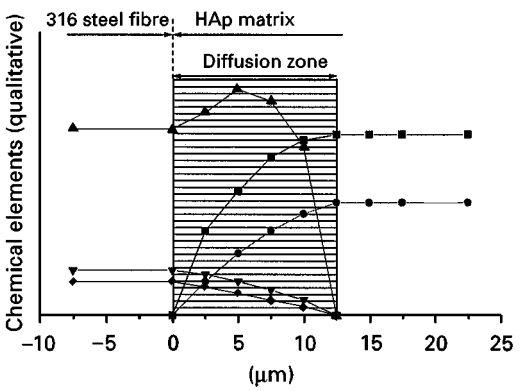
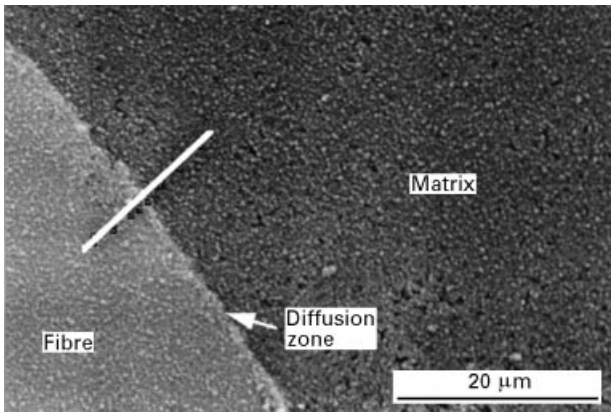
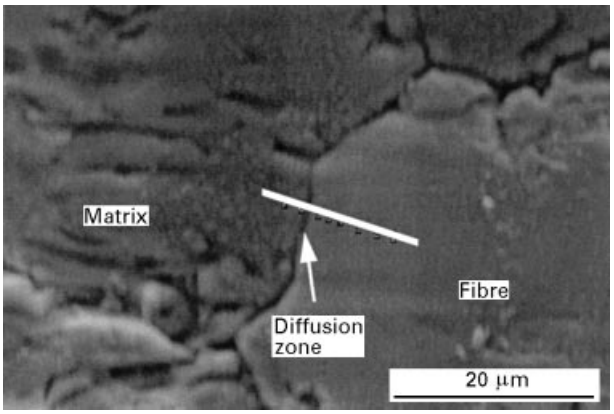


Figure 10 Interdiffusion in the HAp/316L system (sintered in air at 1000 °C). (■) Ca, (●) P, (▲) Fe, (▼) Cr, (◆) Ni.





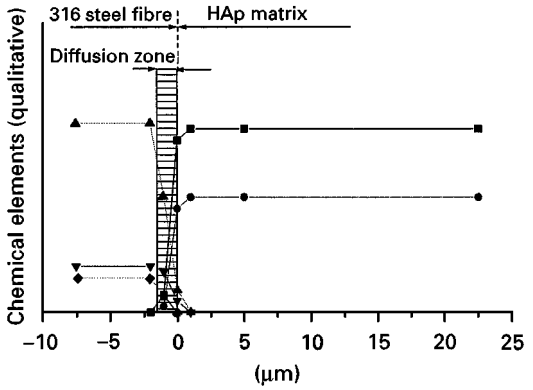


Figure 12 Interdiffusion in the HAp/316L system (hot isostatically pressed, 900 °C, 200 MPa). (■) Ca, (●) P, (▲) Fe, (▼) Cr, (◆) Ni.

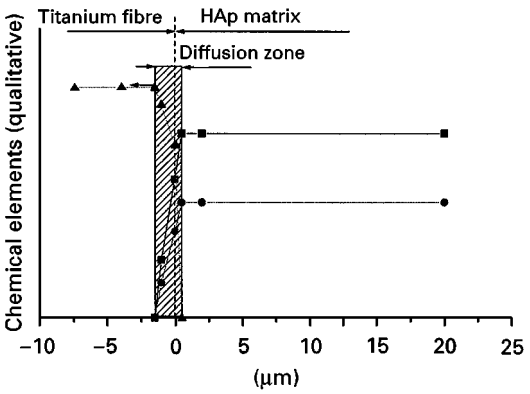
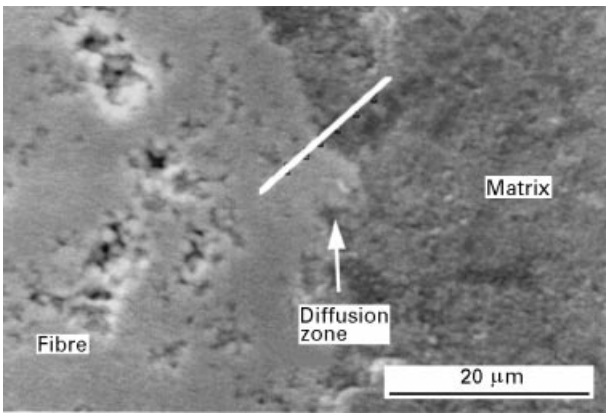
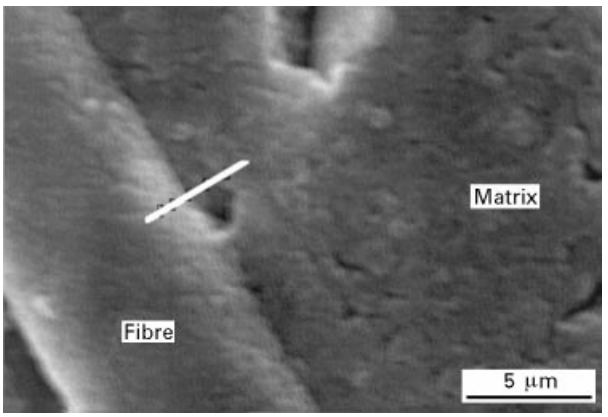


