

硼硅酸盐生物玻璃表面多层结构的形成机理

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摘要: 描述了硼硅酸盐生物活性玻璃在体外含磷溶液中的转变过程, 并采用 XRD、SEM 和 EDS 对反应产物的微观结构、形貌和成分进行了分析。结果显示, 产物为多层结构, 由羟基磷灰石和无定型 SiO₂ 层交替排列而成。此外, 提出了一个定性模型来解释层状结构的形成机制。研究证实, 反应动力学及反应产物的微观结构主要取决于生物活性玻璃的成分和含磷溶液的浓度。

关键词: 硼硅酸盐玻璃; 羟基磷灰石; 形成机理; 生物活性玻璃

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Formation Mechanism of Multilayered Structure on Surface of Bioactive Borosilicate Glass

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Abstract: A conversion process of a bioactive borosilicate glass to a multilayered structure in aqueous phosphate solution was described. Microstructure, morphology and composition of the reaction product were studied using XRD, SEM and EDS analysis. It was shown that a multilayered structure, consisting of alternating hydroxyapatite(HA) and amorphous SiO₂ layers, was formed on the surface of the borosilicate glass. The formation mechanism of the multilayered microstructure was also suggested. Compared with previous work, it was indicated that conversion kinetics and microstructure development of conversion products mainly depended on the composition of the bioactive glass and the concentration of phosphate solution.

Key words: Borosilicate glass; hydroxyapatite; formation mechanism; bioactive glass

Since the initial report on bone-bonding property by Hench et al.^[1], silicate-based bioactive glass, designated as 45S5, has been intensively investigated for biomedical applications. Whereas 45S5 glass exhibits excellent biocompatibility and bioactivity, it is only partially converted to HA when immersed in physiological media. For 45S5 glass particles of size 150 ~ 300 μm , less than 50wt% is converted to HA in an aqueous phosphate solution after several weeks, when

the conversion effectively stops, leaving a core of unconverted glass^[2,3].

Borate glass, based on B₂O₃ network as opposed to the SiO₂ network for silicate glass, has been shown to undergo more rapid and complete conversion to HA in a dilute aqueous phosphate solution^[2,4]. However, the effect of the boron released from the glass on cell must be taken into consideration. It has been shown that high concentration of boron ions dramatically affects cell

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growth^[5,6]. Therefore, it is essential to tailor the glass composition, so that desirable concentration and boron ions release rate can be obtained. The composition of borosilicate glass is between those for silicate and borate glasses. It is confirmed that a minimal effect of boron on cell growth can be achieved by employing bioactive borosilicate glass^[7,8].

The mechanisms of HA layer formation in silicate-based bioactive glasses have been studied and well documented^[9,10]. The conversion of bioactive borate glass to HA follows a process similar to that for 45S5 glass, but without the formation of a SiO₂-rich layer^[2,3]. However, the reports on the formation mechanism of HA on the borosilicate glass surface are still limited^[11].

The objective of the present work is to investigate the conversion process of a bioactive borosilicate glass to a multilayered structure in aqueous phosphate solution. An understanding of the conversion process may be useful for optimizing the glass composition, which in turn controls the bioactivity, degradation and cytotoxicity of the borosilicate glass.

1 Experimental

Borosilicate bioactive glass with the composition (in mol%): 6Na₂O, 8K₂O, 8MgO, 22CaO, 36B₂O₃, 18SiO₂, 2P₂O₅, was prepared by melting the required quantities of reagent grade Na₂CO₃, K₂CO₃, CaCO₃, MgCO₃, SiO₂, H₃BO₃ and NaH₂PO₄·2H₂O (Reagent grade; Fisher Scientific, St. Louis, MO) in a platinum crucible in air for 1 h at 1 100 °C. The melt was cast into a pre-heated graphite mold to give cylindrical samples with a length of 15 mm and a diameter of 5 mm. The obtained samples were annealed for 30 min at a temperature of 450 °C, corresponding to their glass transition temperature.

The conversion reaction was performed by statically immersing the glass samples in 0.25 mol·L⁻¹ K₂HPO₄ solution (100 cm³) with a starting pH value of 7.0 at 37 °C. To ensure that sufficient PO₄³⁻ ions were available to react with Ca²⁺ in the glass to form HA, the dilute phosphate solution was used in the present work instead of simulated body fluid (SBF). After 21 d of immersion, the samples were removed from the solution,

washed with deionized water, and dried at 90 °C.

