

Interface Design and Processing of Bioactive Microporous Calcium Phosphate Coatings on Load-Bearing Zirconia Substrate

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Abstract

This study presents the design and processing of interlocked interfaces of graded bioactive calcium phosphate coatings on a load-bearing zirconia substrate. Such interfacial structures can effectively enhance bonding between the coating and substrate, and suppress the residual stress across the interfacial region. Multiple coating layers with graded interconnected micropore structures, and common phases across the layer boundary have been considered to minimize the likelihood of interfacial cracking/delamination. The Focused Ion Beam (FIB) technique was used to reveal microscopic details of the interlocked interface formed by the common calcium phosphate and zirconia phases in both the microporous coating and the dense substrate. The interface microstructure and phase characteristics in the substrate and coatings were confirmed by means of FIB-SEM and X-ray diffraction (XRD) analysis respectively. A preliminary Finite Element Modelling (FEM) study shows that graded and interconnected micropore structures in multiple coating layers and tailored material composition can further reduce the interfacial residual stresses. The flexural and bonding strength of the composite and coating/substrate interface respectively have been characterized. A preliminary and limited *in vitro* cell test shows that the composite has no cytotoxicity to the fibroblasts. A successful interface design is crucial for bioceramic composite design that combines strength and bioactivity to deliver a potential candidate for load-bearing application.

Keywords: Interface design, interlocked interface processing, calcium phosphate/zirconia composite, mechanical strength, microstructure

1. Introduction

Calcium phosphate bioceramic coatings on load-bearing metal and ceramic bone implants can provide the desirable bioactivity, osseointegration and osteoconductivity^{1–6}. Hydroxyapatite/tricalcium phosphate (HA/TCP) bioceramic scaffolds have recently drawn attention for bone tissue repair application because of their bioactivity, bioreabsorbability and osteoconductivity as well as their open microporous structure, which promotes new bone growth. Unfortunately, HA/TCP scaffolds with open pores larger than 100 μm required for osteoconduction are simply too weak and brittle compared to natural bone^{7–10}. Since even the bending strength of dense HA is around 100 MPa¹¹ or only about one third of the upper strength limit of natural bone¹², significant efforts have been made to create a load-bearing bioceramic composite. Considering the bending strength limit of 300 MPa for compact bone¹², we have fabricated small, layered scaffold constructs exhibiting bending strength over 300 MPa^{13–16}.

The interfacial bonding between the coating and substrate of different ceramics has always been a concern because of the severe dissimilarity in the material compositions and physical properties, which can lead to delamination or coating fracture and thus premature prosthesis failure^{17,18}.

The interface between a bioactive ceramic coating and a strong ceramic substrate can be significantly improved if a strong chemical or ceramic bond can be generated at the interface during a coating-substrate co-sintering process. However, residual stresses are also generated during the co-sintering process owing to differences in the material compositions, layer structures and thermal expansion coefficients, i.e. porous calcium phosphate coating and dense zirconia substrate. This can cause cracks and delamination along the coating/coating and coating/substrate interface. We tested the feasibility of coating-substrate co-sintering, and microporous calcium phosphate coatings successfully deposited on strong zirconia-based substrates by means of a low-density coating-slip deposition process, followed by coating-substrate co-sintering^{13–16}.

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The objective of this study is to process an interlocked interface and investigate material composition and microstructure details across the interface between a microporous coating and load-bearing substrate. Besides the multiple coating layers with graded microporosity, an interlocked boundary across the microporous coating and load-bearing substrate are also investigated. Such an interface design can significantly improve the coating-substrate bonding strength, and reduce the residual stresses caused by the inevitable mismatch in the coefficient of thermal expansion (CTE) and Young's modulus. Therefore, this study pays special attention to the major material phase compositions and microstructure characteristics across the coating-substrate interface. FIB in conjunction with Scanning Electron Microscopy (SEM) was used to examine microstructural details around the interface. A preliminary FEM was performed to understand the effect of graded microporosity and the tailored CTE on the interfacial residual stresses. The graded porous structure of the coating and coating/substrate interface were characterized and preliminary analyses of the bending strength of the composite, bonding strength of the coating/substrate interface and a preliminary *in-vitro* biocompatibility test were conducted to prove the suitability of the proposed composite as a load-bearing bio-implant material.

II. Processing of Microporous Coating/Substrate Interface and Interface Microstructure Design

(1) Material composition and microstructure design for strong interface

A porous ceramic coating and load-bearing dense ceramic substrate with different material compositions and different microstructures have different shrinkage rates when they are co-sintered together from the green state. Furthermore, residual stresses arise owing to the mismatch in the CTE and Young's modulus, which can easily lead to interfacial cracking/delamination between the microporous coating and substrate. Common material phases across the layer-interface and multi-coating layers with graded micropore structures are proposed to promote interfacial bonding on the basis of an interlocked boundary.

Fig. 1(a) illustrates the process for deposition of a microporous hydroxyapatite coating on a zirconia substrate by means of the low-density-slip deposition and co-sintering technique^{13–16}. The slip, consisting of HA powder, polymer particles, water and additives, is applied onto the pre-sintered microporous zirconia-based substrate. Unlike in traditional slip casting, the slip containing the polymer additives is designed to stick onto the microporous substrate after drying. The thermal expansion co-efficient mismatch of the substrate and coatings was reduced by estimating different material compositions for the substrate and coatings, so that after co-sintering they can potentially generate a crack- and delamination-free interface. The addition of alumina and zirconia in the HA coating layers and HA to zirconia substrate was intended to minimize the mismatch of thermal expansion co-efficient between the HA coating and zirconia-based substrate. The density of HA slips, moisture content of the substrate, drying speed of the green coating and control of polymer addition were modi-

fied based on trial and error so that the deposited HA coatings stick to the substrate after drying. Several trials were conducted before a successful green coating was obtained that would stick to the substrate. If the density or drying speed is too high, the green coating cracks, which may lead to coating delamination.