Figure 14 Interdiffusion in the HAp/Ti system (hot isostatically pressed). (■) Ca, (●) P, (▲) Ti.





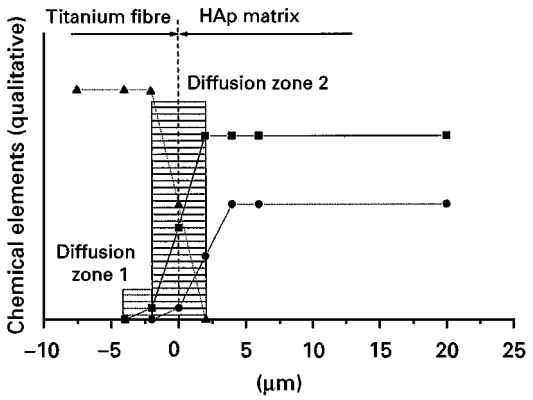


Figure 13 Interdiffusion in the the HAp/Ti system (sintered in air, 1000 °C). (■) Ca, (●) P, (▲) Ti.

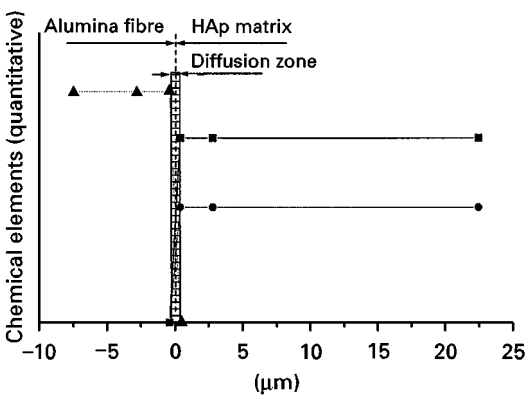


Figure 15 Interdiffusion in the HAp/Al_2O_3 system (sintered in air, 1000 °C). (■) Ca, (●) P, (▲) Al.

3.2.3. HAp–Al_2O_3 System

The HAp–Al_2O_3 system is characterized by the strong chemical stability and inertness of alumina. Neither sintering in air nor hot isostatic pressing leads to the formation of diffusion zones. High-resolution EDS analysis reveals that, if it exists at all, the diffusion zone is likely to be less than 1 μm wide, (Figs 15 and 16).

Fig. 17 summarizes the results of the EDS analysis of all three systems. It compares the different diffusion behaviour of the systems while being sintered in air (1000 °C) or hot isostatically pressed (1000 °C, 100 MPa, argon-atmosphere). Regardless the sintering process applied, it becomes obvious that the interfacial reactions leading to the formation of diffusion zones increases in the order

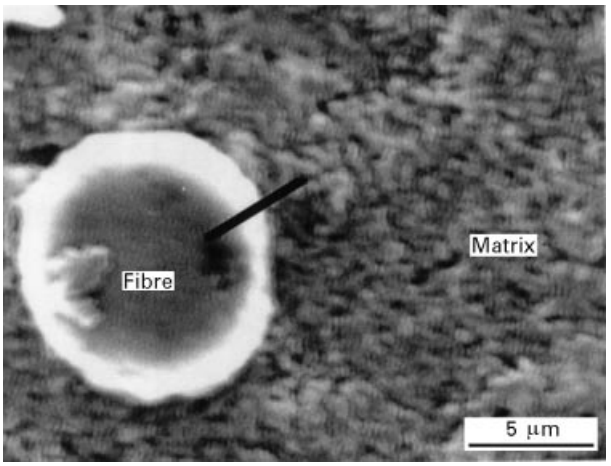
$$\text{diffusion(HAP/Al}_2\text{O}_3\text{)} < \text{diffusion(HAp/Ti)} < \text{diffusion(HAp/316L)}$$

However, the formation of the diffusion zone can be suppressed by applying a process combining high pressure and high temperatures as HIP.

