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Phase stability aspects of various apatite-aluminium oxide composites

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For aluminium oxide-hydroxyapatite composites sintered in air, decomposition of hydroxyapatite to tricalcium phosphate was initiated at temperatures below 1000°C and completed at 1200°C. Composites of aluminium oxide and various apatites (hydroxyapatite, fluorapatite and chlorapatite) as well as the pure materials were hot isostatically pressed at 1200°C for 1 h at a pressure of 160 MPa. Due to the closed system used, the thermal stability was improved and no phase changes were detected in the hot isostatically pressed aluminium oxide-apatite composites. These materials were crushed and thereafter heat-treated in air at several temperatures in order to study the phase stability. In the fluorapatite and chlorapatite based composites, the apatite reacted with the moisture in the air and partly converted to oxyhydroxyapatite and decomposition of the latter phase was initiated. The phase composition in the materials was evaluated by X-ray powder diffraction and the microstructure of the hot isostatically pressed samples was studied in a scanning electron microscope. © *2000 Kluwer Academic Publishers*

1. Introduction

The use of hydroxyapatite (OHAp) as an implant material is restricted to applications where the implant is exposed to low stresses [1, 2]. Thus, efforts have been made to improve the mechanical properties of apatite in biomaterials by OHAp coating or by making an OHAp-oxide composites. To optimise the performance of OHAp containing composite materials, different material compositions can be used in order to achieve the required strength and bioactivity. The reinforcing phase used in combination with OHAp in these composites is usually a high strength ceramic material. One possible candidate for such an additive in bioactive composites is aluminium oxide, an inert high strength ceramic oxide which has been used as an implant material for many years [3].

Preparation and evaluation of the mechanical properties of aluminium oxide and OHAp composites have been discussed in several publications [4–13]. In some cases, the temperature used in the sintering process has been as high as 1400°C [4, 5] and as a consequence, an almost complete decomposition of the OHAp to tricalcium phosphate occurred. When other sintering techniques, such as hot-pressing [6, 7] or hot isostatic pressing [9, 10] are used, it is possible to lower the sintering temperature needed for densification of the composites. However, independent of the sintering technique used, none of the previous studies [4–13] of aluminium oxide-OHAp composites with a fine grained microstructure displayed a sintered compact without formation of tricalcium phosphate when sintered above 1000°C. This indicates that the major problem in this system is to produce composite materials without any decomposition of the OHAp phase.

The problem with decomposition of the OHAp in composites containing an oxide may, however, not be solved simply by reducing the sintering temperature since the decomposition initiates even below 1000°C [13]. If dense aluminium oxide-OHAp composites are to be produced sintering temperatures exceeding the onset temperature of the decomposition of OHAp are needed implying that various efforts to increase the decomposition temperature must be considered. Since it has been shown that the OHAp phase can be preserved up to around 1400°C [14, 15], it would most likely be possible to increase the decomposition onset temperature in the presence of aluminium oxide if the parameters controlling the decomposition are taken into account.

An earlier study has shown that the reaction between aluminium oxide and OHAp can be divided into a two-step reaction mechanism [13]. In the first step, some water is released from the OHAp structure and an oxyhydroxyapatite is formed. Simultaneous with the water release vacancies is formed in the apatite network. When a specific fraction of vacancies is reached in the oxyhydroxyapatite, the second reaction step that involves decomposition of oxyhydroxyapatite to tricalcium phosphate occurs. If the fraction of vacancies formed in the OHAp structure can be controlled and kept below what is required for the decomposition reaction to occur, it may be possible to increase the sintering temperature without accompanying decomposition of the OHAp. One solution would be to sinter the composite under an enhanced partial pressure of water or to use a closed sintering system, thus preventing the apatite phase to decompose. Another way to reduce the fraction of vacancies and thus also the amount of O^{2-} ions might be to use an apatite containing an anion that is not released from the structure at elevated temperatures. Apatites which fulfil these requirements and also are accepted as biomaterials are fluorapatite (FAp) and chlorapatite (ClAp).