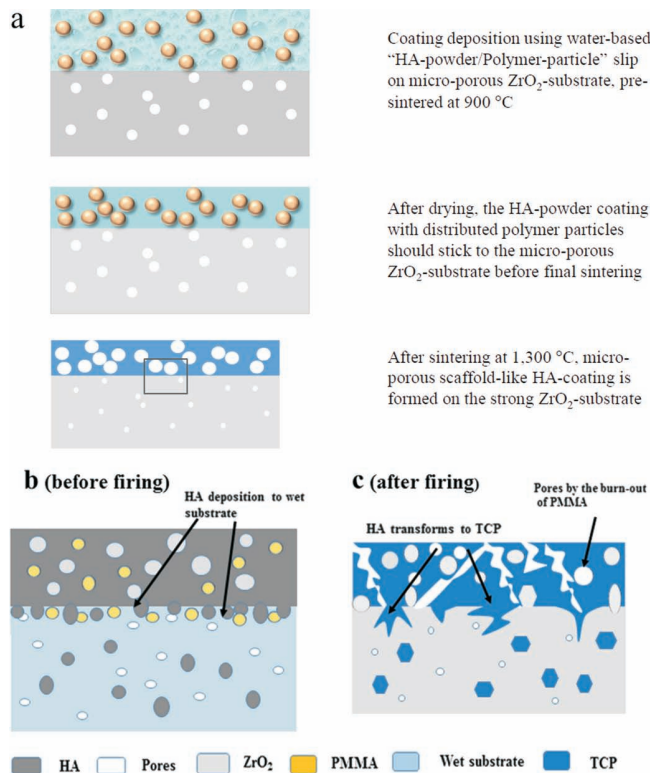


Fig. 1 (a): Deposition of microporous HA/TCP coating on zirconia substrate with low-density slip deposition and co-sintering technique; (b) Deposition of water and HA slurry with pore-forming agents into the microcavities of the pre-sintered wet substrate; (c) Enlarged sketch of the interfacial section encircled in (a) showing a “blurred” or “graded” coating-substrate interface from infiltration of micropores and material compositions across the interface to form mechanical interlocks after sintering at 1300 °C.

The final co-sintering process generates the micropore structures in the HA coating by burning out the polymer particles. Strong chemical interfacial bonding between the HA/TCP coating and zirconia substrate is expected based on the same decomposed phase diffusion along the interface after co-sintering at 1300 °C.

However, special attention is still needed at the interface between the HA/TCP coating and zirconia substrate. The interface region encircled in Fig. 1(a) is enlarged and illustrated schematically in Fig. 1(c). A “graded” or “blurred” interface should also be considered, besides graded HA/TCP coating layers.

Fig. 1(b) illustrates the deposition of the HA slurry into the microcavities of the roughened pre-sintered wet surface before sintering. The pre-sintered substrate was roughened with sand paper for better deposition of the coating slurry and substrate was brushed with water to wet it. The preliminary water deposition into the cavities of the pre-sintered porous substrate allows the solid contents of coating slip filling into the surface microcavities to form a

micro-mechanical interlocked coating-substrate interface with micro-asperities/retentions during co-sintering.

In Fig. 1(c), the HA/TCP coating contains a small amount of zirconia phase (grey area) and the zirconia substrate is incorporated with TCP (blue area), which leads to the “blurred” interface for strong ceramic interfacial bonding. After sintering at 1300 °C, HA transforms into TCP.

(2) Material composition design for coating, transition layer and substrate

The main starting materials used in this study include yttria-stabilized zirconia (3Y-TZP) (TZ-3Y-E < 200 nm, Tosoh Co., Japan), hydroxyapatite (HA) (< 200 nm, Sigma-Aldrich Co., USA), and alumina (α -Al₂O₃) (AKP50, purity > 99.99 %, < 300 nm, Sumitomo, Japan). Polyvinyl alcohol PVA (9 wt%) was used as binder. Starch powders, rice flour, pre-sintered micro-HA particles, and PMMA particles (20–50) μ m, Sigma Aldrich Co. USA) were used as micropore-forming agents in the HA coating.

A number of processing procedures is employed to reduce the residual stresses and to obtain a crack-free interface. Firstly, the coating is deposited in a multilayered fashion with graded composition and porosity and it has been shown previously that this technique assists with the reduction of residual stresses and achieving a delamination-free substrate/coating interface¹³.

In order to minimize the CTE and residual stresses between the micro-porous HA/TCP-coating and load-bearing zirconia-substrate, a thin transition coating layer with compromising micro-pore structures and material compositions is introduced. The final design of the material compositions of top coating layer, transition coating layer and substrate also reduce the mismatch in CTE and Young's modulus.

Although there were chemical reactions between HA and alumina or HA and zirconia and the presence of different micropore structures, CTE of the composite coating and substrate can only be estimated by using the following simplified relations of Turner Model^{19–21} in Eq. (1)

$$\alpha_c = \frac{\alpha_m E_m V_m + \alpha_p E_p V_p}{E_m V_m + E_p V_p} \quad (1)$$

where α , E and V represent the CTE, Young's modulus and the volume fraction of the matrix (m) and the secondary particles (p). The Young's moduli of HA, α -Al₂O₃ and ZrO₂ (3Y-TZP) are available in the literature, i.e. $E_{HA} = 100$ GPa²², $E_{Al_2O_3} = 401$ GPa²³ and $E_{ZrO_2} = 222$ GPa²⁴. The CTE values of the composite coating and substrate calculated with Eq. (1) are listed in Table 1. These values were calculated before the co-sintering process. The compositions of the coatings and substrate were estimated to reduce the CTE mismatch between the HA coating and zirconia-based substrate. From estimation, the transition layer close to the substrate (zirconia containing 30 vol% HA) has 10 vol% Al₂O₃. It should be mentioned that the estimation was for fully dense layered composite. The presence of porosity in the coating layers can significantly change the calculated results. Porosity in coating layers is another influencing factor, not expressed by Eq. (1), is considered experimentally based on trial and error. The HA

decomposition above 1000 °C in the presence of Al₂O₃ and ZrO₂ has not been considered.

After the coating process, thermal and intrinsic residual stresses are generated inevitably owing to significant mismatch of the CTE and Young's modulus of the coating and the substrate. Different processing techniques are employed to reduce residual stresses and to obtain a crack-free coating/substrate interface. Additionally, HA is added in the substrate and ZrO₂ in the transition coating layer, TCP can form in the composite, thus improving the substrate-coating bonding. The presence of porosity and common phase TCP diffusion between the coating and substrate interface reduces the CTE mismatch.

