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Porous hydroxyapatite coating on strong ceramic substrate fabricated by low density slip coating-deposition and coating-substrate co-sintering

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Abstract

This study aims at developing a process technique, which can deposit porous scaffold-like hydroxyapatite (HA) coatings on strong ceramic substrates. As a first trial, micro-porous HA coatings on strong zirconia-based substrates are fabricated by the following technique—consisting of low-density HA-slip coating-deposition on the micro-porous substrates pre-sintered at 900 °C, and coating-substrate co-sintering at 1300 °C. The final co-sintering process ensures a strong bonding between the HA coating and the zirconia-based substrate after minimizing the mismatch in thermal expansion coefficients by adding alumina in HA coating and HA in zirconia-based substrate. The presence of porosity in the HA coating also reduces the mismatch. HA decomposition during the co-sintering process is discussed.

Keywords: Functionally graded coatings; C. Mechanical properties; D. Apatite; D. ZrO_2; E. Biomedical application

1. Introduction

Hydroxyapatite (HA), in particular HA scaffolds, have attracted increasing attention in recent years for potential bone implant applications because they are bio-resorbable and osteoactive. The key concern for such applications is the low bending strength of HA scaffolds due to their open pore structures as even the strength of dense HA is only around 100 MPa or less or about one-third of the upper bending strength limit of natural bones.[1] To overcome the concern on low bending strength of man-made HA, dense HA coatings on strong ceramic or metal substrates have been explored to combine the attractive bio-properties of HA coating with the strength of strong substrates. For instance, various coating processes including sol–gel,[2,3] laser and induction plasma,[4] slurry/suspension dipping,[5,6] thermal/plasma spray[7] and electrophoretic deposition[8] have been attempted. A sol–gel derived HA coating on a ceramic substrate is normally very thin, e.g. less than 5 μm, which limits its applications. Fully sintered zirconia and alumina have been also used as substrates in the slurry dipping or sol–gel deposition processing,[5,9,10] and decomposition of HA is not an issue as HA coating is typically formed at temperature less than 1000 °C. However, a strong ceramic bond between HA coating and dense ceramic substrate may not be achieved easily, and the coating thickness is also limited because of the fully dense substrates. Despite of the development of those compromising HA composite designs, the problem of low load-bearing capacity of HA scaffolds remains unresolved.

Pure HA has been sintered from nano-powders from 900 °C up to around 1300 °C.[11–16] Such a temperature range is also useful to nano-sized zirconia and alumina powders. For instance, the upper limit of 1300 °C can be used as the sintering temperature for nano-sized zirconia and alumina powders, and the lower limit of 900 °C can be used as the pre-sintering temperature so that pre-sintered green zirconia and alumina parts can be green machined. In fact, it has been a common practice that ultra-fine grained zirconia (3Y-ZTP) blocks pre-sintered at around 1000 °C are green-machined to the required dental crown geometries at dental labs, followed by dental porcelains coatings and final firing.[17,18]

In this study, we explore a new processing method, which can potentially combine the bio-properties of HA scaffolds and the load bearing capacity of zirconia. The method can be summarized as follows: HA coatings with graded porosity are

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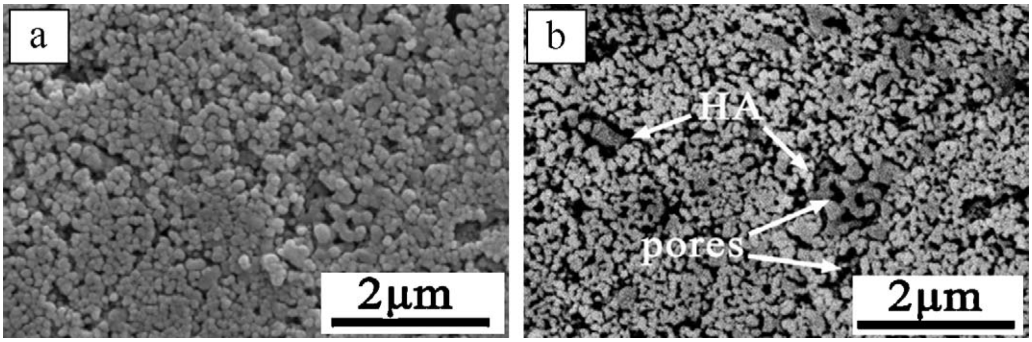

