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THE INTERMEDIATE GLASS STUDY IN HYDROXYAPATITE AND ALUMINA BONDING

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HAp와 알루미나 결합에 있어서의 중간 유리상연구

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Several intermediate glasses are investigated to bond the alumina and the hydroxyapatite (HAp). The chemical compositions of the intermediate glasses are chosen as $CaO-Al_2O_3$. The mole ratio of CaO/Al_2O_3 is changed from 0.5 to 3.0. The lowest melting is observed at 1355℃ in the specimen of CaO/Al_2O_3 at the mole ratio of 2. With increasing contents of Al_2O_3, the melting temperatures gradually increase and a number of pores are observed. The sectional microstructure shows that the good wetability is observed in higer contents of CaO specimens. This implies that the good wetability is obtained in the mole ratio range of $CaO/Al_2O_3 \geq 2$. The phase transformations are observed after heat treatment but the major peaks of HAp still exist.

알루미나와 Hydroxyapatite(HAp)의 결합을 연구하기 위하여 9 가지의 중간 유리상을 연구하였다. 그 중간상의 화학 조성은 $CaO-Al_2O_3$에서 정하였으며 CaO/Al_2O_3의 몰 비율은 0.5 에서 3 까지 변화 시켰다. 가장 낮은 용융은 CaO/Al_2O_3의 몰 비율이 2이고 1355℃때 나타났다. Al_2O_3의 양을 증가시킴에 따라 용융점은 점점 높아 졌고 많은 기공들이 발견 되었다. 단면 조직 조사에 따르면 높은 CaO양 시편에서 양호한 흡수접착을 발견할 수 있었고, 이것은 CaO/Al_2O_3 비가 2보다 큰것에서 더좋은 흡수접착을 얻을 수 있음을 의미한다. 열처리후 상변태는 발견되었으나, HAp의 중요한 피크는 그대로 남아 있음을 알 수 있다.

Key words : Intermediate, Glass, Hydroxyapatite, Bonding, Wetability

I. INTRODUCTION

It is well known that the hyrdroxyapatite (HAp) has good biocompatibility and it is used as the bio-implant materials.[1,2] However, the usage of HAp is limited because of the low fracture strength. Thus it is not directly used for substitution of human bone but used as the filler materials in the voids of broken bone.

The coating of HAp to alumina is needed to study to satisfy both the strength and the biocompatibility. Thus, the intermediate glass phases are investigated with the variations of CaO/Al_2O_3 compositions in order to find the good wetability between the alumina and the HAp.

According to Ji and Marquis[3], the phases which can be found between HAp and Al_2O_3 are $Ca_3Al_2O_6$, $CaAl_2O_4$, $CaAl_4O_7$, $Ca_5Al_6O_{14}$, $Ca_{12}Al_{14}O_{33}$. Prof. Shaoxian et al. studied the bonding between the HAp and the alumina substrate in order to make surgical implants. They used the glass phases to bond the alumina and the HAp. The glass is melted at 1000℃ and the wetting is observed good.[4]

Thus, the possible intermediate glass phases are chosen according to those of Ji and Marquis and the phase diagram of $CaO-Al_2O_3$ (Fig. 1) in this study.[5]

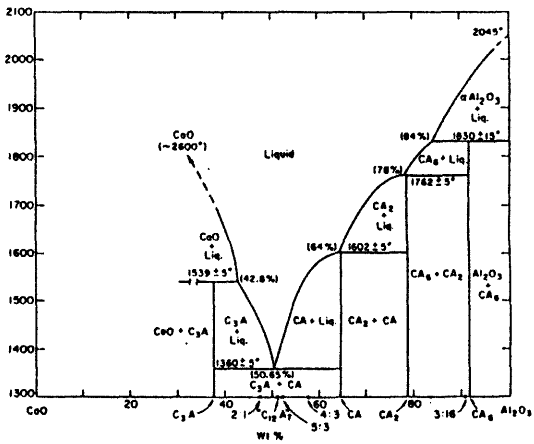


Fig. 1 Phase Diagram of CaO-Al2O3

II. EXPERIMENTAL PROCEDURE

The 5 intermediate phases are chosen according to the $CaO-Al_2O_3$ phase diagram (Fig. 1), in which the mole ratio of CaO/Al_2O_3 changes from 1.428 to 2. In addition to this, the 4 possible intermediate phases which was reported by Ji and Marquis are investigated.[3] Thus, the chemical compositions of 9 intermediate phases are shown in Table 1.