Field emission scanning electron microscopy (FE-SEM, S-4700; Hitachi, Japan) was used to observe the surfaces and cross-sections of the reaction products. The surfaces were observed using conventional techniques. To observe the cross-sections of the samples, the samples were embedded into epoxy resin, followed by grinding with SiC paper and polishing with diamond paste. Composition analysis of the reaction products was carried out using energy-dispersive X-ray (EDS) in the FE-SEM at an accelerating voltage of 10 kV, and with a spot size of 0.02 μm. X-ray mapping by EDS microanalysis was used to determine the elemental distribution in the polished cross-section. The reaction products were removed gently from the sample surface, and then were ground into powder and analyzed by XRD (Model D/mas 2550 v; Rigaku; The Woodlands, TX) using Cu Kα radiation (λ=0.154 06 nm) in a step-scan mode (0.05° 2θ per step) in the 2θ range of 10°~60°.

2 Results and discussion

Fig.1 shows XRD pattern of the powder ground from the product resulting from the reaction between the borosilicate glass and 0.25 mol·L⁻¹ K₂HPO₄ at 37 °C. The diffraction pattern of a standard HA is also shown in this figure for comparison. The diffraction peaks of the reaction product correspond to those of the standard HA, indicating the formation of HA layers during the reaction. The low intensity and broad width of the diffraction peaks indicate the information of

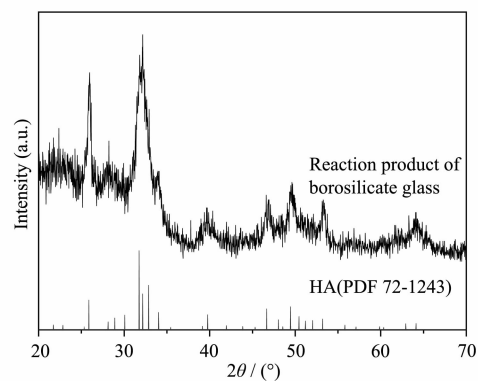


Fig.1 XRD patterns of conversion product resulting from the reaction between borosilicate bioactive glass and 0.25 mol·L⁻¹ K₂HPO₄ at 37 °C

nano-sized weak crystals^[4]. SEM micrographs of the glass surface after immersion for 21 d in the phosphate solution are shown in Fig.2. It is clear that the surface of the borosilicate glass is fully covered by a fine particulate layer. High-resolution SEM image (Fig.2 (b)) shows that the surface consists of a porous network of nanometer-sized, plate-like crystals. On the basis of

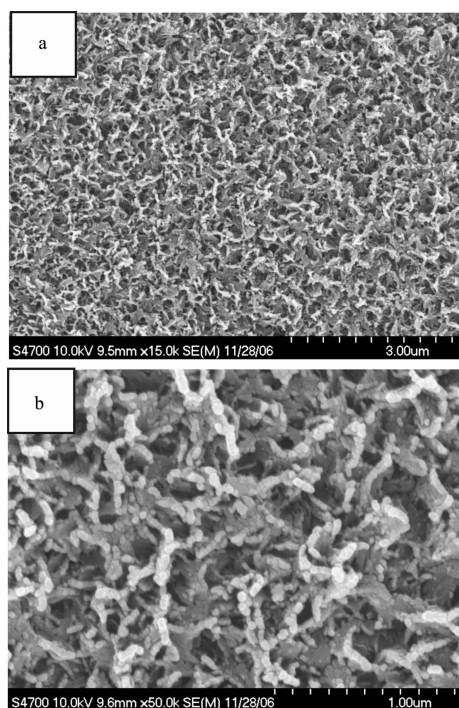


Fig.2 SEM micrographs of the glass surface after immersion for 21 d in the phosphate solution

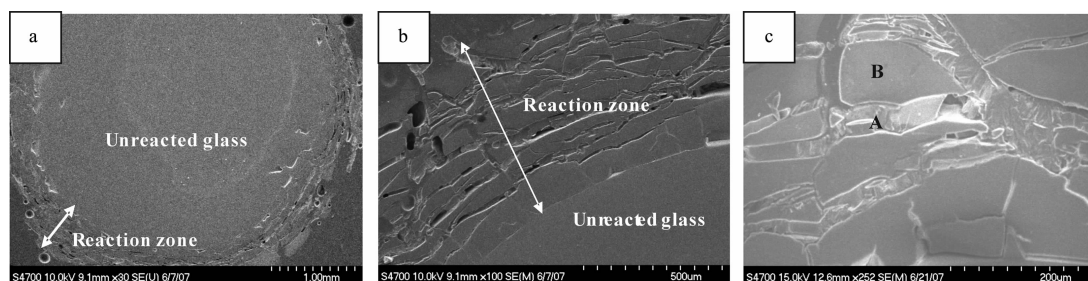


Fig.3 SEM micrographs of a cross-section of the glass sample after immersion for 21 d in the phosphate solution