The zirconia-substrate is composed of 70 vol% ZrO₂ and 30 vol% HA. The substrate was pre-sintered at 900 °C¹³. The slip for the transition coating layer, consisting of 70 vol% HA, 20 vol% ZrO₂, 10 vol% Al₂O₃, and 10 wt% starch, was introduced between the microporous HA-coating and porous zirconia-based substrate. 300 wt% of water as solvent, 5 wt% of polyvinyl alcohol (PVA) solution ($C = 9$ wt%) as polymer binder and 0.5 wt% of Dolapix as dispersant were added to form the HA-coating slip for the transition layer and was ball-milled for 24 h before application to the substrate. The substrate was roughened with SiC paper and was wetted with a brush for better deposition of the coating slip. The substrate was pre-sintered at 900 °C for 2 h. The pre-sintered substrate is microporous¹³. The pre-sintering process used in this study is new and unique. The pre-sintering process makes green machining or roughening of the substrate possible. Surface roughness improves the mechanical interlocking of the coating³⁷. The roughened cavities and porosity provide favourable sites for bonding with the HA coating. The coating slurry gets into the cavities created by roughening and pores during deposition. As a result, the HA particles with additives get into the substrate. After drying and chemical reaction during sintering, these cavities and pores become bonding sites for the coating. After sintering and chemical reaction, HA transforms to TCP. The TCP from coating diffuses to the substrate and zirconia from substrate diffuses to the coating. These diffused sites can work as bonding sites and interlock the coating with the substrate. As a result, the coatings become interlocked with the substrate. The moisture contained in the coating influences the deposition process. That is why the substrate was wetted prior to coating slurry deposition.

The substrate with the transition coating was dried for 24 h and pre-sintered again at 900 °C. Finally, the slip for the green HA-coating contains 90 vol% HA, 10 vol% Al₂O₃, 10 wt% starch, 30 wt% PMMA and 15 wt% rice flour as pore-forming agents. The top coating slurry was also ball-milled for 24 h before being applied. After the top HA coating had been applied with a soft brush, the green top coating was dried for another 24 h and the coating/substrate composite was pre-sintered at 900 °C before it was finally co-sintered again at 1300 °C. 10 wt% and 25 wt% starch powder is added to the transition coating and top coating respectively to improve the overall interconnectivity of the coatings.

Table 1: CTEs of HA, zirconia, alumina, HA top coating (with 10 vol% alumina), transition layer (with 20 vol% zirconia and 10 vol% alumina) and zirconia substrate (with 30 vol% HA).

Materials /composites	HA	Zirconia (3Y-TZP)	Alumina (α -Al ₂ O ₃)	HA top coating (with 10 vol% alumina)	HA transition layer (with 20 vol% zirconia and 10 vol% alumina)	Zirconia substrate (with 30 vol% HA)
Coefficient of thermal expansion (CTE) (10 ⁻⁶ /K)	13.6 [21]	10.8 [22]	8.3 [23]	12.0–12.9	11.7–12.2	11.3–11.6

The optimal processing procedures employed in the production of final composite have been identified on the basis of trial and error.

(3) Phase composition, sample preparations, and microstructure characterization

The phase change of the coating layer after heat treatment was characterized using X-ray diffraction (Siemens D5000 diffractometer, Munich, Germany) using CuK α ₁ radiation at a scanning rate of 1.2°/min. The sample used for XRD is a bulk composite with coating.

Two different types of coating-substrate samples were prepared. Samples for a large cross-section overview have thicker calcium phosphate coatings (around 160 μ m), as the coating thickness is not a concern for mechanical sectioning and polishing. Samples for delicate Focused Ion Beam (FIB) milling/cutting need to have thinner coatings (around 30 μ m) so that the coating-substrate cross-section can be exposed in a reasonable time frame. However, the material compositions for all coating layers were kept constant for all samples, despite the variation in the coating thickness.

For analysis of the coating/substrate interface microstructure, the samples were embedded in the resin (Epofix epoxy, Struers A/S, DK-2750 Ballerup, Pederstrupvej84, Denmark) and polished with diamond grinding plates with a final size of 1 μ m. The resin embedding was necessary to preserve the porous structure during sectioning and polishing¹⁵. A large-scale porous cross-section was observed by means of Field Emission Scanning Electron Microscope (FESEM) Zeiss 1555 (Oberkochen, Germany). Focused ion beam-scanning electron microscopy (FIB-SEM) (FEI Helios Nano Lab Dual Beam, Hillsboro, Oregon USA) was used to characterize the inner interface microstructure details. The cross-sections of the coatings on the zirconia-based substrate were prepared using the Ga⁺ ion beam at 30 kV and 21 nA to cut the holes, with cleaning of the section face done at 30 kV with 6.5 nA current.

(4) Interfacial residual stress analysis with 2-D finite element modelling

Preliminary and limited 2-D Finite Element Modelling (FEM) was performed to understand the residual stress along the “clear” interface between the porous HA coating and dense zirconia substrate with big mismatches of CTE and Young’s modulus. Three plane FE models were built

for analysing the effect of different coating porosity (no porosity, uniform large porosity and gradient porosity) on the interfacial residual stress. Half models with symmetrical boundary conditions were used. The properties of HA and zirconia were $\alpha_{\text{HA}} = 13.6 \times 10^{-6}/\text{K}$ ²³, $\alpha_{\text{ZrO}_2} = 10.8 \times 10^{-6}/\text{K}$ ²⁴, $E_{\text{HA}} = 100 \text{ GPa}$ ²⁵, and $E_{\text{ZrO}_2} = 280 \text{ GPa}$ ²². A thermal loading of -1280 °C was carried out to simulate the cooling from 1300 °C to 20 °C.

A 4-node bilinear axisymmetric quadrilateral, reduced integration, hourglass control element of (type CAX4R in Abaqus) is used. The total number of elements used for modelling is 14 480. The mesh density near to the interface between HA and zirconia is very high to resolve the thermal stress distribution accurately. Symmetry boundary condition is used on the left-hand side, which reduces the number of elements and computational time. All the other sides (top, bottom and right-hand) are kept free so that the stress can be developed accurately at the interface between HA and zirconia without any boundary effect. The initial temperature of both materials is set to 1300 °C. They are allowed to cool down at 20 °C (room temperature). The simulation is performed for 1 day. This time is enough to make sure that the system is in thermal equilibrium at the end of the simulation.

(5) Characterization of mechanical properties

The load-bearing capacity of the calcium phosphate and zirconia composite was measured in a three-point bending (3-p-b) test. A total of five samples (3 mm $\times$ 4 mm $\times$ 40 mm) were tested in 3-p-b using an Instron 4301 testing machine (Instron Company, Norwood, MA 02062–2643, USA). The crosshead speed was 0.5 mm/min and the jig span was 20 mm. All the coating-substrate faced the loading roll and the coating faced the spanners. For control, we used five samples identical in size which consisted only of the substrate (ZrO₂ + 30 vol% HA) without the porous coating.