Table 1. The Chemical Compositions of 9 Intermediate Glass Phases

(wt. %)

Sample No.	1	2	3	4	5	6	7	8	9
CaO	62.3	35.5	21.6	47.8	52.4	50.54	48.6	146.4	44
Al_2O_3	37.7	64.5	78.4	52.2	47.6	49.46	51.4	53.6	56
CaO/Al_2O_3*	3	1	0.5	1.67	2	1.857	1.714	1.57	1.428

* : Mole Ratio

The first grade of chemical reagent was used in this experiment. Especially the powder of Al_2O_3 is the products of Hanawa and Hayashi Chemicals in Japan and the CaO is the products of Dong Yang Chemicals in Japan.

The exact weight of each powder was measured using electronic digital balance and the each specimen powder was grinded and mixed with the mortar and the pestle. The 1 g of the intermediate glass phases were pressed at 3500 psi for 2 min. in 10 mm diameter moulding die. Thus, the 10 mm diameter discs of the intermediate phases are obtained.

The HAp was made by the reaction of $Ca(OH)_2$ and H_3PO_4. Firstly the adequate amount of $Ca(OH)_2$ is added in distilled water and the HAp precipitates in $Ca(OH)_2$ solution by the dripping of H_3PO_4. The ratio of Ca/P would maintains 1.67 at all the time during the reaction and the solution is stirred. The HAp precipitations are dried using vacuum drying oven. Then the HAp precipitations are heat treated at 900℃ for 3 hours in order to make the HAp phase. The same pressing procedure are adopted for HAp and the 10 mm diameter discs are obtained for this experiment.

The 25 mm X 25 mm X 1.2 mm α alumina substrates are used for the basement.

The α alumina(substrate), the intermediate glass and the HAp stacked sequentially. Then the specimen was heat treated from 1350℃ to 1400℃ for 6 hours in the air atmosphere. The ramp rate of heating and cooling was fixed at 300℃/hour. After heat treatment, the HAp was analysed using X-ray diffraction. In order to investigate the sectional microstructure of bonded specimen, the transverse section of bonding specimen was cold mounted, polished and coated with gold for the scanning electron microscopy.

III. RESULTS AND DISSCUSSION

The bonding characteristics of specimen are observed and they are listed in Table 2.

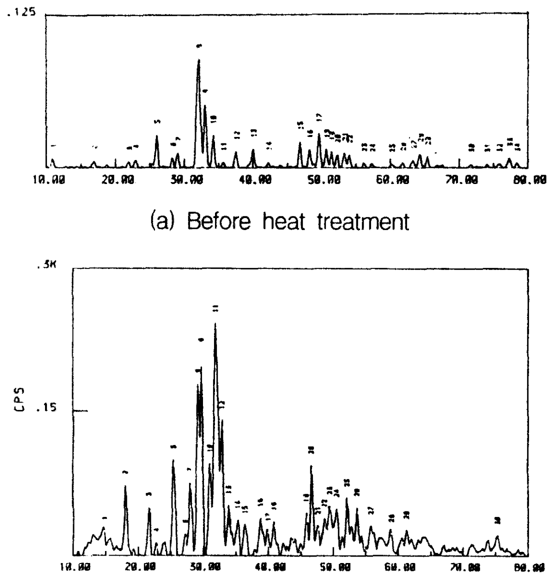
Table 2. The Bonding Characteristics of Intermediate Glass Phases at Several Temperatures, Which Was Observed by the Naked Eye