The aim of this work has been to investigate the possibility of avoiding decomposition of different apatites in composites containing aluminium oxide when a closed sintering process is used.

2. Experimental

FAp and ClAp were produced by a solid-state reaction between mixed powders of tricalcium phosphate (Merck), CaF_2 (Acros) and $CaCl_2$-$2H_2O$ (Merck), respectively. For the reaction to take place the powder mixtures were heated for 6h at 1000°C. The OHAp powder (Merck) used was of commercial quality. Composite powders consisting of 40 vol% aluminium oxide (AKP 30, Sumitomo) and 60 vol% of OHAp, FAp and ClAp respectively were produced by ball milling. The powder mixtures were calcinated at 500°C for 2 h and then cold isostatically pressed (CIP) at 300 MPa. The green bodies were coated with boron nitride powder, sealed in steel tubes and thereafter hot isostatically pressed (HIP) at 1200°C and 160 MPa for 1 h. After the HIP procedure, crushed HIPed composites were heat-treated at various temperatures up to 1250°C for one hour in air. Composite powders of aluminium oxide- OHAp were also sintered in air at temperatures up to 1200°C for 2 h. The phases present in the sintered compacts, HIPed materials and heat-treated powders were characterised by their X-ray powder diffraction (XRD) patterns obtained with a Guinnier-Hägg camera using Cu $K_{\alpha 1}$ radiation and Si as an internal standard. The obtained photograms were evaluated by means of the SCANPI system [16] and the unit cell parameters were determined with the PIRUM computer software [17] using the least square method. The standard deviations of the obtained cell parameters were always below 0.002 Å. The microstructure of polished samples was studied in a scanning electron microscope (SEM) and the weight losses upon heating of the pure apatites and composites were studied in a thermogravimetric (TG) unit (Setaram TAG24) using a heating rate of 3 degrees per minute. The measurements were made in argon and covered the temperature range from room temperature to 1500°C. The density of the composites was measured by the Archimedian method.

3. Results and discussion

The HIPed aluminium oxide-apatite composites reached densities above 96% of the theoretical values and the microstructure given in Fig. 1 indicates a homogeneous dispersion of the two phases. The porosity consisted of small pores which were well distributed throughout the compact.