Fig. 1. Micro-porous HA-containing ZrO_2 substrate pre-sintered at 900 °C.

deposited on micro-porous zirconia-based ceramic substrates pre-sintered at 900 °C using low-density HA-slips with different material compositions and micro-pore generators. The crucial slip property is that deposited HA coating should stick to the micro-porous substrate after drying, rather than forming a separate HA layer away from the substrate as in a normal slip casting process. If the deposited HA coating layers stick to the substrate and if the mismatch in thermal expansion coefficients is sufficiently reduced, the final coating-substrate co-sintering process can potentially generate a strong bonding between the scaffold-like HA coating and the strong zirconia substrate.

Therefore, the primary objective of the present study is to develop this unique low-density HA-slip coating-deposition and coating-substrate co-sintering process so that the resultant HA composites will have micro-porous surface characteristics, similar to those of HA scaffolds, and sufficient strength from the support of strong zirconia cores. Processing issues and problems encountered during experimental trials, such as HA decomposition, will also be discussed although our main focus for this study is to produce the composites as many processing details still need to be further studied.

2. Materials and methods

The key starting materials used in this study are yttria stabilized zirconia (3Y-TZP) (TZ-3Y-E, <200 nm, Tosoh Co., Japan) and hydroxyapatite (HA) (<200 nm, Sigma–Aldrich Co., USA). According to the available information in the literature,[8,19] their thermal expansion coefficients are $\alpha_{HA} = 13.6 \times 10^{-6}$/K and $\alpha_{ZrO2} = 10.8 \times 10^{-6}$/K. Therefore, alumina ($\alpha$-$Al_2O_3$) (AKP50, purity >99.99%, <300 nm, Sumitomo, Japan) with a thermal expansion coefficient of 8.3×10^{-6}/K[17] can be used to tailor the mismatch between the HA coating and zirconia based substrate.

The substrate is zirconia with 30 vol.% HA power, formed through die pressing, then pre-sintered at 900 °C for 2 h. This pre-sintering step removes all polymer binders and additives leading to a micro-porous substrate as shown in Fig. 1. HA powers, or alternatively pre-sintered HA micro-particles, in the substrate not only help controlling the substrate micro-porosity required for the HA coating deposition, but also provide favorable bonding sites with the HA coating. The pre-sintering process also make green-machining of the substrate possible as often implants need to be machined into desired shapes. To test the feasibility of green-machining, some zirconina substrates were roughened with 600 grit SiC papers before the HA-coating deposition.

The low-density HA-slips are prepared using distilled water and HA powders together with sodium tripolyphosphate ($Na_5P_3O_{10}$) (99%) as the dispersant, silica sol (30 wt.%) and PVA solution (10 wt.%) as the binders, and ball milled for 24 h. The density of HA slips, porosity and moisture content of the pre-sintered HA-containing zirconia substrate are modified through trial-and-error so that the deposited HA coating layers stick to the substrate after drying. The moisture contained in the micro-porous substrate also influences the coating deposition process. The low density HA-slip coating-deposition and coating-substrate co-sintering process is illustrated in Fig. 2.

To test the feasibility of the current processing method for deposition of multilayered HA coatings on the strong zirconia substrate with graded composition and porosity, tri-layer HA coatings are processed. In the green body, the top layer is pure HA but with different porosity, the middle HA layer contains 30 vol.% ZrO_2, and the under layer has 16.5 vol. % of Al_2O_3. To design a graded porous structure in the HA coatings, 15 wt.%, 30 wt.% and 45 wt.% starch powders are added in the under layer,