Specimen	1	2	3	4	5	6	7	8	9
1350 ℃	△	X	X	X	△	X	X	X	X
1355 ℃	○	X	X	X	○	X	X	X	X
1360 ℃	○	X	X	○	○	○	○	X	X
1370 ℃	○	X	X	○	○	○	○	○	X
1380 ℃	◎	X	X	○	◎	◎	○	○	○
1400 ℃	◎	○	X	○	◎	◎	◎	○	○

* X : No Melting, No Bonding
△ : Half Melting, Half Bonding Strength
○ : Melting, Good Bonding
◎ : Complete Melting, Bonding

At 1350℃, the specimen 1 and 5 shows half melting and a little bonding strength. However the other specimens are not melted at all. With slightly increasing temperatures, the specimen 1 and 5 are only melted and bonded at 1355℃. With further increasing the temperatures, the more Al_2O_3 contained specimen melted gradually. It is thought that this is due to the high melting temperatures of Al_2O_3. At 1380℃, the melting and bonding of the intermediate glass phases except specimen 2 and 3 are observed. The mole ratio of CaO/Al_2O_3 of the specimen 2 and 3 is 1 and 0.5 respectively. The highest contents of Al_2O_3 specimen 3 only remains unmelted at 1400℃. Thus, it is concluded that the melting temperatures of the intermediate glass phases are increased with increasing contents of Al_2O_3 in this experiment. In other words, the lower melting temperature of the intermediate phases is observed in higher contents of CaO specimens.

The changes of HAp are investigated with X-ray diffraction analysis. The results of X-ray diffraction before and after heat treatment are shown in Fig. 2. Slightly different phases are observed but the major peaks of HAp still remain. This suggests that the temperatures 1360℃ can change the properties of HAp.



(a) Before heat treatment

(b) After heat treatment

Fig. 2 The X-ray diffraction pattern of HAp before and after heat treatment (1360℃, 6 hours)

The 5 specimens were chosen for the investigation of microstructures of the intermediate glass phases bonding at 1360℃. The scanning electron micrographs of bonding sections of the intermediate phases are shown in Fig. 3.

As shown in Fig 3, the complete bonding is observed between the alumina and the intermediate phases as in specimen 1 and there is no pores observed. It is also hard to find the clear boundary between the HAp and the intermediate phases. This suggests that the bonding is still good between them. In contrast to specimen 1, a lot of large and small pores are observed in specimen 4. However, it seems that the boundary between the alumina and the intermediate phases is bonded well. The microcracks are observed in between the HAp and the intermediate phases. This implies that the bonding characteristics of specimen 4 is not so good as specimen 1. With increasing CaO contents, there are few number of small pores in the intermediate phases as in specimen 5. The good wetability is observed between the intermediate phase and the alumina and it is hard to find the boundary between the HAp and

