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# Coating of hydroxyapatite on various substrates via hydrothermal reactions of Ca(edta)$^{2-}$ and phosphate

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Hydroxyapatite was coated on various substrates such as 12 mol % ceria-doped tetragonal zirconia (12Ce-TZP), 3 mol % yttria-doped tetragonal zirconia (3Y-TZP), alumina, monetite coated titanium (Ti/$CaHPO_4$) and calcium titanate coated titanium (Ti/$CaTiO_3$) via hydrothermal reactions of Ca(edta)$^{2-}$ and 0.05 M $NaH_2PO_4$ at initial pH 6 and 160–200 °C for 0.5–6 h. Rod-like particles of hydroxyapatite precipitated to form film on the substrates above 160 °C. The morphology of the film changed significantly depending on the characteristics of substrate, i.e. hydroxyapatite entirely coated the surfaces of 12Ce-TZP, Ti/$CaHPO_4$ and Ti/$CaTiO_3$ plates, but sparsely deposited on 3Y-TZP and $Al_2O_3$ plates. Film thickness increased with time (ca. 20 and 90 μm on 12Ce-TZP plates for 0.5 and 6 h, respectively, at pH 6 and 200 °C). The adhesive strength of the film for the substrate was in the order, 12Ce-TZP/hydroxyapatite(28 MPa) > Ti/$CaTiO_3$/hydroxyapatite (22 MPa) > Ti/$CaHPO_4$/hydroxyapatite (9 MPa).

## 1. Introduction

Hydroxyapatite (($Ca_{10}(PO_4)_6(OH)_2$)) is a main component of bone mineral [1] and has received much attention for its application to orthopedic surgery [2]. The clinical use of hydroxyapatite as a load-bearing implant, however, is limited because of its mechanical brittleness. Materials with excellent mechanical strength and chemical stability such as titanium alloys, alumina, zirconia, etc. have been used for orthopaedic implants [3], but the biocompatibility of these materials is poor. Attention has therefore been focused on the formation of a hydroxyapatite coating on these materials. Hydroxyapatite films formed by heat treatment such as plasma spraying, spattering, etc., tend to differ from bone apatite in chemical composition [4, 5]. The process of using simulated body fluid [6] to form a hydroxyapatite film on a material is a novel technique, but the growth rate with this method is quite slow. In previous papers [7–9] we reported that hydroxyapatite films could be formed quickly on the surface of titanium substrates by the hydrothermal reactions in Ca(edta)$^{2-}$ – $PO_4^{3-}$ mixed solutions above 150 °C after pre-coating of monetite ($CaHPO_4$) or calcium titanate ($CaTiO_3$) (where edta is ethylenediaminetetraacetic acid). In the continuation of our study on the hydrothermal synthesis of hydroxyapatite film, a series of tests were conducted to investigate the formation of hydroxyapatite film on ceramic materials.

## 2. Experimental procedure

### Chemicals

All chemicals were of reagent grade and used without further purification. Mixed Ca(edta)$^{2-}$ – phosphate solutions (0.05 M Ca(edta)$^{2-}$, 0.05 M $NaH_2PO_4$) were prepared using stock solutions of 0.5 M $CaCl_2$, 0.2 M $Na_2H_2$edta, 0.5 M $NaH_2PO_4$, and 0.1 M NaOH just before the reaction. The solution pH was adjusted with 1 M NaOH using a pH meter at room temperature.

### Substrates

The plates (ca. 6.2 mm diameter and 2 mm thickness) of 12 mol % ceria doped tetragonal zirconia, and 3 mol % yttria doped tetragonal zirconia were prepared using TZ-12Ce and TZ-3Y powders (Toso Co.) and designated as 12Ce-TZP and 3Y-TZP, respectively. To avoid low temperature degradation in a moist atmosphere of yttria-doped tetragonal zirconia [10, 11], 3Y-TZP was sintered at a temperature as low as 1300°C. Alumina plates were prepared using AKP-15 powders (Sumitomo Chemical Co.). The sintering conditions, relative densities and grain sizes of the plates prepared are summarized in Table I. Unless especially mentioned, as-sintered ceramic plates were used without polishing. Monetite coated titanium and calcium titanate coated titanium plates were prepared by treating titanium plates (Niraco Co., purity > 99.9%, 10 mm × 10 mm × 1 mm)

