CHAPTER 6

SUMMARY AND CONCLUSION

HAp powders were synthesized in this work from the precipitation reaction between $Ca(NO_3)_2.4H_2O$ and $(NH_4)_2HPO_4$ in base medium. To successfully produce HAp powders, we have found that the pH of the reaction mixture between $Ca(NO_3)_2.4H_2O$ solution and $(NH_4)_2HPO_4$ solution must be kept constant at the value of 11 to 12 all the time. The reaction mixture must be boiled, and kept on stirring for more than 3.5 h before boiling. The employed synthesizing procedure of HAP powders used in this work is summarized as a flow chart in Fig.2.11. Fully densed specimens with a relative density of 98 % the theoretical density have been found to obtain by single-end die press the synthesized powders to 3 MPa and subsequently wet-bag isostatic press to 250 MPa, and finally sinter at 1200°C for 1 h. The XRD pattern and IR spectrum of the prepared specimens (Figs.2.14 and 2.15) indicate that specimens thus prepared are monophase HAp and there was no occurrence of OH^- vacancies in their crystal structure. SEM examinations of the thermally-etched surface of the polished specimens (Fig.2.17) show that their grain structure is equiaxed and their average grain size is 1.8 ± 0.1 μm.

The Vickers-produced damage patterns on monophase HAp specimen surfaces are found to consist of a square impression and two crack systems, i.e.the median/radial crack and lateral crack (Figs.4.1-4.3). The median/radial crack, which is the likely source of premature failure, is found to be easily initiated. its size is relatively large even at the indentation load as low as 1 N (Fig.4.1). The intersection of lateral crack to specimen surface, which causes surface chipping, is also observed even at this 1 N indentation load. Thus these observations indicate that HAp specimens fabricated in this work are highly susceptible to microcrack formations due to handling damages, thus resulting in both strength degradations and surface removals. From the direct measurement of the impression diagonals and the median/radial crack lengths from damage patterns due to Vickers and Knoop indentations as a function of indentation load (Figs. 4.5-4.8 ,4.11), the following average mechanical properties of

monophase HAp specimens are found : hardness H, 5.3 $\pm$ 0.4 GPa; stiffness E, 274.4 $\pm$ 3.1 GPa; and fracture toughness T,0.9 $\pm$ 0.1 $MPam^{1/2}$.

The results of the indentation-strength tests (Fig.4.15) illustrates that strengths of the monophase HAp ceramics tend to follow the -1/3 power law dependence of strength on indentation load. Therefore the indentation-strength results indicate that it has a single-value fracture toughness and its strength is strongly dependent on the pre-existent crack size. The physical insight into the conclusion that the HAp ceramics has a single - value toughness is available from the results obtained from optical and SEM examinations that its cracks always propagate through the grains (Figs. 4.4 and 4.16) and no grain-interlocked bridgings are found at crack interfaces. Thus the toughening mechanisms of grain-interlocked bridgings, which can dissipate energy from the loading system and results in the increase of fracture toughness as the crack length increases (T-curve) as described in Sect.3.5.1, are not possible in the monophase HAp ceramics. These results indicate that the grain boundary toughness has a higher value than its average fracture toughness, therefore cracks tend to propagate through the grains (intragranular) rather than along the grain boundaries (intergranular). Accordingly, eventhough it should have lock-in thermal expansion mismatch stresses due to its noncubic structure as in many monophase ceramics displaying the T-curve, the grains cannot be clamped by these lock-in stresses since cracks do not propagate along the grain boundary. Therefore in the next part of this work, no attempt was made to modify its microstructures by changing grain sizes and shapes, but Y_2O_3-ZrO_2 was dispersed into the HAp matrix to promote phase-tranformation toughening.