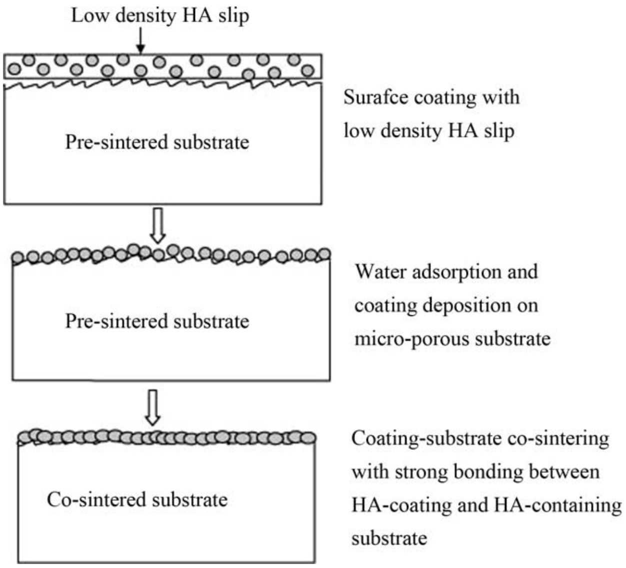

Fig. 2. Schematic diagram of the low-density HA-slip coating-deposition and coating-substrate co-sintering process.

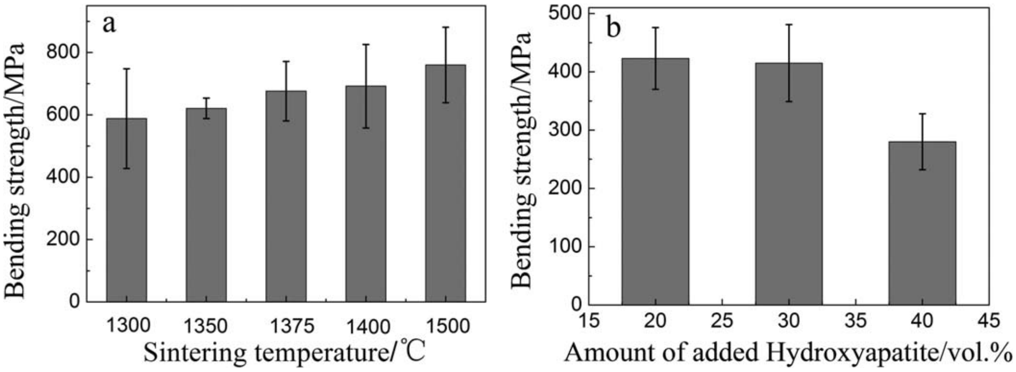

Fig. 3. Bending strengths of (a) pure 3Y-TZP versus sintering temperature and (b) 3Y-TZP with HA addition versus the amount of added HA.

middle layer and top layer respectively as the pore forming agent. The mixed slips were stirred for 10 min with a magnetic stirrer after adding starch.

The addition of alumina and zirconia in the HA coating layers is to minimize the mismatch of thermal expansion coefficients between the HA coating and ZrO_2 based substrate, e.g. following the existing methods.[20,21] From estimation, the HA-under layer close to the zirconia substrate (containing 30 vol.% of HA) should contain around 16.5 vol.% Al_2O_3. It should be mentioned that the estimation is for fully dense layered composites. The presence of porosity in the coating layers can significantly change the calculated results, and HA decomposition above 1000 °C due to the presence of ZrO_2 and Al_2O_3 has not been considered.

After preparation of the micro-porous zirconia-based substrate and appropriate low-density HA-slips, coating layers are applied on to the substrate using a soft brush, following the order of under layer, middle layer and top layer. By controlling the density of HA slips and moisture content of the substrate, the deposited green HA layers can stick to the substrate even after drying. The HA-rich coatings and substrate are dried in wet air for 24 h and in dry air for another 24 h, then finally co-sintered at 1300 °C for 2 h. The total HA-coating thickness is around 40 μm. The same sintering conditions including the peak temperature of 1300 °C are also used to sinter pure HA and zirconia samples for comparison.

The three-point-bending strengths of the 3Y-TZP-based substrates with/without HA-rich coatings and pure 3Y-TZP samples were measured with an Instron 4301 testing machine with a loading rate of 0.5 mm/min. All those samples were polished with a final surface finish of 1 μm. The sample dimension was 3 mm × 4 mm × 40 mm. The span was 20 mm. 5 tests were done for each sample. Indentation tests were also carried out along the coating/substrate interface to check the interfacial bonding condition. The selected load was 5 kg and holding time was 30 s.