TABLE I Sintering conditions and relative densities and grain sizes of sintered bodies of 12Ce-TZP, 3Y-TZP and alumina used

| Substrate | Sintering conditions | | Relative density (%) | Grain size (μm) |
|---|---|---|---|---|
| | Temperature (°C) | Time (h) | | |
| 12Ce-TZP | 1500 | 5 | 99.9 | 2.5 |
| 3Y-TZP | 1300 | 5 | 85.3 | 0.3 |
| $Al_2O_3$ | 1600 | 5 | 94.3 | 1.0 |

in 0.05 M $Ca(edta)^{2-}$ – 0.05 M $NaH_2PO_4$ mixed solution at pH 5 and 160 °C for 2 h, and 0.01 M $Ca(edta)^{2-}$ solution at pH 13 and 250 °C for 6 h after polishing them with No. 60 emery paper and No. 240 emery paper as reported [8, 9], and designated as Ti/$CaHPO_4$ and Ti/$CaTiO_3$, respectively.

### Preparation of hydroxyapatite film

A piece of each plate and 15 ml of $Ca(edta)^{2-}$ – $NaH_2PO_4$ solution were placed in a 20 $dm^3$ PTFE (polytetrafluoroethylene) vessel which was inserted in a SUS 304 sealed stainless tube, which in turn was immersed in an oil bath. The bath was raised to the desired temperature at a heating rate of 1.5 °C/min and kept there. After heat treatment, the sealed tube was taken out from of the bath and cooled in air. The treated plates were washed with distilled water and dried at room temperature using a vacuum desiccator for 1 day.

### Analysis

The morphology of the hydroxyapatite film was observed by scanning electron microscopy (SEM, JEOL, T-50). The crystalline phase of the film was identified by X-ray diffraction analysis (Shimadu Co., XD-D1) using nickel-filtered CuKα radiation. The film thickness was measured from the SEM photographs of cross sections of the plate. The concentrations of Ca and P in solution were determined by inductively coupled plasma atomic emission spectroscopy (Seiko Co., SPS-1200A). The adhesive strength of the film for the substrate was determined using an arrangement shown in Fig. 1. A pair of titanium jigs with a base 6 mm in diameter were attached to the outer surface of the film formed on the substrates with epoxy resin (Sumitomo 3 M Ltd., Scotch-Weld SW2214). After leaving the arrangement for 1 d for complete solidification of the adhesives, the adhesive strength of the film was measured by applying a tensile stress to the interface of the apatite and substrate using an Instron-type testing machine (Shimadu, Autograph AK-20kNG) at a crosshead speed of 1 mm $min^{-1}$, until a fracture occurred. Three measurements were done for each data point.

## 3. Results and discussion

Ceramic plates were treated in 0.05 M $Ca(edta)^{2-}$ – 0.05 M $NaH_2PO_4$ solutions at initial pH 6 and various temperatures. No precipitation was observed below 140 °C, whereas white precipitates were observed above 160 °C and increased with increasing temperature (Fig. 2) as expected from the thermodynamic calculation [8]. The degree of precipitation in the presence of 12Ce-TZP is higher than that of 3Y-TZP. The increase in solution pH would be attributable to the following reaction.

$$10\ Ca(edta)^{2-} + 6\ HPO_4^{2-} + 4\ H_2O$$
$$\rightarrow Ca_{10}(PO_4)_6(OH)_2 + 10\ Hedta^{3-} + 2\ OH^-$$

The X-ray diffraction profiles of the surfaces of 3Y-TZP plates treated in 0.05 M $Ca(edta)^{2-}$ –0.05 M $NaH_2PO_4$ solutions at initial pH 6 and 200 °C for various period are shown in Fig. 3. The tetragonal to monoclinic phase transformation of Y-TZP did not proceed at all under the present reaction conditions. The diffraction peaks corresponding to hydroxyapatite appeared after 0.5 h and the peak intensity increased with time. It is notable that the hydroxyapatite film prepared showed a larger peak intensity ratio for (300)/(211) than that of JCPDS 9-432, indicating the preferred orientation of hydroxyapatite crystals.