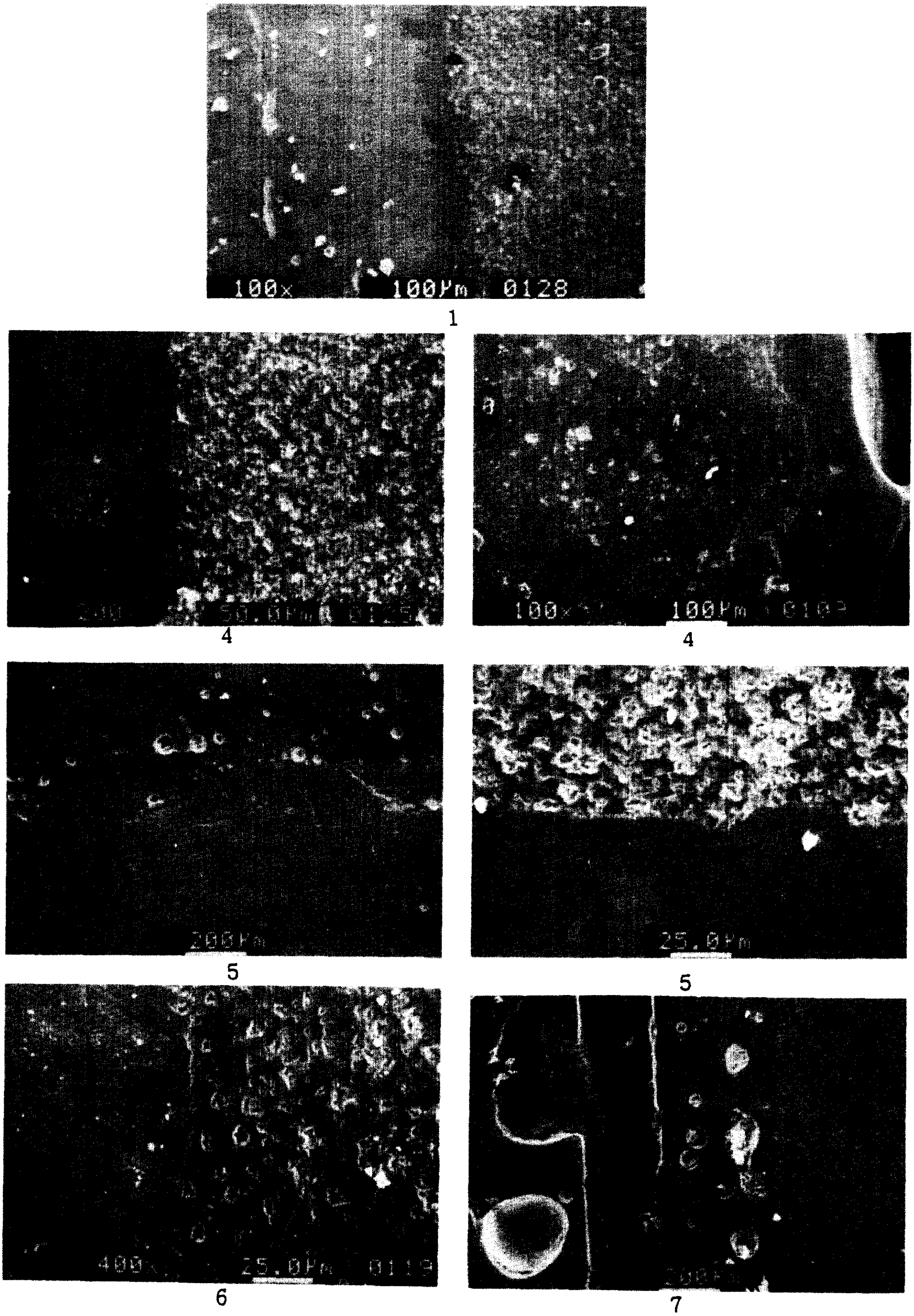


Fig. 3 The bonding microstructures of HAp, intermediate phases and alumina, which was heat treated at 1360℃ for 6 hours.

the intermediate phase. This suggests that the bonding characteristics of specimen 5 is good compared to specimen 4. With increasing contents of Al_2O_3 (compared to specimen 5), the number of large and small pores are also increased in the intermediate phase as in specimen 6 and 7. The separate boundary between the alumina and the intermediate phase is clearly observed in specimen 6. This suggests that the wetting properties is poor in specimen 6. There are several cracks observed in the HAp and the intermediate phases in specimen 6 and 7. When considering the influence of the mole ratio of CaO/Al_2O_3 to the number of pores in the intermediate phase, the size and number of pores is increased with decreasing the mole ratio of CaO/Al_2O_3. Especially there is no pores in specimen 1 which has the mole ratio CaO/Al_2O_3, 3.0.

Ⅳ. CONCLUSIONS

(1) The good wetability is observed in the specimen which contains the mole ratio of $CaO/Al_2O_3 \geq 2$ in the experiments of 1360℃ for 6 hours

(2) The numbers and sizes of pores in the intermediate phase are increased with decreasing the mole ratio of CaO/Al_2O_3 in the range of $1.67 \leq CaO/Al_2O_3 \leq 1.857$. The wetability is getting worse with decreasing the mole ratio of CaO/Al_2O_3.

(3) The phase transformations of HAp are observed during heat treatment at 1360℃ for 6 hours. However, the HAp is still remained as a major phase.

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