4. Conclusion

Composite materials containing hydroxyapatite as matrix phase and 20 wt % fibres of alumina, 316L-stainless steel or titanium as reinforcement phase, were processed by two different methods: sintering in air, and HIP.

The density of the fibre composites can be varied by choosing a suitable ceramic process and suitable fibre geometry. More importantly, employing the appropriate sintering technology enables the composite to be



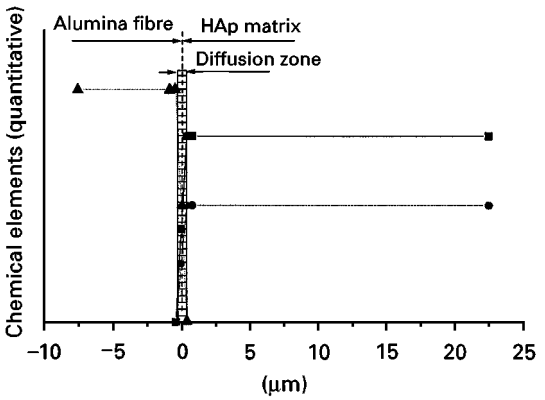


Figure 16 Interdiffusion in the HAp/Al_2O_3 system (hot isostatically pressed, 1000 °C). (■) Ca, (●) P, (▲) Al.

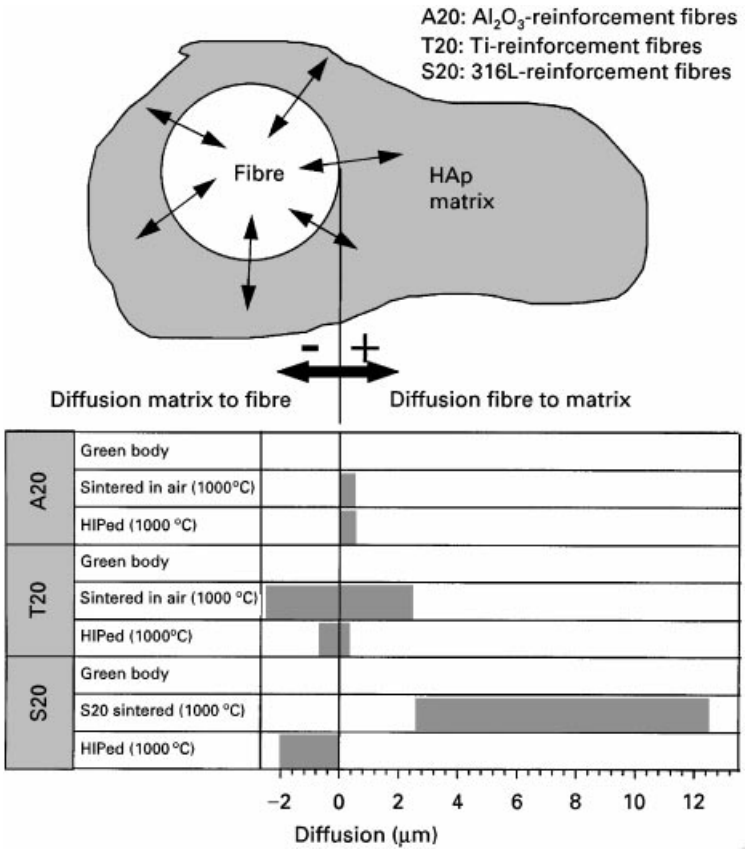


Figure 17 Interdiffusion in the different HA-reinforced composites.

formed with controlled interdiffusion. The nature of the type of reinforcement fibre in combination with the sintering method strongly determines the tendency to form diffusion zones. To achieve a strong matrix–fibre bond, interdiffusion may be desired. However, the influence of the interfacial reactions on the formation of calcium phosphates different from HAp [14] has to be taken into account, and thus it might be an advantage to control the diffusion process.

These studies demonstrate that a metal–fibre reinforcement of HAp is possible in order to achieve a product with desired properties.

Acknowledgements

This work has been supported by the German Research Foundation. The authors thank E. Merck AG, Darmstadt/Germany, for the supply of hydroxyapatite powder, and Bekaert Fibre Technologies BV, Zweregem, Belgium, for the supply of titanium fibres. The invaluable contributions of Mr D. Koch, Materials Science Institute Aachen/Germany, and Mr Roger Müller-Courté, regarding the preparation of the samples, and of Mr Christian Ragoss, regarding the green body production, is gratefully acknowledged.

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Received 24 February
and accepted 25 September 1997