The scanning electron micrographs of the surfaces of 12Ce-TZP, 3Y-TZP and $Al_2O_3$ after hydrothermal reactions at initial pH 6 and 200 °C for 4 h are shown in Fig. 4. Rod-like crystals of hydroxyapatite, ca. 50 μm

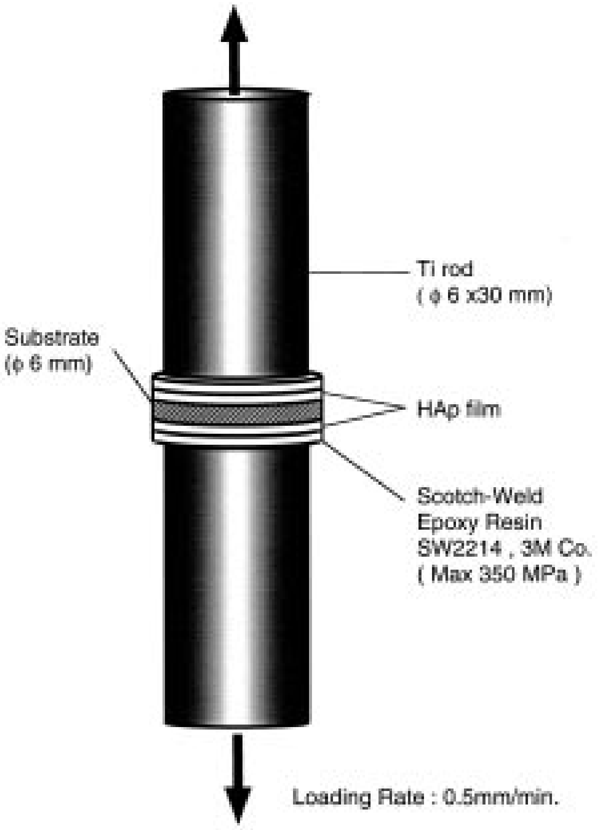

*Figure 1* Arrangement for measuring the adhesive strength of the hydoxyapatite film for the substrate.

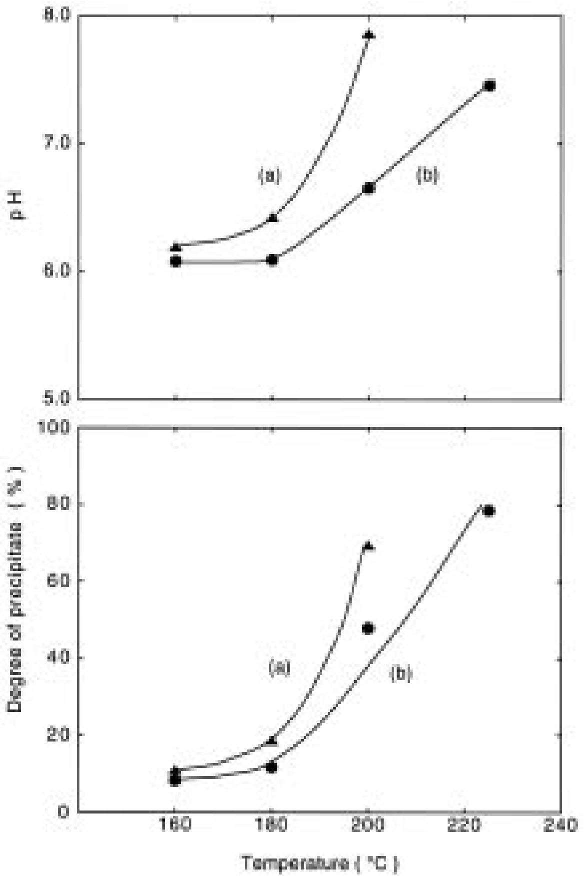

*Figure 2* Degree of $Ca^{2+}$ precipitation and change in solution pH by the hydrothermal reactions of (a) 12Ce-TZP and (b) 3Y-TZP plates in 0.05 M $Ca(edta)^{2-}$ – 0.05 M $NaH_2PO_4$ mixed solutions.

