Controlling calcium phosphate formation on calcium silicate thin film

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Statement of Purpose: It is well known that bioglasses are able to form calcium phosphate quickly in simulated body fluid. Present authors previously reported calcium phosphate forming ability of calcium silicate thin film synthesized by electron beam evaporation. In this report, controlling the rate of calcium phosphate formation on calcium silicate thin film was studied by pretreatment and/or post treatment.

Methods: Commercially pure titanium foil and silicon wafers were used as substrates. Electron-beam deposition system was employed to deposit calcium silicate. Selected pretreatment was Ar-ion beam cleaning which was conducted in the same vacuum chamber just before the deposition. Post treatment was heat treatment. Processing temperature was ranged from 200^0C to 800^0C. Then the specimens were immersed into PBS (phosphate buffered saline). The morphological change with different immersion time was observed by scanning electron microscopy. The composition, crystallinity and film stress were evaluated by X-ray photoelectron spectroscopy, X-ray diffractometer and laser scanner, respectively.

Results/Discussion: In case of SC37 (30 wt.% SiO_2 and 70 wt.% CaO) as a evaporant, calcium phosphate was formed just after immersion into PBS, but both calcium silicate layer and calcium phosphate layer were peeled off. Oxide films formed by vacuum process were oxygen deficient in nature if no oxygen treatment was incorporated during deposition. Post heat treatments at 400^0C and 800^0C in air were performed as an oxygen treatment. Calcium silicate which was post treated at 400^0C was not peeled off until the termination of 1 week immersion in PBS. Calcium silicate heat treated at 800^0C also did not show flaking problem but it showed more active calcium phosphate formation. As increased processing temperature, the tensile stress of thin film decreased and fissures were observed high temperature conditions – 600 ~ 800^0C. The stress reducing was general phenomena of annealing. It might retard the calcium phosphate formation. However fissures by different thermal expansion coefficient offered increased reactive area and the edge of fissures might act as a nucleation site for calcium phosphate formation. Crystallinity of the film by different thermal treatment conditions was investigated. As-received calcium silicate film showed amorphous phase. As temperature condition increased, only small γ-Ca_2SiO_4 and β-Ca_2SiO_4 was observed after 400^0C and 800^0C heat treatment, respectively. Development of crystal phase might affect on calcium phosphate forming reaction. However the calcium phosphate mechanism on different crystal phase has not been distinguished yet.

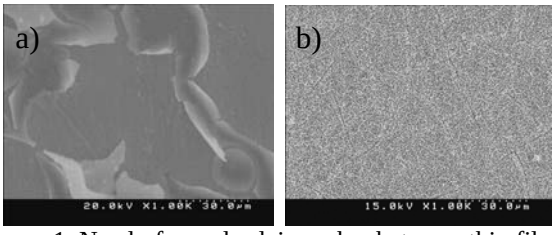

Figure 1. Newly formed calcium phophates on thin films. (a) agressively formed calcium phosphate on as-deposited calcium silicate (immersion time in PBS : 1hr) (b) well developed calcium phosphate on heat treated calcium silicate at 400^0C (Immersion time in PBS : 1 week)

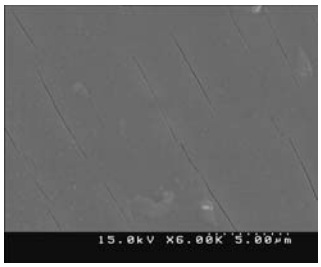

Figure 2. Fissures of calcium silicate thin film after 800^0C post heat treatment.

Conclusions: Calcium silicate thin film showed aggressive calcium phosphate formation and poor adhesion just after calcium phosphate formation. Post heat treatment in air settled this problem and controlled the reactivity.

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