The coating/substrate tensile adhesion tests were conducted in compliance with the method given in ASTM C633–01. The size of the five square samples was 15 mm $\times$ 15 mm $\times$ 3 mm. Two steel rods with diameters of 10 mm were made for connecting the sample and testing machine fixture. Araldite super strength A & B glue was used as bonding agent, which can reach maximum strength after 24 h. The steel rods with sample adhering to them were pin-fixed into the testing machine, which provided a self-

aligning function. The loading speed was 0.1 mm/min. Five tests were performed on the sample with double-layered coatings. The bonding strength is calculated based on the maximum load/contact area. In order to check the coating/substrate interfacial bonding condition and the microstructure of the coating, the fracture surface resulting from bonding strength test was observed with SEM.

(6) In-vitro cell test

A preliminary *in vitro* cell test was also conducted to investigate if the porous scaffold-like coating has any cytotoxicity and whether cells can attach, proliferate and grow on the coating surfaces. This test was employed because some other minor phases besides the TCP main phase are contained in the coating, the effect of which cannot be predicted for the amount resulting from processing on the cells.

More details of the *in-vitro* test are given in our previous paper¹⁵.

III. Results and Discussion

(1) Large overview of the coating-substrate cross-section and coating surface

Based on the above-graded interface composition and microstructure design illustrated in Fig. 1(c), microporous calcium phosphate coatings were successfully fabricated on zirconia-based substrate in a newly developed low-density-slip coating-deposition and coating-substrate co-

sintering process. The well-polished cross-section was observed with SEM to pre-check the coating/substrate interface structure. Figs. 2(a and b) clearly show the coating is composed of two layers varying in thicknesses and porosity. The 10- μm -thick transition coating layer has micropores smaller than 10 μm in diameter. The top coating layer has a thickness of around 150 μm with hierarchical porosity, the larger pores in the top coating ranging from 20 μm to 150 μm . Figs. 2(a) and 2(b) show that the coatings are crack-free and with an open gradient architecture. Fig. 2(c) presents the as-sintered surface microstructure of the porous coating. The connecting part of the bigger pores possess a micro-sieve structure with 1–3- μm pores generated from HA decomposition to form TCP with gassy water release and the sintering of HA micro-particles^{14, 15}. Considering the size of the pores, the SEM observation indicates that the larger pores result from PM-MA particles and rice flour burnout whereas the smaller ones and the micro-sieve structure are mainly derived from starch powder and HA particles sintering. An SEM close-up overview of the double-layered TCP-based coating cross-section is shown in Fig. 2(d). The coating shows the two layers, with the top coating consisting of TCP, whereas the transition coating contains ZrO_2 and Al_2O_3 (white phase). The main phase in the transition coating is TCP (grey phase). The black phase is the resin that flows through the interconnected pores when the sample is embedded in the resin.

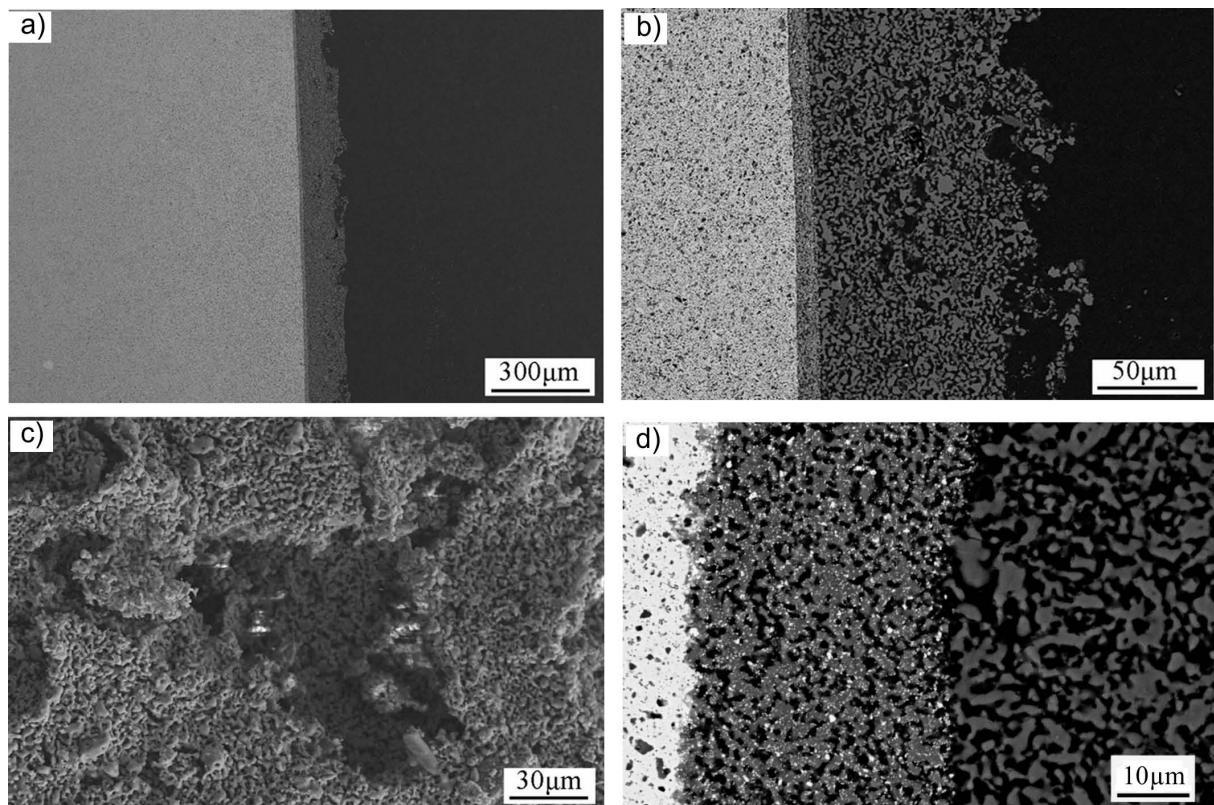


Fig. 2 (a): Overview of a polished TCP-coating/zirconia-substrate cross-section; (b) Higher-magnification view of the encircled area in (a) showing a 10- μm -thick transition layer between the TCP coating and zirconia-substrate, and larger pores in the top TCP coating layer that were created by burnout of rice flour particles; (c) as-sintered surface of the TCP coating, showing bigger pores from burnout of rice flour particles and micro-sieve structures of TCP-coating with micropores around 3 μm ; (d) Close-up cross-sectional view of the substrate/transition coating/top coating interface.

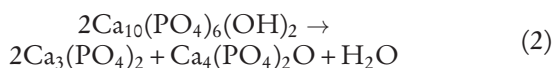
The open porous structure with good interconnectivity in bone implants is believed to have a notably positive effect on the osteoconductivity and bone in-growth rate^{26–28}. Woodard *et al.*²⁹ also demonstrates that the hierarchical microporosity might be helpful for implant material to increase osteoconductivity required for bone regeneration. In addition to the porous structure in the coating, the interfacial bonding condition is the other big concern for the coating-substrate composite implants. The large overview of the cross-section and direct observation indicates that the interfacial bonding between the coating and the zirconia substrate is excellent as there is no delamination and cracking along the 1.2-mm-long interface.