To reveal the cross-section microstructures within the triple HA coatings and along the interfaces, samples were sectioned and mounted in resin, and then polished by diamond grinding plates with a final surface finish of 1 μm. Morphology and microstructure of the coating and the substrate were observed using a field emission scanning electron microscopy (FESEM) of Zeiss 1555.

3. Results and discussion

The three-point-bending test results are shown in Fig. 3. The strength of pressureless sintered pure zirconia (3Y-TZP) increases with the increasing sintering temperature. However, even at 1300 °C, pure zirconia still has a bending strength of about 588 MPa, and a zirconia-based substrate with 30 vol.% HA starting powder has a strength of about 415 MPa, which is four times of the optimum strength of around 100 MPa obtained from dense HA fully sintered at 1300 °C. The bending strength of the zirconia based ceramic composite with micro-porous HA coatings is between 350 and 425 MPa depending on the HA coating micro-structures and residual stresses in the composites. Therefore, our preliminary processing results demonstrate that the desirable combination of a porous scaffold-like HA-coating and a strong ceramic core/substrate is achievable in principle. Such a composite could be potentially used as a load-bearing bone implant if thicker HA coatings with larger open pores can be further built on the top of the existing composite system.

Fig. 4 shows a pre-sintered zirconia substrate sample with three different surface sections. Region 1 is covered by only one HA-rich coating (under layer), Region 2 is covered by two HA-rich coatings (under and middle layers), and Region 3 is composed of three HA-coatings (under layer, middle and top layers). As can be seen, all three coatings are crack free, and the third region with the triple coating layers has a rougher surface because of its more porous structure, which shows potentially

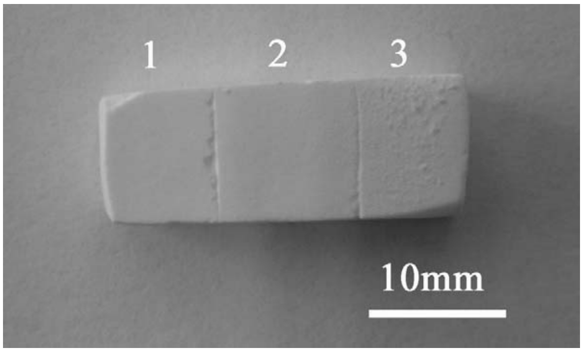

Fig. 4. Photographs of co-sintered crack free HA coatings on ZrO_2 based substrate. 1, single layer; 2, double layers; 3, triple layers.