length and 5 μm diameter, precipitated and entirely coated the surface of as-sintered 12Ce-TZP plates (a). On the other hand, hydroxyapatite sparcely precipitated on the surface of as-sintered 3Y-TZP (c) and alumina (d). The difference in the morphology of hydroxyapatite film may be attributed to the difference in the surface roughness of the substrate. To confirm the effect of surface roughness, a similar experiment was carried out using 12Ce-TZP ground by No. 80 diamond plate. As seen in Fig. 4(b), a uniform hydroxyapatite film did not form after grinding. These results indicated that large flaws induced limited numbers of nuclei to precipitate hydroxyapatite. Consequently, hydroxyapatite sparcely precipitated when large flaws existed on the surface. Therefore, it may be concluded that appropriate surface roughness is necessary to form a uniform hydroxyapatite film.

The time dependence of the hydroxyapatite film thickness on the 12Ce-TZP plate is shown in Fig. 5. The thickness increased with time at each temperature.

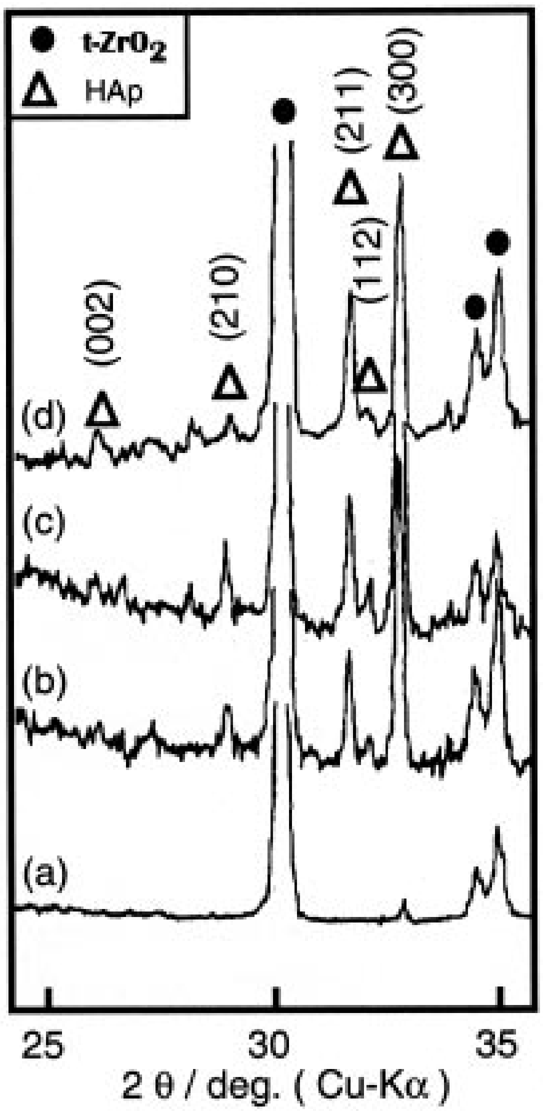

*Figure 3* X-ray diffraction patterns on the surface of 3Y-TZP plates after hydrothermal reactions in 0.05 M $Ca(edta)^{2-}$ – 0.05 M $NaH_2PO_4$ mixed solutions at 200 °C for various periods. (a) 0.5 h, (b) 1 h, (c) 2 h, (d) 4 h.

Although the degree of calcium ion precipitation increased with increasing temperature (see Fig. 2), the film formed at 160 °C was thicker than those at 180 and 200 °C, indicating that hydroxyapatite precipitated on the surface of 12Ce-TZP plate selectively at 160 °C, whereas it precipitated not only on the plate but also in the solution above 180 °C.