(2) Material compositions in adjacent layers and interfacial chemical bond

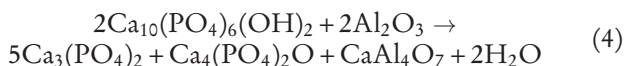
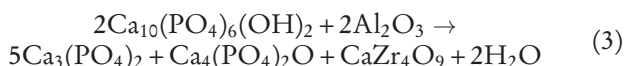
Sections of the same material compositions across the interface of two adjacent ceramic layers can form a strong chemical bond during the sintering process, leading to the *in-situ*-formed micro mechanical interlocks across the interface. As a result, the previously distinct interface formed from the coating deposition process becomes “blurred”, or the interface is graded or “smeared”.

XRD analysis shows the phase composition of the TCP-rich coatings and the substrate. In the top coating, the final phases are TCP, TTCP ($\text{Ca}_4(\text{PO}_4)_2\text{O}$), $\alpha\text{-Al}_2\text{O}_3$ and CaAl_4O_7 (Fig. 3a). In contrast, the transition coating phases are TCP, TTCP ($\text{Ca}_4(\text{PO}_4)_2\text{O}$), ZrO_2 , CaZr_4O_9 and CaAl_4O_7 (Fig. 3b). The main phases in the substrate are ZrO_2 , TCP and CaZr_4O_9 (Fig. 3c).

HA can decompose to form TCP and TTCP when subjected to temperatures over 1350 °C as illustrated in Eq. (2) below. Some of the TCP and TTCP can be rehydrated to HA when the sintering temperature is lowered below 1100 °C. The detailed phase transformation process is reported elsewhere^{30,31}.



Because zirconia and alumina promote the decomposition of HA at the temperature below 1300 °C, the reactions can be described by means of the following equations¹⁵.



In our samples, we could not trace HA in the sintered coatings. The common phases in different layers promote strong interfacial bonding formed through sintering.

(3) Observation of interfacial microstructures using FIB-SEM

FIB is able to rapidly prepare site-specific cross-sections through coatings by sputtering, avoiding detrimental processes associated with mechanical polishing such as deformation, smearing and the closing of the existing cracks by abrasion. In this study, we used the FIB-SEM technique to analyse the interfacial bonding state and detailed interface structure. The specimen is milled using the ion beam and tilted to an angle ($\theta = 52^\circ$) so that the newly created surface can be imaged.

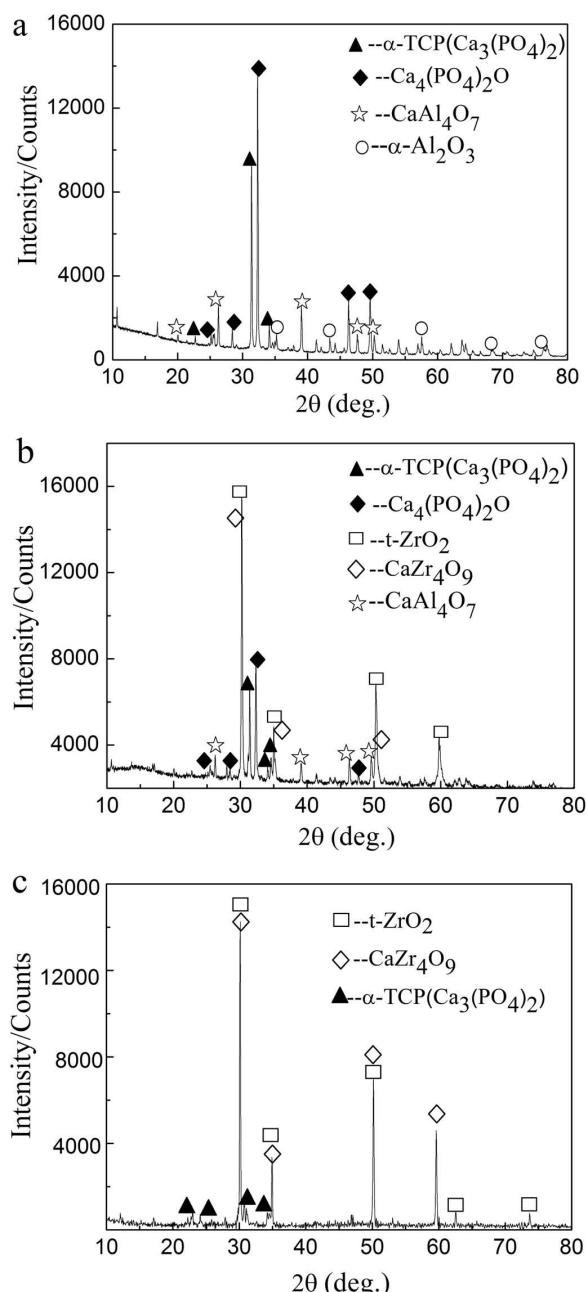


Fig. 3: XRD patterns showing the phase compositions of (a) top coating, and (b) transition coating and (c) the substrate.

After FIB milling, the coating-substrate interface and coating interior are exposed for direct SEM observation, as shown in Fig. 4(b). The strong ceramic bonding was achieved along the coating-substrate and transition-top coating layer interface, which is distinctly supported by the magnified images and close-ups shown in Figs. 4(c)-(f). The HA in the substrate and coating has transformed to TCP after final sintering, as indicated in XRD analysis, which is not harmful to the mechanical properties of the composite, but beneficial to forming a strong ceramic bonding interface. The inter-diffusion of the common TCP (blue zone) and zirconia (grey zone) phases in the coating and substrate makes a significant contribution to the strong interfacial bonding, which is highly aligned with the sketch presented in Fig. 1(c). The microporous structure of the coating is helpful for releasing the residual stress along the interface to reduce the likelihood of interfacial-cracking/delamination.