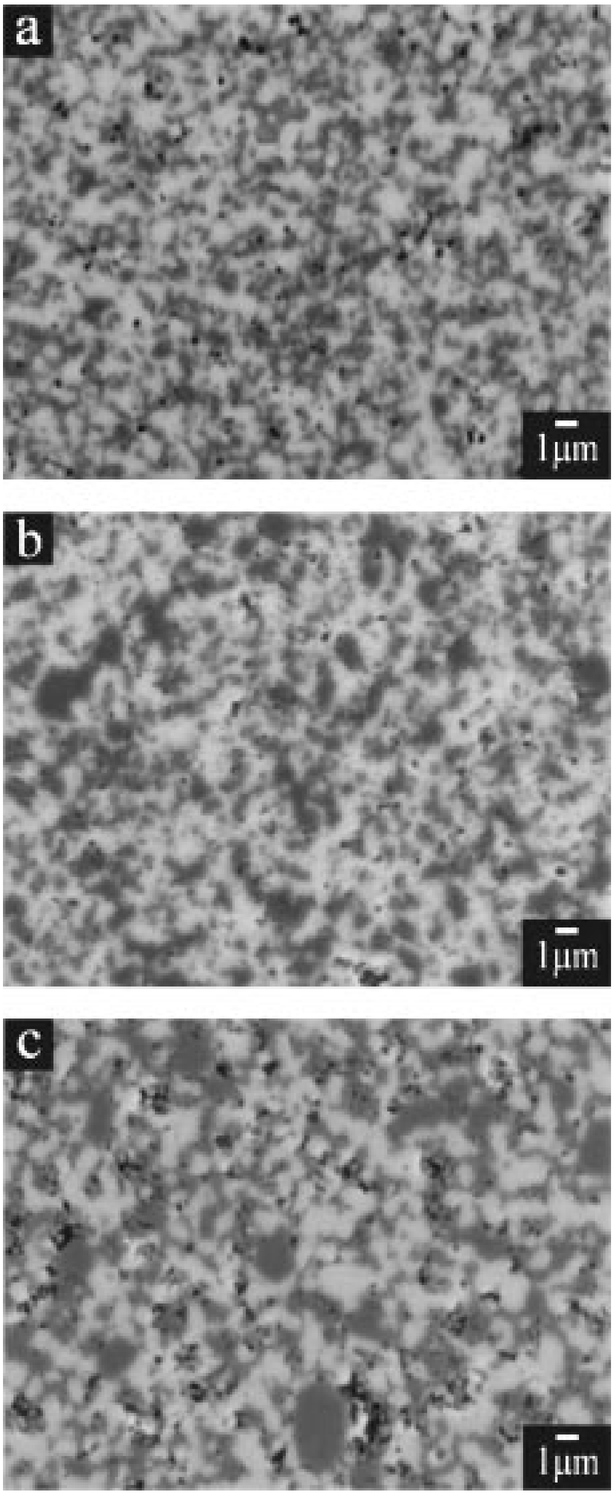

Figure 1 Microstructures in HIPed composites of (a) aluminium oxide-FAp, (b) aluminium oxide-OHAp, (c) aluminium oxide-ClAp.

3.1. Aluminium oxide-OHAp

When the aluminium oxide-OHAp composite powder is sintered in an open system, the accompanying loss of water from OHAp creates vacancies in the apatite structure and an oxyhydroxyapatite phase is formed. This oxyhydroxyapatite is close to be in equilibrium with the actual atmosphere and temperature. Due to the open porosity of the powder compacts a fast release of water was allowed when heated and the thermal stability of the oxyhydroxyapatite formed was assumed to be lower compared to OHAp and further reduced as the

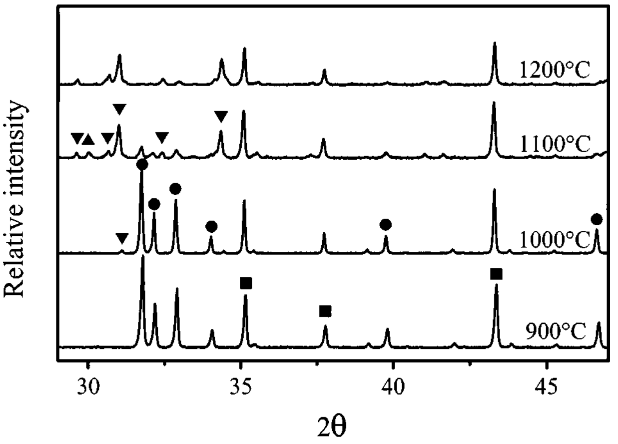

Figure 2 XRD patterns of aluminium oxide-OHAp composite powders sintered in air for 2 h at selected temperatures: (●) OHAp, (■) aluminium oxide, (▼) tricalcium phosphate, (▲) calcium aluminate.

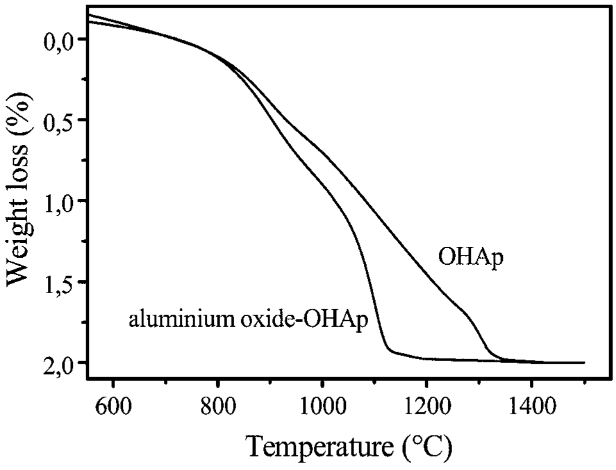

Figure 3 Thermogravimetric analysis of OHAp and aluminium oxide-OHAp composite powder (40 vol% aluminium oxide, 60 vol% OHAp) recalculated as OHAp.