Fig.4 shows a secondary electron image and the corresponding X-ray maps of O, Si, Ca, P and B. Based upon the compositional information from the X-ray maps, the light phase is enriched in P and Ca, whereas the dark phase mainly contains Si, O. Because Si is firmly bound to B, a small amount of B is also found in this phase, as observed in Fig.3 B(K). The concentrations of the major elements present in the multilayered product, determined by EDS semi-quantitative analysis,

aforementioned XRD result, the plate-like crystals formed on the glass surface are determined to be HA crystals. These results are in agreement with our previous observation for the conversion reaction of borosilicate glass^[2,4].

Fig.3 shows SEM micrographs of a polished cross-section of the glass sample reacted for 21 d in the phosphate solution. It is noted that the cross-section consists of a reaction zone surrounding an unreacted glass core. For the sample shown, with a cross-section of 5 mm in diameter, the thickness of the reaction zone is $\sim 500 \mu\text{m}$. The volume fraction of the reaction product is therefore approximately 10%. The presence of a large amount of remaining glass phase provides an indication that the conversion reaction is insufficient during the short reaction period. As observed in Fig.3 (b), the reaction product has a multilayered structure. Moreover, a few cracks are also found across the section of the sample. In the present experiment, the sample was mounted in epoxy resin prior to SEM observation. The cracks present in the cross-section are therefore believed to be caused by the differential volume changes during the curing of the epoxy resin^[11]. A higher magnification SEM image (Fig.3(c)) indicates that the reaction zone consists of alternating layers of a light phase A and a dark phase B.

are listed in Table 1. The data are based on an average of four measurements at different positions in the phase. It should be noted that the concentrations of B and C are not determined because of the insensitivity of the technique to low atomic number elements^[11]. According to the above analysis, it is deduced that the light phase corresponds to HA, while the dark phase is composed of Si-rich material. As indicated in Fig.1, HA is the only crystalline phase detected by XRD, therefore the Si-

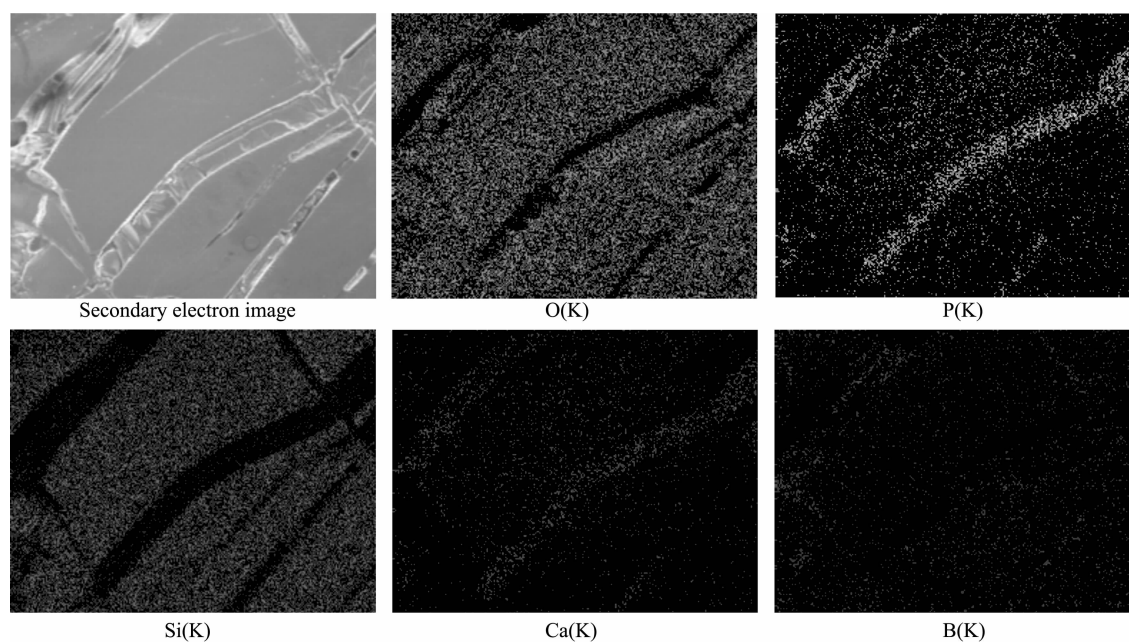


Fig. 4 Secondary electron image and corresponding X-ray maps of O, P, Si, Ca and B