The TCP and zirconia phases provide strong ceramic bonding sites and micro-mechanical interlocks at the interface between the substrate and transition coating layer, as shown in Fig. 4(f). It is proven that the macro- and micro-mechanical interlocked structures at the interfaces of layered composite biomaterials could improve the interfacial bonding quality and overall mechanical properties, e.g. tensile strength³². For the presented coating-substrate composite, the interfacial micro interlocks are joined by mechanical bonding and strong ceramic bonding generated from the inter-penetration and inter-diffusion of the common phases in the coating and substrate during final co-sintering. The interfacial residual thermal stresses are reduced, which increases interfacial bonding without any delamination. The actual micropores/material distribution in the coating and substrate are close to the interface, consistent with the design sketch shown in Fig. 1(c). Fig. 4(c) shows that the transition and top coating layer bond quite well since they have the main common phase of TCP. The multi-coating layers with graded micropore structures and common materials of TCP and zirconia across the layer-interface make the coating-substrate interface microstructure more blurred to form a strong interfacial bond, avoiding the interfacial-cracking/delamination. In addition to the excellent adhesion to the substrate, the presented coating has submicron/nanopores (Fig. 4(d) and (f)) resulting from the transformation of HA to TCP during the sintering process, accompanied by gassy water release and burnout of the starch powder^{14,16}. It is demonstrated that nanoscale surface features of implant materials are promising to enhance the tissue regeneration capacity^{33,34}. The micropores connect to each other to increase the interconnectivity and form longer channels to potentially assist cell migration in enhancing osseointegration and bone regeneration.

(4) Effect of porosity on residual stresses at interface from numerical simulations

Fig. 1(c) proposes a graded microstructure for the coating to improve the interfacial bonding quality and avoid interfacial-cracking/delamination by reducing the residual thermal stress at the coating-substrate interface. Snapshots of the interfacial opening stress are shown in Fig. 5.

The maximum residual stress (Table 2) at the interface decreases from 527 MPa for sample without porosity to 503 MPa and 414 MPa respectively for samples with uniform and gradient porosity, whilst the interfacial shear stress exhibits a similar trend. The FEM results indicate that the distribution of porosity, which could be highly reduced by gradient porosity in the coating, is one of the dominating factors in the development of residual stress at the interface after heating and cooling.

(5) Interfacial residual stress between composite coating and substrate with tailored CTEs

For the material design of presented coating-substrate composite, the zirconia substrate contains 30 vol% HA before final sintering, and the HA transition coating is incorporated with 20 vol% zirconia and 10 vol% alumina, which notably increases the similarity of the CTE and Young's modulus between the coating and substrate to

make a more "blurred" interface. The interfacial residual stress is reduced owing to reduced mismatch of CTE and Young's modulus between the coating and substrate. Based on the FEM results the interfacial residual opening stresses along the graded interface decrease notably to 37.9 MPa, 36.2 MPa and 29.8 MPa from 527 MPa, 503 MPa and 414 MPa, respectively for the coatings without porosity, with uniform porosity and with graded porosity for the composite coating and composite substrate (Table 3). With the combination of FEM results and thermal expansion coefficient estimation for the composite coating and substrate, it can be concluded that the interfacial opening stress could be greatly reduced by the similar composition of the coating and substrate with tailored CTEs, as well as the graded porosity of the coating. Strong interfacial bonding between the microporous HA/TCP coating and porous zirconia substrate is achieved by the "blurred" interface composition and microstructure design. Although in our case, HA is transformed into TCP after sintering at 1300 °C, the direct observation of the coating/substrate interface in Fig. 2 proves that the coating/substrate interface is free from cracks and delamination. The combined contribution of porosity, graded porous coating architecture, transformation of HA to TCP, tailored CTEs of the graded coating, and common phase diffusion reduces the interfacial stress (Fig. 5) and creates a crack- and delamination-free interface.

Table 2: The maximum interfacial opening stress and shear stress values for pure HA coating on pure zirconia substrate.

Samples with various porosity	No porosity	Uniform large porosity	Gradient porosity
Interfacial opening stress (MPa)	685	654	538
Interfacial shear stress (MPa)	181	153	160

Table 3: The maximum interfacial opening stress and shear stress values for HA composite transition coating (with 20 vol% zirconia and 10 vol% alumina) on zirconia composite substrate (with 30 vol% HA).

Samples with various porosity	No porosity	Uniform large porosity	Gradient porosity
Interfacial opening stress (MPa)	37.9	36.2	29.8
Interfacial shear stress (MPa)	2.0	5.5	6.8