Scanning electron micrographs of the surfaces of 12Ce-TZP, Ti/$CaHPO_4$, and Ti/$CaTiO_3$ plates coated with hydroxyapatite before and after the adhesive strength tests are shown in Fig. 6. All plates were uniformly coated with hydroxyapatite film. The thick-

TABLE II Thickness and adhesive strengths of hydroxyapatite films on various plates

| Substrate | Hydroxyapatite film | | Adhesive strength (MPa) |
|---|---|---|---|
| | Formed temperature (°C) | Thickness (μm) | |
| 12Ce-TZP | 200 | 41.0 | 28.3 (17.7–40.3) |
| Ti/$CaHPO_4$ | 180 | 9.8 | 9.2 (8.1–10.2) |
| Ti/$CaTiO_3$ | 180 | 5.0 | 22.1 17.5–26.3) |

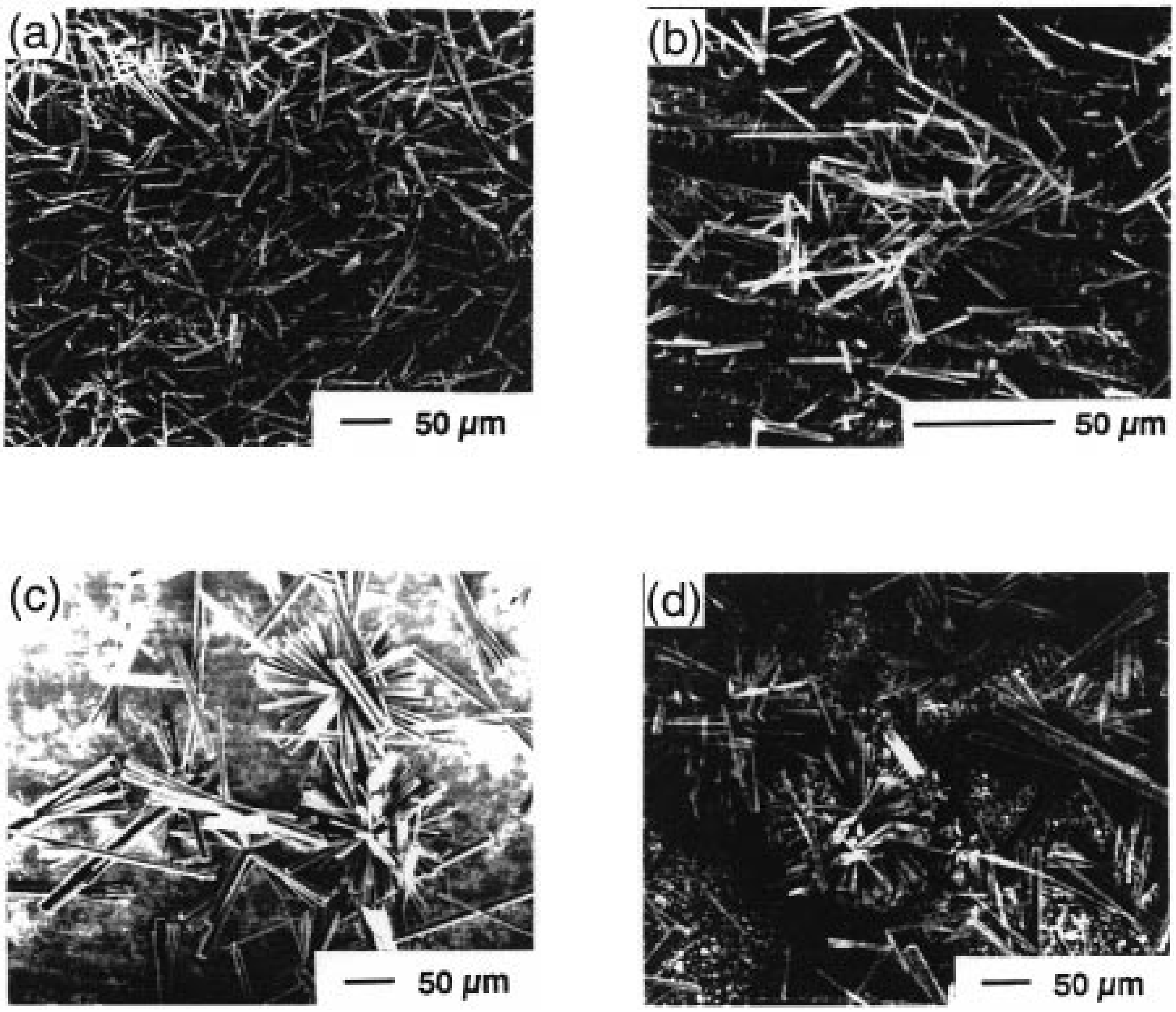

*Figure 4* Scanning electron micrographs on the surface of (a) as-sintered 12Ce-TZP, (b) 12Ce-TZP ground with a diamond plate (80#), (c) as-sintered 3Y-TZP and (d) as-sintered $Al_2O_3$ after hydrothermal reactions in 0.05 M $Ca(edta)^{2-}$ – 0.05 M $NaH_2PO_4$ mixed solutions at 200 °C for 2 h.