fraction of vacancies increases in connection with the water release. When the fraction of vacancies formed was sufficient for decomposition of oxyhydroxyapatite to take place in contact with aluminium oxide, calcium aluminates and tricalcium phosphate, which are the more stable phases, were formed. In the composite prepared, decomposition of OHAp was detected after sintering at 1000°C in an open system (Fig. 2). The major part of the OHAp decomposed as early as 1100°C, and was not possible to detect in the XRD pattern after sintering at 1200°C.

The decomposition of OHAp in the presence of aluminium oxide can then be divided into two reaction steps according to the following reactions [13]

$$\mathrm{Ca_{10}(PO_4)_6(OH)_2} \rightarrow \mathrm{Ca_{10}(PO_4)_6(OH)_{(2-2x)}O_x} + x\mathrm{H_2O} \qquad (1)$$

$$\mathrm{Ca_{10}(PO_4)_6(OH)_{(2-2x)}O_x} + \mathrm{Al_2O_3} \rightarrow 3\ \mathrm{Ca_3(PO_4)_2} + \mathrm{CaAl_2O_4} + (1-x)\ \mathrm{H_2O} \qquad (2)$$

Thermogravimetric measurements were used to study how presence of aluminium oxide influences the release of water from the apatite structure at elevated temperatures. The thermogravimetric curves of OHAp powder and aluminium oxide-OHAp composite powder are shown in Fig. 3. The weight loss from OHAp containing composites were recalculated as weight loss of pure OHAp, and was then compared to that of pure OHAp. At lower temperatures, adsorbed water was released and the remaining amount of removable water from the structure in pure OHAp and in the OHAp containing composite was similar at 700°C. Above this temperature, the continuous weight loss will correspond to water removed from the OHAp structure implying that the number of vacancies and O^{2-} ions formed at the former OH^- positions increases with increasing temperature. When the critical fraction of water lost from the OHAp structure is reached, decomposition occurs according to reaction 2. Thus, the water loss rate from OHAp in the composite will increase compared to the pure OHAp. Around 1050°C the enhanced mobility in the fine grained composite powder will further increase the reaction rate. At 1150°C almost all water is lost from OHAp and only traces of the apatite phase is found in the XRD pattern. This can be compared to the OHAp sample where the water was not completely removed until about 1350°C.

In a closed system, only a small part of the OH^- ions can leave as water. The majority of the OH^- ions will thus remain in the structure and the equilibrium in reaction 1 shifts to the left. This decreases the fraction of vacancies created, and makes the apatite phase more stable also in contact with aluminium oxide. The improved stability allows the use of a higher sintering temperature. The XRD phase analysis of aluminium oxide-OHAp composites HIPed at 1200°C for one hour, revealed that no phases other than OHAp and aluminium oxide were present as seen in Fig. 4. Using an optimised sintering process it will most likely be possible to produce almost fully dense composites of aluminium oxide and OHAp containing a limited amount of or no decomposition products. The XRD phase analysis of HIPed aluminium oxide-OHAp composites heat treated in air, revealed that tricalcium phosphate was formed when temperatures above 1200°C were used. This is a significant increase in temperature