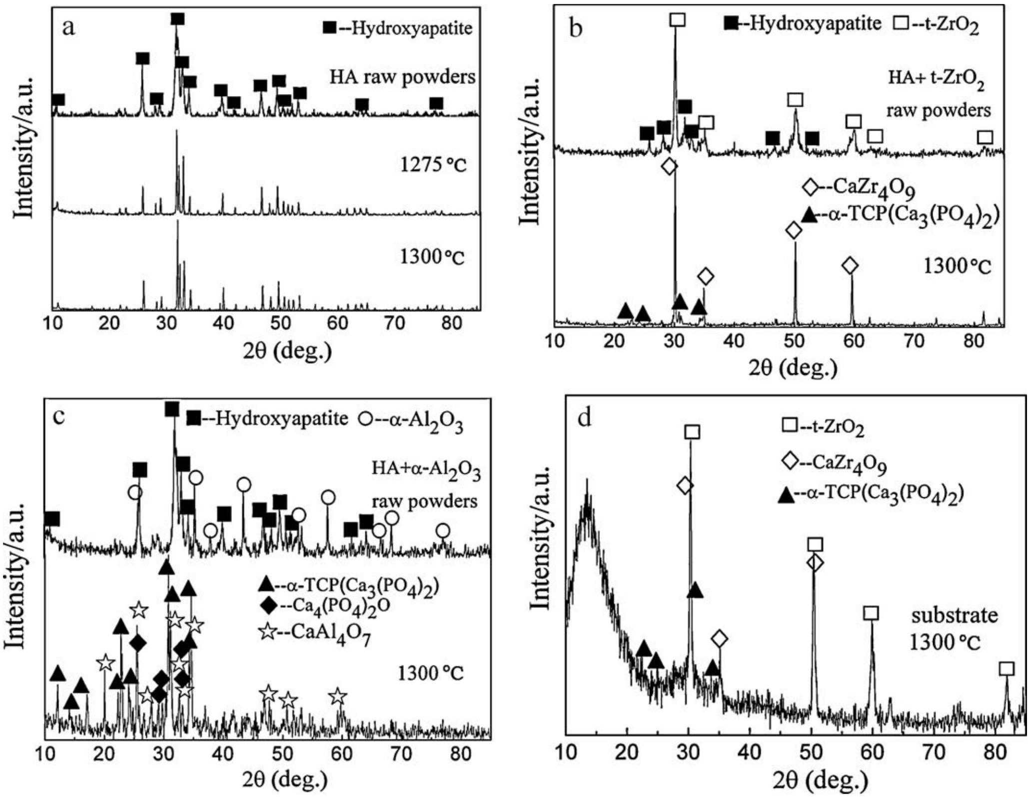

Fig. 5. XRD patterns of the triple-layer coating: (a) top layer of pure HA; (b) middle layer; (c) under layer; and (d) substrate.

much thicker HA coatings with larger open pore structures can be built on the top of it.

To understand the phase compositions of the three HA-rich coating layers and zirconia-based substrate, XRD analysis was carried out, and the results are shown in Fig. 5. It can be seen from Fig. 5(a), only pure HA can be identified in the top layer after co-sintering at 1300 °C for 2 h, as no diffraction peak of TCP can be found in the XRD pattern. The thermal decomposition or stability of HA is related to the Ca/P ratio, partial pressure of oxygen/water vapour in the sintering atmosphere, preparation method (wet chemistry or solid phase reaction), sintering additives. So the decomposition temperature is various for different commercial or in-house HA powder. Some HA powders/coatings can be thermal stable over 1250 °C or even 1300 °C in air,[6,21] the XRD result in Fig. 5(a) is consistent with those findings. This is promising as the XRD result shows thicker HA coatings with larger open pores to be deposited on the existing layered system shown in Fig. 4 can retain the pure HA after the co-sintering process.

The XRD results in Fig. 5(b) and (c) shows that the main phases of the under layer are α-TCP, TTCP, α-Al_2O_3 and $CaAl_4O_7$, and the main phases of the middle layer are α-TCP and $CaZr_4O_9$. The HA contained originally in the under and middle layer has decomposed to TCP and TTCP during the co-sintering process at 1300 °C due to the presence of alumina and zirconia. However, it should be emphasized that HA decomposition will be limited to those thin transitional layers. If it does not affect the bonding strength between the zirconia-based substrate and the top HA-coating, and if the main phases, α-TCP, TTCP, are not harmful, HA decomposition generated during the co-sintering process should not be a major concern. For instance, it has been reported that calcium phosphate bone cement con-

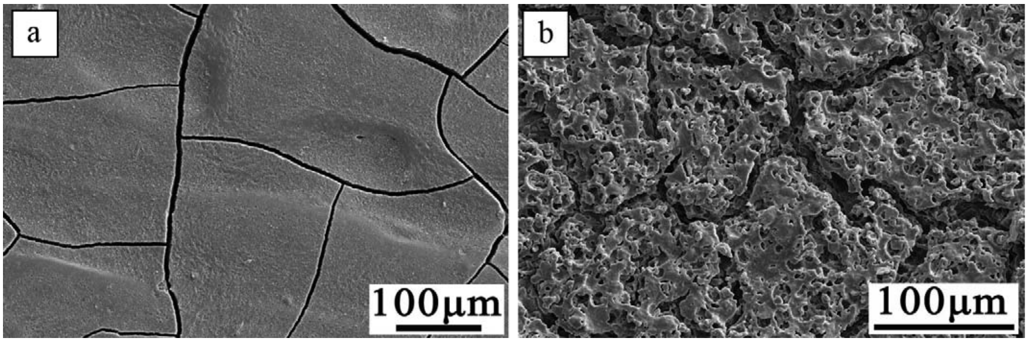

Fig. 6. Surface morphologies of cracked coatings: (a) dense green coating after drying; (b) porous finally sintered coating.