It has been found in this work that to be able to obtain 3YZ-HAp composite without being broken during the processing, the reduction of the differential shrinkage between HAp and 3YZ is needed and it is necessary to uniformly distribute 3YZ in HAp matrix by the coprecipitation technique (Sect.5.1). The employed fabrication procedure of 3YZ-HAp composite used in this work is summarized as a flow chart in Fig.5.2. The obtained 3YZ-HAp specimens are found to have a relative density of only 87 % the theoretical density whereas the monophase HAp specimens can be prepared with a relative density as high as 98 % the theoretical density. The XRD pattern (Fig.5.3) indicates that a thermally decomposition of HAp

into α-TCP and β-TCP second phases occurs in the HAp matrix of the 3YZ-HAp specimens. However, its IR spectrum (Fig.5.4) indicates that there was no occurrence of OH^- vacancies in their crystal structure. SEM examinations of its thermally-etched surfaces (Fig.5.7) show that the HAp matrix has the same grain structure as that of the monophase HAp ceramics, i.e. an equiaxed structure, but its grain size of 8.8 $\pm$ 1.0 μm is larger than that of the prepared monophase HAp ceramics which has a value of 1.8 $\pm$ 0.1 μm. Its SEM micrograph (Fig.5.7A) indicates that there is a uniform distribution of ultrafine particles, which might be tetragonal zirconia precipitates, and pores within its HAp matrix whereas none of them is evident in the SEM micrograph of the monophase HAp ceramics (Fig.5.7B). In addition, its SEM and optical micrographs (Fig.5.8) illustrate that there is a uniform distribution spherical agglomerates, which might be 3YZ agglomerate, of the average size of 20.0 + 1.5 μm within its HAp matrix. Microcracks initiated during the processing have been observed on its surfaces (Fig.5.9).

The Vickers-produced damage patterns on 3YZ-HAp surfaces (Figs.5.10 - 5.12) are also found to consist of a square impression and two crack systems, i.e. the median/radial crack and lateral crack, as those on the monophase HAp surfaces. However, its impression diagonals are found to be longer than those of the monophase HAp ceramics subjected to the same indentation load (Fig.5.12), indicating that the 3YZ-HAp composite has a lower value of hardness than that of the monophase HAp ceramics. Furthermore,its lengths of the median/radial crack traces are found to be shorter than those of the monophase HAp ceramics subjected to the same indentation load (Fig.5.12), indicating that its fracture toughness has a higher value than that of the monophase HAp ceramics. It has also been found that the intersection of lateral crack with the specimen surface only occurs in the 3YZ-HAp composite at the indentation loads $\geq$ 40 N whereas it starts to occur in the monophase HAp ceramics at the indentation load as low as 1 N, thus indicating that the 3YZ-HAp composite has a higher resistance to surface removals due to contact damages than the monophase HAp ceramics.

SEM and optical micrographs of the crack path on the surface of 3YZ-HAp composite (Fig.5 14) illustrate that the crack propagates through the grains of HAp matrix (intragranular), but when it encounters the spherical agglomerates, which might be 3YZ, it either propagates through or go around them. By directly measuring the impression diagonals and the

median/radial crack lengths from the damage patterns due to Vickers and Knoop indentations as a function of indentation load (Figs. 5.15 - 5.19), the following average mechanical properties of the 3YZ-HAp composite are found : hardness H, 1.7 $\pm$ 0.1 GPa; stiffness E, 121.4 $\pm$ 2.5 GPa ; fracture toughness T, 1.2 $\pm$ 0.1 $MPam^{1/2}$.

The results of indentaion-strength tests indicate that strengths of the 3YZ-HAp composite are significantly higher than those of the monophase HAp ceramics in large-crack size domain, although this is offset by lower strengths in the small-crack size domain (Fig.5.20). They indicate that the strengths of 3YZ-HAp composite are almost completely independent of the crack size whereas those of the monophase hydroxyapatite ceramics are strongly dependent on the crack size. This crack insensitivity achieved by uniformly dispersing tetragonal zirconia containing 3 mol % Y_2O_3 into the HAp matrix is a highly desirable property in the applications as prosthetic materials which are subjected to mechanical loads, because it offers the prospect of a single, well- defined stress level, without regard to the size of a critical crack. Such implant will be much less susceptible to strength degradations due to subsequent damages occurring during the actual use. The mechanism responsible for the crack-insensitive strength of the 3YZ-HAp composite might be achieved by the process of phase-transformation toughening described in Sect.3.5.2.

It is of challengeable to try to improve our established processing technique to produce 3YZ-HAp composite which preserve the quality of crack-insensitive strength shown here and at the same time attain even higher strength levels.