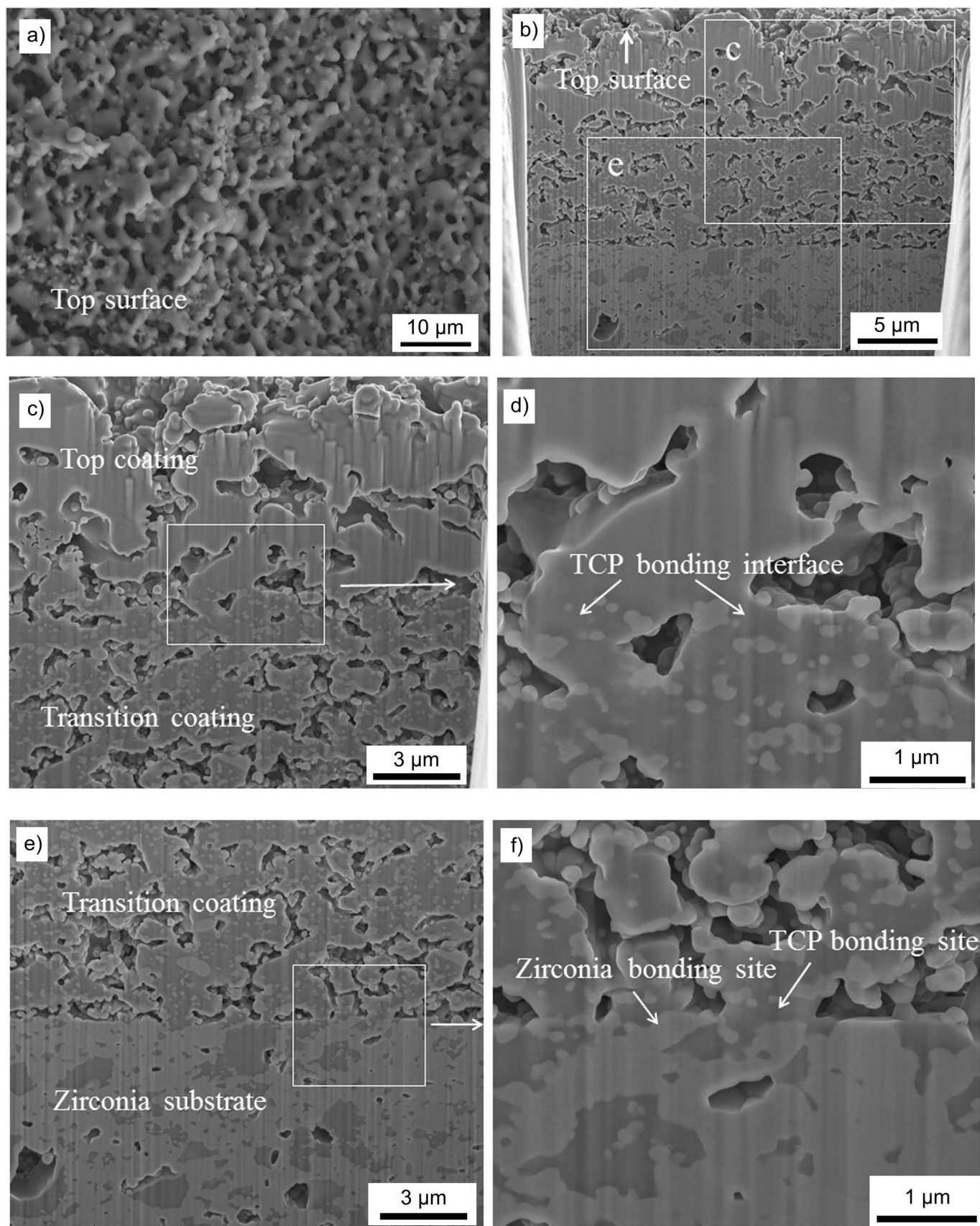


Fig. 4: FIB-SEM micrographs showing interfacial microstructure between the TCP-rich coating/TCP-containing zirconia substrate: (a) as-sintered microporous TCP coating surface selected as FIB milling area; (b) exposed coating/substrate interface after FIB cutting, as in Fig. 3 (b); (c) Enlarged view of the interface between the microporous top and transition TCP coating layers; (d) Close-up of the rectangle area in (c) showing the TCP ceramic bonding interface; (e) Enlarged view of the interface between the transition coating and zirconia matrix substrate; (f) Close-up of the rectangle area in (e) showing TCP/zirconia ceramic bonding sites along the coating-substrate interface, and the micropores/material distribution in the coating and substrate close to the interface, corresponding to Fig. 1(c).

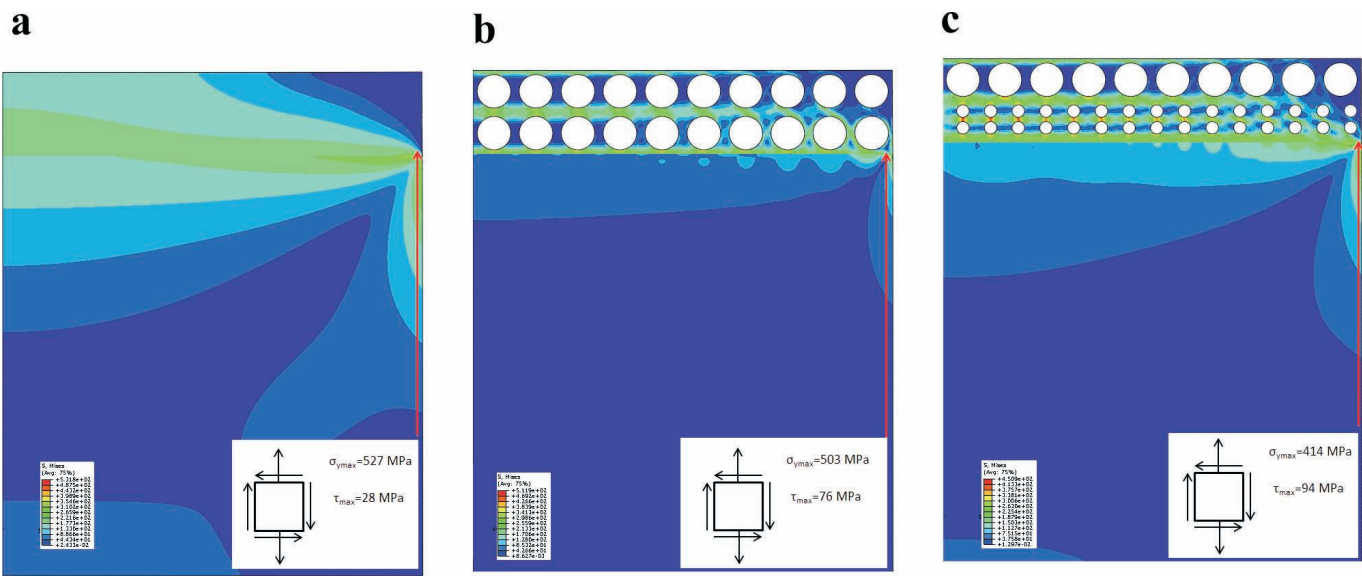


Fig. 5: Finite element modelling image of thermal-residual stress for pure HA coating on zirconia substrate (a) without porosity; (b) with uniform and large porosity; (c) with gradient porosity.

Table 4: Flexural strength results of the composite with and without the coating.

Samples		Bending Strength (MPa)				Average (MPa)	SD (MPa)
Substrate without coating	488	415	426	410	490	445.8	39.87
Substrate with coating		468.23	473	557.26	393.41	510	480.4
							60

(6) Mechanical testing of the coating/substrate composite

The 3-p-b test showed that the coating/substrate composite has the bending strength of 480.8 ± 60 MPa. The average bending strength of the zirconia-based substrate without coating is 446 ± 39.87 ¹⁴. After coating deposition and co-sintering, the HA/TCP-containing zirconia substrate with scaffold-like HA/TCP coatings has bending strength between 393 and 557 MPa, depending on the coating thickness and microstructure and the residual stresses within the composites. Table 4 shows the flexural strength results of the composite with and without the coating.

The bonding strength of the TCP coating and zirconia-based substrate interface was 24 MPa. From the SEM image in Fig. 6, it is clear that there is a mixed mode of failure. Cohesive failure happens within the coating layers and adhesive failure along the coating-substrate interface. In Fig. 6, the white area is the substrate (adhesive failure) and the grey area is the TCP coating (cohesive failure). Cohesion failure indicates that the obtained results are not the actual adhesion strength between the coating substrate interfaces ³⁵. Also, the adhesion failure area is less than the cohesive failure area, which indicates that the substrate/transition coating interface is stronger than the value measured. For the sample with double TCP-rich coating layers, the fracture took place within the top coating because it is more porous and weaker than the transition

coating. For the sample with only the 10-μm-thick transition coating layer, the fracture still mainly occurred within the coating and partially at the coating-substrate interface, as shown in Fig. 6 (white area is the exposed substrate). This indicates that interfacial bonding strength between the presented microporous TCP coating and zirconia-based substrate is higher than the values measured.

