CHAPTER 1

INTRODUCTION

1.1 Research backround

In the present day, the development of new materials for the effective repair of the skeletal system is an outstanding goal of biomaterials science. By the discovery of bioglass by Hench in 1971, various kinds of bioactive materials that are close to human bone have been developed. Active bioceramic $Ca_{10}(PO_4)_6(OH)_2$ hydroxyapatite (HAp) was ideal for using as materials of artificial bone **[1-2]**. Biological apatites are characterized by means of crystal size in the order of nanometers, poor crystallinity, nonstoichiometry, and a variety of ionic substitutions **[3-5]**. Since hydroxyapatite provided a biocompatible capability of a strong chemical bond with natural bone, it can induce future tissue in growth and future formation of chemical bonding to achieve fixed function. Unfortunately, even hydroxyapatite has an excellent biocompatibility though its mechanical properties of low strength and high brittleness restrict the application only on bone repair. Therefore, combining the biocompatibility and bioactivity of hydroxyapatite with the high strength and toughness of metals such as titanium should be a good idea.

According to the mechanical properties of titanium metal, which is close to human bone, it has been used as implant materials over the past decade. Titanium metal, however, is bioinert **[6]** which is normal characteristics of metal implants. Moreover, titanium metal and its alloys have high strength and excellent corrosion resistance in living body.

Bone tissue is constituted of a mineral phase, which accounts for about 60-70% of the dry weight and is mainly nonstoichiometric carbonate apatite(Figure 1.1), and of an organic matrix where collagen is the main component **[7-8]**. This complex structure has the significant meaning for design of bone substitutes. It seems that composite is suitable material to serve this meaning. Reinforcement by whiskers or fibers is acceptable method to improve the mechanical properties of composite matrix. In order to preserve both bioactivity and biocompatibility of hydroxyapatite, calcium phosphates with controlled morphology are required for the development of composites in biomedical application. Calcium phosphates are needed because these materials will not detoriorate the bioactivity and biocompatibility of hydroxyapatite. Moreover, calcium phosphates can induce hydroxyapatite to deposite and grow on itself [9-22].

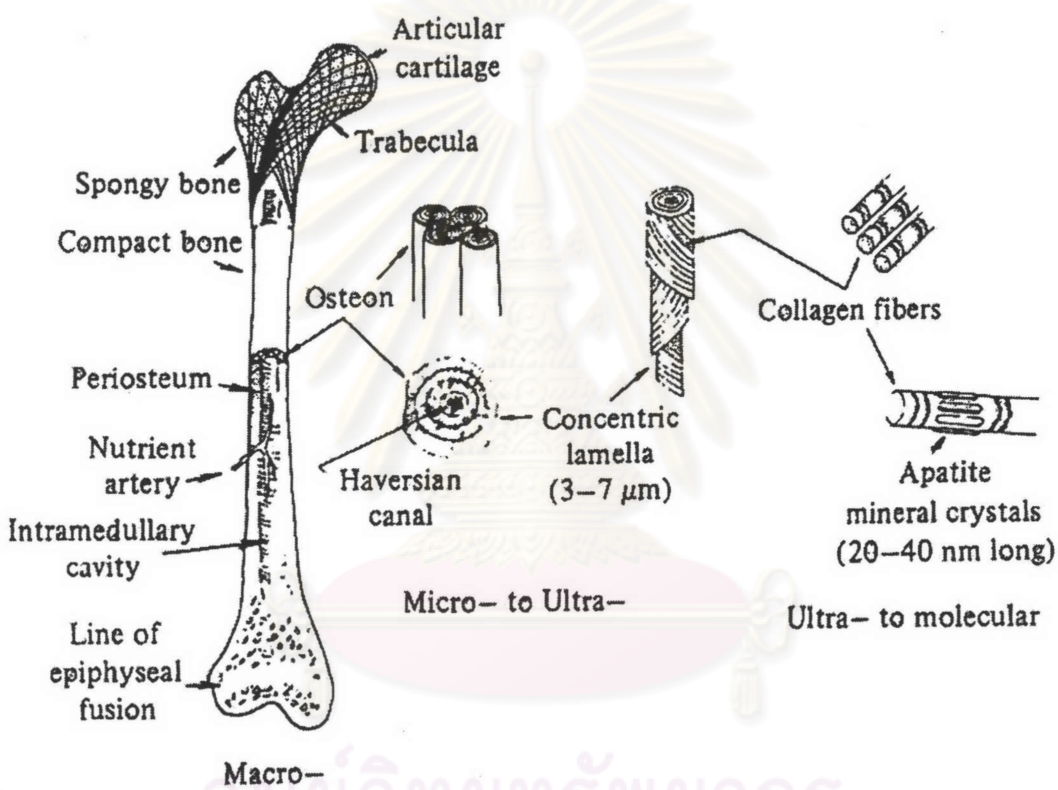

Figure 1.1 The structure of human Bone.

From all above information, coating surface by calcium phosphates and/or hydroxyapatite should be the good candidate to improve the bioactivity of titanium. The methodologies of deposition techniques are varieties such as sol-gel [23], RF magnetron sputter [24], ion beam dynamic mixing [25-26], pulse laser deposition [27], electrophoretic deposition [28], and electrocrystallization [29]. Currently, the most widely applied coating procedure is the plasma spray technique [30]. The major problem for the plasma spray is the decomposition and phase transformation of hydroxyapatite during the spray coating process. According to very high temperature of plasma, cracking/peeling of calcium phosphates coating films may be occurred.

Electrochemical deposition of calcium phosphate bioceramic coating has recently attracted considerable attention [31-34]. Because of a variety of advantages of the method of the coating fabrication such as a low process temperature, the ability to deposit on porous or complex shapes of substrate, and the simple control of deposition thickness. Hydroxyapatite, which is one form of calcium phosphates, was electrochemically deposited in several solutions at elevated temperature and accompanied with other unstable calcium phosphates.

Though, the easiest way to induce any hydroxyapatite from electrochemical deposition is adding some ions such fluoride and magnesium into electrolyte. It is known that fluorine is one of the elements contained in biological apatites because fluoride ions have been found in saliva and blood plasma. Moreover, it is also required for normal dental and skeletal development, and has been suggested to prevent the risk of dental cavies [35].

For biomimetic study, a biologically active bone-like apatite on titanium surface is needed. According to Kokubo et. al., the bone-like apatite formation on bioactive materials *in vivo* can be reproduced even in a simulated body fluid (SBF) with ion concentrations nearly equal to human blood plasma [36]. Therefore, the SBF has been widely used for formation of bone-like apatite on various kinds of implant materials *in vitro*.

1.2 Objectives

In this study, formation of calcium phosphate and hydroxyapatite thin film on titanium substrates by electrochemical deposition in both aqueous and non- aqueous solutions were attempted. Moreover, formation of hydroxyapatite was induced by adding fluoride ions into both aqueous and non-aqueous systems. In addition, bone-like apatite grown by biomimetic process in SBF was also investigated.