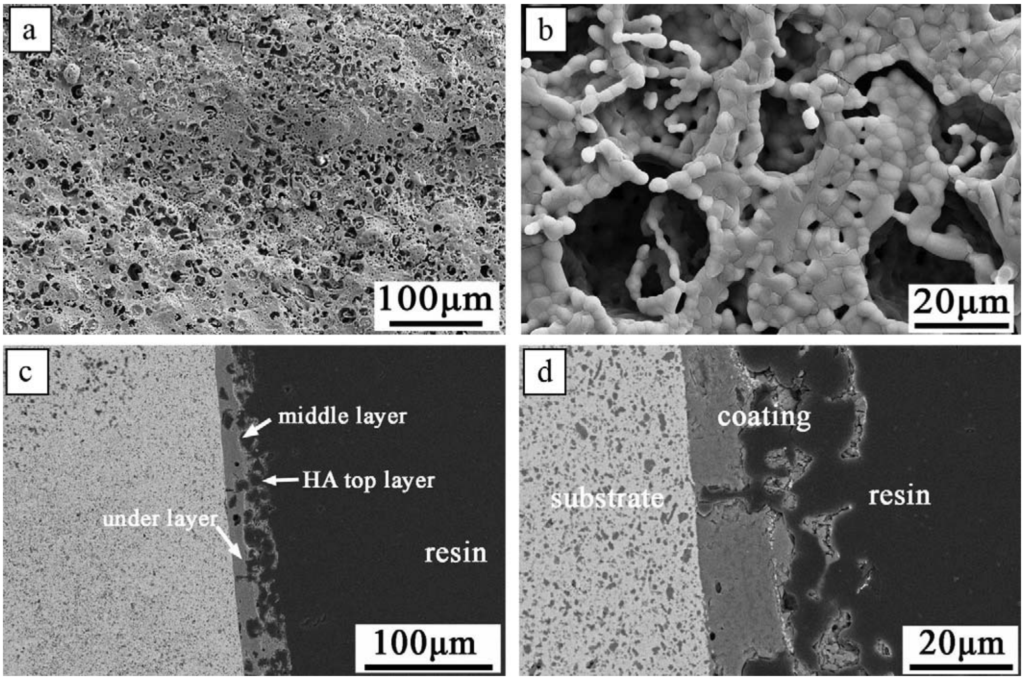

Fig. 7. As-sintered surface morphologies of crack free graded porous HA coating: (a) overview; (b) details; and side surface microstructure: (c) back scattered diffraction (BSD) image showing the overview; (d) BSD image showing the detailed porous structure and coating/substrate interface.

tains TCP, HA and other bioactive phases,[22] and that biphasic calcium phosphate ceramics consisting of HA/β-TCP or HA/α-TCP are more bio-active than pure HA alone, and the biological behavior of the biphasic ceramics is superior in new bone formation.[23]

In summary, based on the XRD results, the layered HA composite produced in this study consists of pure HA top-coating, TCP-based transitional layers, and ZrO_2-based substrate containing TCP.

Low-density water-based HA-slips are required for deposition of thin transition layers onto the micro-porous substrate, or implant core without inducing cracking at the green stage. Addition of polymer binders is necessary at this stage. To avoid cracking after the final co-sintering process, appropriate micro-porous structures need to be generated in the transition layers besides incorporating small percentage of Al_2O_3/ZrO_2 in the slip. If the density of HA based slip is or drying speed for the deposited coating is too high, crack would occur in the green body, as shown in Fig. 6(a), which may also lead to coating delamination. If delamination has not occurred even after coating-substrate co-sintering, coating-cracking in the green stage is not a major issue as in Fig. 6(b).

After the density of HA slips, the moisture content of the pre-sintered zirconia-based substrate, as well as the drying speed of the coating and the contents of polymer additives in the slips, were properly adjusted through trial-and-error, desirable HA-coating structures have been produced as shown in Fig. 7.