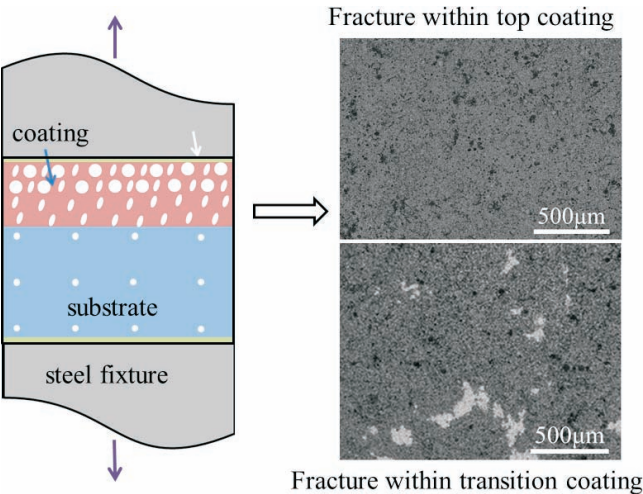


Fig. 6: Sketch of coating adhesion tests, and typical SEM image of the fracture surface that occurred in the top TCP-coating layer containing larger micropores (cohesive failure), and failure close to the coating-substrate (lighter phase) interface for adhesion tests with only the 10-μm-thick transition layer containing smaller micropores (adhesive failure).

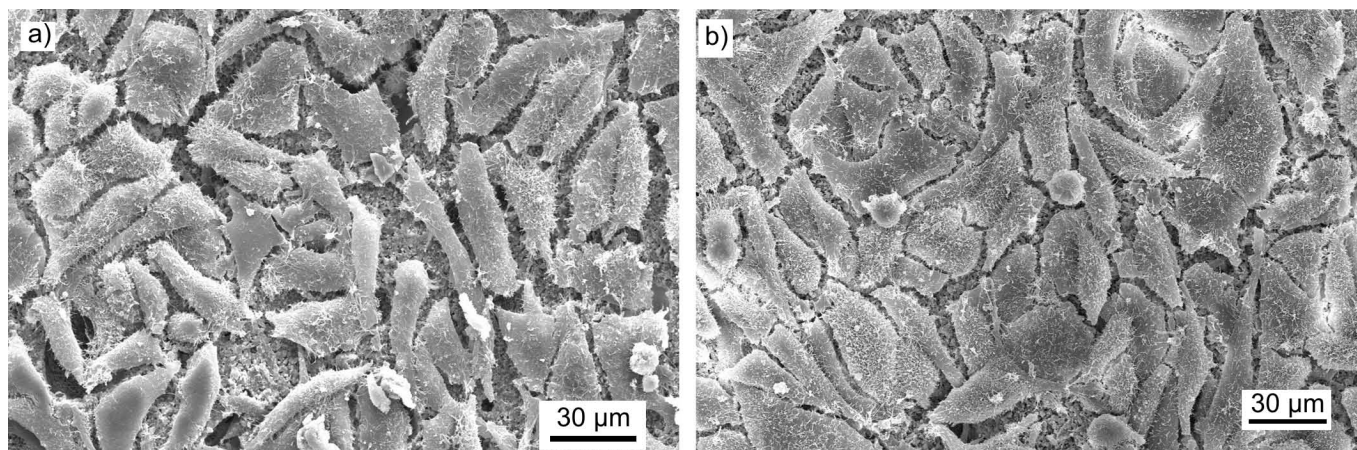


Fig. 7: SEM images showing the morphologies of cells proliferated on the surfaces of (a) transition coating and (b) top coating.

(7) In-vitro test results for the coating

The cytotoxicity of the coatings was evaluated and the relative growth rate (RGR) was calculated after the L929 mouse fibroblast cells growing for 72 h. The RGR values of transition/top coatings and control materials are 92 ± 1.41 , 91 ± 1.41 , and 93 respectively. It is obvious that the RGR values of the coatings are close to those of negative control materials, which means that the cells can proliferate well on the non-cytotoxic calcium phosphate coating. The results further indicate that various compositions and porous structures of the three coating layers have virtually no influence on the cellular response.

The morphologies of the cells cultured on the coating surfaces for 72 h were observed with SEM.

The cells attached and spread well on the scaffold surface with some cytoplasmic extensions (Fig. 7(a) and (b)), suggesting that the porous structure features and interconnectivity of the scaffold layers are suitable for cell spreading and growth. The results are in agreement with the cellular response

This is consistent with other reports in the literature³⁶, which show a good *in vitro* cellular response on calcium phosphate surfaces.

IV. Conclusions

The main achievement of this work is to design and develop a unique processing technique to create a successful bioactive/load-bearing coating/substrate interface without any cracks or delamination. The bond strength between the coating layer and the strong substrate is a very critical factor. Separation of the coating layer from the implant during service in the human body results in adverse effects on the implants and the surrounding tissue caused by detached particles³⁸. The main reason for using HA coating on load-bearing substrates is to maintain the mechanical properties of the substrate, such as load-bearing ability, and, at the same time, to take advantage of the coating's chemical similarity and biocompatibility with the bone. But the stability of the HA coating is the most critical factor to ensure the success of this type of implant. Furthermore, the method used to deposit HA powder onto the substrate could influence the coating characteristics such as its adhesion strength and reliability³⁹.

The method used to deposit the coating on the pre-sintered rough substrate and co-sintering of the coating/substrate make the current approach better than others. The coating slurry was deposited not only on the substrate but also into the cavities created by the roughening process of the pre-sintered substrate. The chemical reaction and the diffusion of the common phases during the sintering process helps to build the bone bonding sites into the substrate. In the physiological environment, HA/TCP will be replaced with bone cells and these bonding sites into the substrate will increase the bone-bonding ability of the composite. The good interface will also help to stop the separation of the coating layer.

This study focussed on a graded and micro-interlocked interface design as well as graded micropore structures in TCP coatings. Diffusion of common material phases across the layer-interface and multi-coating layers with graded micro-pore structures promotes the interfacial bonding on the basis of an interlocked boundary. This bio-functional coating/load-bearing substrate composite has been manufactured using a slip coating and coating/substrate co-sintering technique. The resulting 150-μm-thick coating has a graded porous structure with nano/submicron pores and micropores, and the TCP coatings are non-cytotoxic to the cells and suitable for cell spreading and growth. The coating/substrate composite exhibits very good bending strength and strong interfacial bonding. The interface design manufactured in this study can be applied in other ceramic coating-substrate systems to promote interfacial bonding quality. This porous bio-coating/strong substrate composite provides a potential promising alternative for load-bearing bone implant replacement application.

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