nesses of the hydroxyapatite films were 41.0, 9.8 and 5.0 μm, respectively, and the adhesive strength of the film was in the order, 12Ce-TZP/hydroxyapatite (28.3 MPa) > Ti/$CaHPO_4$/hydroxyapatite (22.1 MPa) > Ti/$CaHPO_4$/hydroxyapatite (9.2 MPa) as shown in Table II. The adhesive strengths of the films in 12Ce-TZP/hydroxyapatite and Ti/$CaHPO_4$/hydroxyapatite systems were ca. twice that in the Ti/hydroxyapatite system formed by the biomimetic process using a simulated body fluid [12]. After adhesive strength tests of 12Ce-TZP/hydroxyapatite, Ti/$CaHPO_4$/hydroxyapatite and Ti/$CaTiO_3$/hydroxyapatite specimens, 12Ce-TZP, Ti and $CaTiO_3$ appeared, indicating that fracture occurred between 12Ce-TZP and hydroxyapatite, Ti and $CaHPO_4$, and $CaTiO_3$ and hydroxyapatite, respectively.

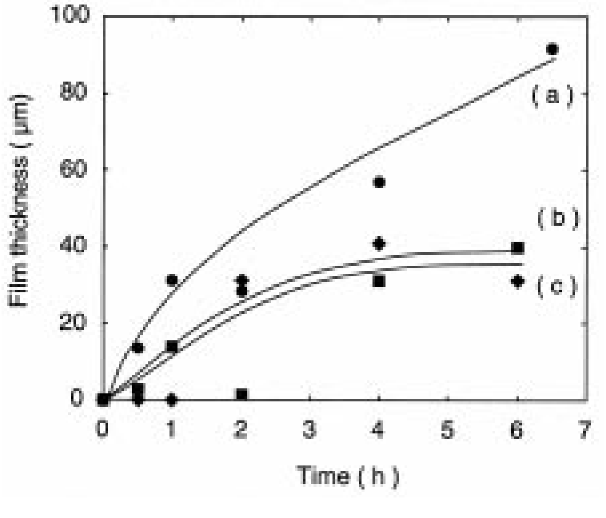

*Figure 5* Time dependence of the thickness of hydroxyapatite film on 12Ce-TZP plates in 0.05 M $Ca(edta)^{2-}$ – 0.05 M $NaH_2PO_4$ mixed solutions at various temperatures. (a) 160 °C, (b) 200 °C, (c) 180 °C.

## 4. Conclusion

(1) Hydroxyapatite was coated on 12Ce-TZP, 3Y-TZP, alumina, Ti/$CaHPO_4$ and Ti/$CaTiO_3$ plates via hydrothermal reactions of 0.05 M $Ca(edta)^{2-}$ and 0.05 M $NaH_2PO_4$ at pH 6 and 160 – 200 °C for 0.5–6 h.

(2) Hydroxyapatite entirely coated the surfaces of 12Ce-TZP, Ti/$CaHPO_4$ and Ti/$CaTiO_3$ plates, but sparsely deposited on 3Y-TZP and $Al_2O_3$ plates.

(3) Film thickness increased with time (ca. 20 and 90 μm on 12Ce-TZP plates for 0.5 and 6 h, respectively, at pH 6 and 200 °C).