SEM in Fig. 7(a) shows that the coating has a crack free micro-porous surface, which potentially allows further deposition of thicker HA-coatings with large open pore structures desirable for bone replacement implants. SEM in Fig. 7 (b) shows that the open pores in the HA coating vary in size from 1 μm to about 15 μm, and there are secondary submicron pores in the HA coating. An overview of the multi-layered HA coating cross-section is shown in Fig. 7(c). The interfacial bonding between the 40 μm-thick HA coating and zirconia-based sub-

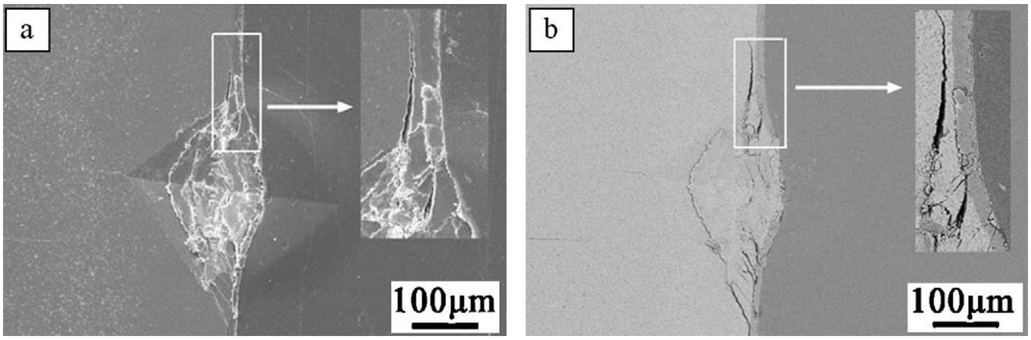

Fig. 8. (a) Secondary electron (SE2) and (b) back scattered diffraction (BSD) images showing the diamond indentation imprints along the interface of HA coating and HA containing zirconia substrate.

strate is excellent. Fig. 7(d) shows a close-up of the cross-section and its open pore structure.

Micro-indentation tests were also carried out along the coating/substrate interface to check the interface bonding condition. It can be seen from the insets of Fig. 8(a) and (b) that the indentation crack did not propagate along the coating/substrate surface, but extended within the substrate. Even after the indentation has induced extensive damage in the contact area, the HA coating is still connected to the substrate. Therefore it can be concluded that the HA coating bonds well with the zirconia-based substrate. Considering the overall good mechanical strength, bio-functions of the micro-porous HA coating and the excellent interfacial bonding between HA-coating and zirconia-based substrate, the layered HA composites provides a useable alternative as a load-bearing bone implant once thicker HA coating with larger open pores are further deposited on the system.In conclusion, this paper has shown that graded micro-porous HA-coatings can be deposited on strong ceramic substrates using our newly developed low-density slip-deposition and co-sintering process. Further work is needed if TCP from decomposition of HA at thin transition layers is concerned in terms of bio-function although our current work shows it does not influence the interfacial bonding between the HA-coating and zirconia-based substrate.

4. Conclusions

A low-density HA-slip coating deposition and coating/substrate co-sintering process has been developed and used to fabricate multi-layered HA composites consisting of micro-porous scaffold-like HA coating on strong zirconia-based substrate. While HA-decomposition indeed has occurred during the co-sintering process in the transition layers and zirconia-based substrate, the mirco-porous HA coating still bonds well to the substrate though the transition layers containing TCP. The micro-porous top-coating surface of pure HA provides a suitable base for further deposition of thicker HA coatings with larger open pores suitable for bone replacement implant applications.

The advantages of this new HA-coating deposition method can be summarized as follows. (1) The pre-sintered zirconia-based substrate can be conveniently green-machined into a desirable shape and dimension, and preparation for fixing can also be done at this stage, which is necessary for bone implants. (2) HA-coating is deposited after green-machining and fixing preparation, which provides the freedom to build scaffold-like HA-coatings with different pore structures and thicknesses at different locations of an implant. (3) Porous HA implant parts produced in this way do not have sharp edges, not desirable as implants, which however will occur if machined from common HA scaffolds fabricated by the current state-of-art solid freeform method. (4) A strong ceramic bond between porous HA-coating and strong zirconia implant core can be formed during the coating-substrate co-sintering process although HA decomposition to TCP occurs within thin transition layers. (5) Thicker HA-coatings with micro-pores larger than 100 μm required for bone replacement implants can be potentially built on the existing HA-coatings with micro-pores less than 20 μm.

It will also be useful in the future to study the possibility of stabilizing HA with addition of sintering additives or using other strong ceramics as matrix if HA decomposition should be avoided by any cost.

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