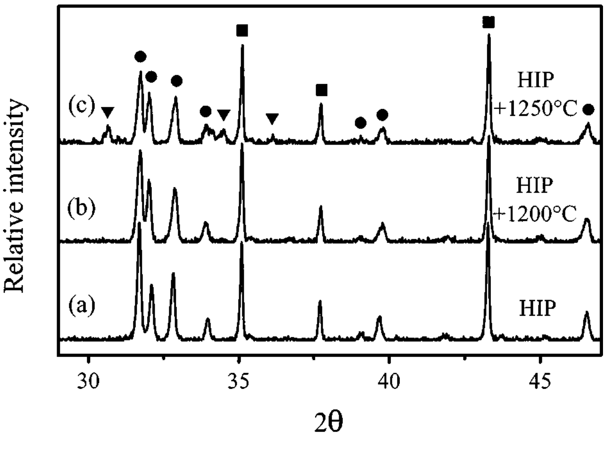

Figure 4 XRD patterns of (a) HIPed aluminium oxide-OHAp, (b) HIPed aluminium oxide- OHAp post heat-treated in air for 1 h at 1200°C and (c) HIPed aluminium oxide-OHAp post heat-treated in air for 1 h at 1250°C: (●) OHAp, (■) aluminium oxide, (▼) tricalcium phosphate.

before decomposition of OHAp is detected compared to aluminium oxide-OHAp composite powder sintered in air, where it was found that decomposition of OHAp initiates below 1000°C and decomposes completely at 1200°C.

The difference in the phases formed after exposure of composite powder and HIPed material to elevated temperatures indicates some kinetic restrictions that prevent the reaction to occur in the HIPed material. This improved thermal stability in the densified material may be explained by the connectivity between the two phases. For the phase transformations to occur, a volume change is needed and this may be opposed in the densified material. Another contribution may be that the apatite crystallites are located without connection to the surface. The release of water will then be retarded and this can inhibit the reaction since a certain fraction of vacancies must be present in the OHAp before the decomposition according to reaction 2 is initiated. On the other hand when the composite powder is sintered, the most stable phases are easily formed without any restrictions around the contact points of OHAp and aluminum oxide grains.

3.2. Aluminium oxide-FAp

Only the pure phases of aluminium oxide and FAp were possible to detect in the XRD pattern of HIPed samples and HIPed samples post heat-treated at 1200°C (Fig. 5). The X-ray powder patterns of composite powder or HIPed samples heat-treated in air at 1250°C or above, revealed the presence of tricalcium phosphate. The reason for this might be that the F^- ions react with the water in air at high temperatures and is accordingly replaced either by OH^- or O^{2-} ions or by a vacancy. Depending on the temperature and the composition of the apatite formed an uptake or a release of water may thereafter occur for the apatite to reach equilibrium. When the fraction of vacancies is sufficient in the presence of an aluminium oxide grain, decomposition to tricalcium phosphate and formation of calcium aluminates may proceed.

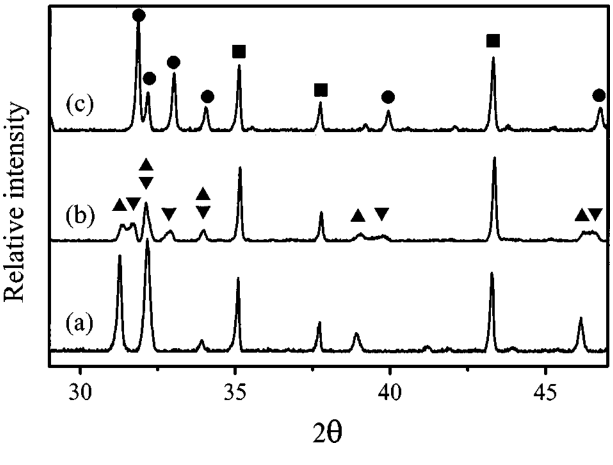

Figure 5 XRD patterns of (a) HIPed aluminium oxide-ClAp, (b) HIPed aluminium oxide-ClAp post heat-treated in air for 1 h at 1200°C and (c) HIPed aluminium oxide-FAp: (●) FAp, (▲) ClAp, (▼) OHAp, (■) aluminium oxide.