(4) The adhesive strength of the hydroxyapatite film for the substrate was in the order, 12Ce-

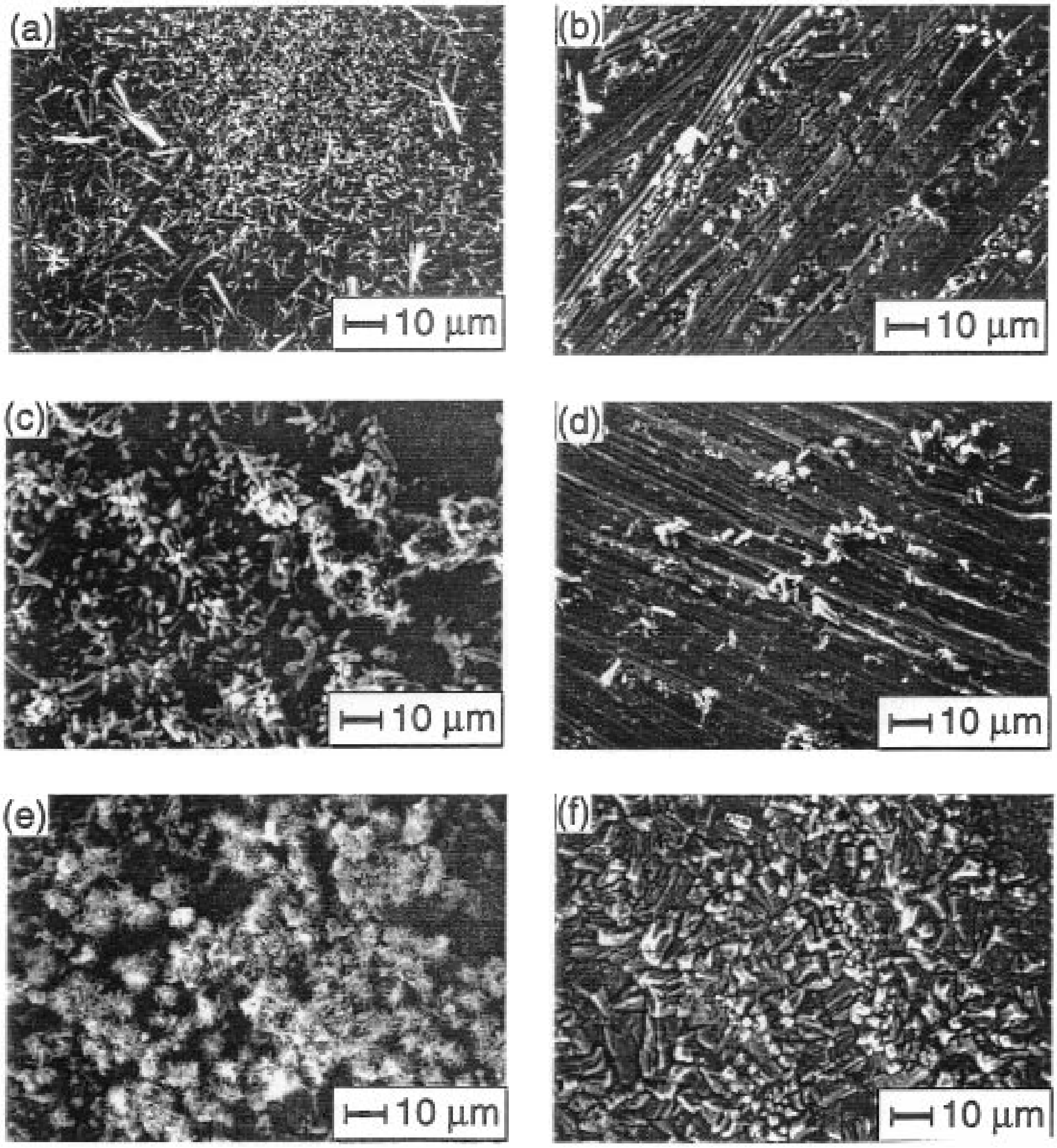

*Figure 6* Scanning electron micrographs of the surfaces of 12Ce-TZP, Ti/$CaHPO_4$ and Ti/$CaTiO_3$ plates coated with hydroxyapatite film before and after the adhesive strength test. (a), (b): 12Ce-TZP, (c), (d): Ti/$CaHPO_4$, (e), (f): Ti/$CaTiO_3$, (a), (c), (e): before test, (b), (d), (f): after test.

TZP(28 MPa) > $CaTiO_3$ coated Ti (22 MPa) > Ti/$CaHPO_4$ (9 MPa).

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