Table 1 Compositions (at.%) of the light and dark layers of the reacted glass

Layer	Si	Na	K	Mg	Ca	P	O
Light(A)	1.2	0.2	0.5	0.7	27.8	17.2	52.4
Dark(B)	15.1	0.4	0.6	1.0	5.3	3.8	88.9

rich material is presumably an amorphous SiO_2 -rich phase.

For the present borosilicate glass, the mechanism for HA layer formation is expected to follow a set of dissolution-precipitation reactions similar in nature to those in the 45S5 bioglass system. The initial reaction involves a preferential extraction of alkalis(Na^+ , K^+) and boron ions from the glass, and at the same time the B-O network structure of the glass is attacked, as indicated in Fig.5(a). Subsequently, soluble silicon passes into the solution as a result of breakdown of the glass network as the conversion reaction proceeds. Condensation and re-polymerization of Si-OH lead to the formation of a SiO_2 -rich layer on the glass surface depleted in alkalis and boron ions. Diffusion of Ca^{2+} from the glass through the

Si-rich layer and the reaction with PO_4^{3-} from the surrounding solution lead to the precipitation of an HA layer on the top of the Si-rich layer(Fig.5(b)). It is shown that the conversion reaction is controlled by the concentration of ions in the solution or diffusion of ions across the SiO_2 -rich layer^[11,12]. In the present work, the conversion rate to HA is more rapid due to the low chemical durability of borosilicate glass and the high concentration of PO_4^{3-} in aqueous phosphate solution. Thus, the ions in the solution are rapidly consumed. However, the presence of SiO_2 -rich and HA layers on the glass surface reduces the removal of ions into surrounding solution, so that the ionic concentration in the solution is remarkably decreased, and the reaction stops until the ionic concentration increases to a value where

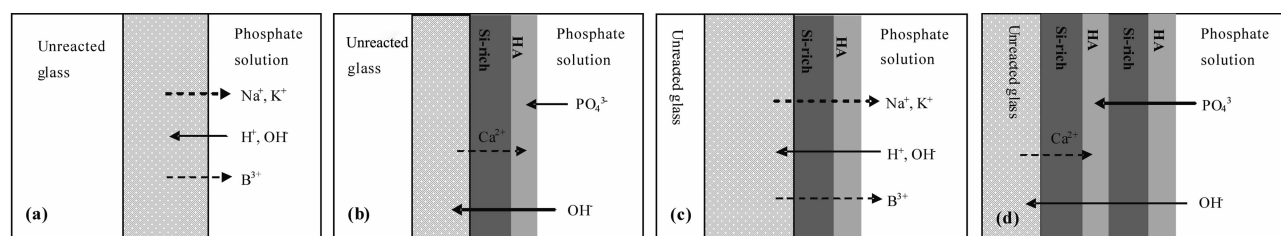


Fig.5 Qualitative model for the conversion reaction of a bioactive borosilicate glass to a multilayered structure

the reaction can proceed again (Fig.5 (c)). The process repeats itself, and consequently an alternating multilayered structure is developed on the surface, as shown in Fig.5(d).

In recent report, Li and Rahaman et al.^[11] carried out a conversion reaction of a borosilicate glass under two different conditions, referred to as “intermittent” and “continuous”. A similar multilayered structure, consisting of alternating HA and amorphous SiO₂ layers, was observed in the intermittent experiment. However, in the present work the multilayered microstructure is formed under continuous condition. Therefore, it is believed that the nature of the experiments does not appear to be a crucial factor. Comparatively, the composition of the bioactive glass and the concentration of used phosphate solution are more essential to control the conversion kinetics and microstructure development of conversion products.

3 Conclusions

A multilayered structure, consisting of alternating HA and amorphous SiO₂ layers, was formed on the surface of a borosilicate glass by immersing it in 0.25 mol · L⁻¹ K₂HPO₄ solution at 37 °C. A qualitative model is suggested to explain the formation mechanism of the multilayered structure during the conversion reaction. It is indicated that compared with the nature of the exper-

iments, the composition of the bioactive glass and the concentration of used phosphate solution appear to be more essential to control the conversion kinetics and microstructure development of conversion products.

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