3.3. Aluminium oxide-ClAp

The ClAp phase is less thermally stable than FAp and OHAp in an open system [18]. However, the XRD pattern of HIPed aluminium oxide-ClAp composite showed no decomposition of the ClAp (Fig. 5). When a HIPed aluminium oxide-ClAp composite was heat-treated in air at 1200°C, a split of the apatite peaks arose. The new peaks formed originate from ClAp close to the surface of the grains where Cl^- is replaced by OH^-, O^{2-} or a vacancy [19]. When the temperature is high enough and the fraction of vacancies increases and makes contact with aluminium oxide, the solid state reaction was initiated with formation of tricalcium phosphate and calcium aluminates.

3.4. Cell dimensions

The cell dimensions of the apatites increased in the aluminium oxide-apatite composites compared with those for pure apatites (Table I). These changes in the apatite cell were significant larger than the observed standard deviations (<0.002 Å) and may be caused by a minor interface-reaction, compositional changes or internal stresses in the composite.

No phase changes were detectable from observing the XRD pattern in the HIPed aluminium oxide-apatite composites. However, this only indicates that no reaction large enough to be detected occurred between the two phases. A far more complex case, and difficult to detect, would be the occurrence of a low calcium deficiency in the apatite structure. Such a deficiency may, in that case, be due to a slight diffusion of calcium from the apatite to a connected aluminium oxide grain during the sintering process.

Precipitated OHAp usually has a slightly larger cell than OHAp obtained from solid state synthesis, which in some cases is due to non-stoichiometry with a low Ca/P ratio or additional water in the structure [20]. When such calcium deficient OHAp is heated, a mixture of OHAp and tricalcium phosphate is produced [14] while the apatite structure is maintained in calcium deficient FAp [21] and calcium deficient ClAp [22]. As a consequence, the composition of calcium deficient FAp or ClAp directly reflects the composition of the individual apatites, while the composition of heat-treated calcium deficient OHAp reflects an overall composition of a OHAp-tricalcium phosphate mixture. Thus, the influence of calcium deficiency in OHAp on cell

TABLE I Cell dimensions of HIPed samples

Sample	*a*-axis (Å)	*c*-axis (Å)
ClAp	9.6047(7)	6.8066(7)
ClAp (aluminium oxide-ClAp)	9.610(1)	6.818(2)
FAp	9.3677(4)	6.8890(5)
FAp (aluminium oxide-FAp)	9.3778(9)	6.892(1)
OHAp	9.4154(6)	6.8826(8)
OHAp (aluminium oxide-OHAp)	9.430(1)	6.892(2)
aluminium oxide	4.7593(3)	12.997(1)
aluminium oxide (aluminium oxide-ClAp)	4.7594(3)	12.995(1)
aluminium oxide (aluminium oxide-FAp)	4.7581(7)	12.994(2)
aluminium oxide (aluminium oxide-OHAp)	4.7573(5)	12.992(2)

parameters is difficult to evaluate in aluminium oxide-OHAp composites.

4. Conclusion

Decomposition of OHAp in aluminium oxide-OHAp composites was initiated at temperatures below 1000°C in air. With the use of a closed system, it was possible to reduce the fraction of vacancies formed and thereby improve the thermal stability of OHAp. The temperature at which the decomposition reaction of OHAp is initiated in an aluminium oxide-OHAp composite can then be increased. After hot isostatic pressing at 1200°C no decomposition of the OHAp was detected. This increase in the reaction onset temperature indicates that the reaction mechanism discussed is valid, and that the decomposition of OHAp (reaction 2) was possible to keep at a low level or even eliminate. A temperature of 1200°C was also used for densification of aluminium oxide-FAp and aluminium oxide-ClAp composites without any detectable phase changes. In an open system, both FAp and ClAp reacted with aluminium oxide after exchange of F^- and Cl^- by OH^-, O^{2-} or a vacancy, resulting in a reduced stability of the structures. Biological and mechanical evaluation of these composite materials will be more relevant than previous ones when it is possible to control the phase composition of the aluminium oxide-OHAp composites during the densification process. If the biological properties of these oxide-apatite composite materials turn out to be satisfactory the use of apatite containing materials in medical applications may expand.

Acknowledgements

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