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Study on Microstructure and Nanomechanics Properties of Antibacterial Bone China

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Abstract: Fracture appearance, surface and nanomechanics properties of antibacterial ceramics containing rare earth phosphate composite antibacterial materials were characterized and measured by SEM, AFM and Nanoindenter, respectively. Results show that grain of fracture surface of antibacterial ceramics grows uniform refinement topography of bubble break-up appears at the surface, which is flat and has liquid character, by adding the phosphate composite containing rare earth, nevertheless needle-like crystal and granular outgrowth form at fracture surface and surface of common ceramics, respectively. Young's modulus of antibacterial ceramic film is 74.397 GPa and hardness is 8.134 GPa, which increses by 4.4% and 1.6% comparing with common ceramics, respectively. Loading curves of two kind of ceramics have obvious nonlinear character under 700 nm and linear character between 700 ~ 1000 nm, and unloading curve have obvious linear character.

Key words: AFM; nanoindenter; characterization; nanomechanics; antibacterial ceramic; rare earths
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Transition metals with strong antibacterial properties such as silver, zinc and copper are often used in preparing inorganic antibacterial materials[1~2]. A great deal of effort has been devoted in recent years to developing composite phosphate antibacterial materials produced by means of ion exchanging methods due to composite phosphate having adsorb function, ion changing function and catalyzing function. Researches show that the antibacterial property can be obviously increased by each other when transition metals such as silver, zinc and copper are used together with rare earth in preparing composite phosphate antibacterial materials[3~5]: The composite phosphate antibacterial materials containing rare earth can produce a lot of hydroxylic free radicals (·OH), which can kill bacteria efficiently in the surface of ceramic. However nanomechanics properties of this kind of function materials have not been reported, which districts the application in the engineering field. Obvious surface topography was measured by atomic force microscopy AFM. It is tested that nanoindenter is an excellent tool to the measurement of nanomechanicas properties of bone bacterial china through the experiments. In this article, microstructure characterization and nanomechanics properties of antibacterial ceramic were studied, which can support evidence for the widespread engineering application and the improvement of craft and ingredients.

1 Experimental

1.1 Preparation of sample

Sample Zinc oxide, calcium carbonate and aluminum hydroxide powders were weighed up pro ratio and mixed thoroughly by vigorous stirrer. Then the uniformly mixed powders were slowly put into phosphoric acid solution of 40 ~ 60 ℃ and a concentration about 40% while stirring the solution. When the reaction finished, the slurry temperature was lowered of itself to about 30 ℃ before it was put into the mill and was mulled after putting silver nitrate and cerium nitrate solution into the mill; after neutralizing, flush

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out, filtrating, baking the slurry and mulling in super fine mill, the composite phosphate inorganic antibacterial material containing rare earth was prepared[4]. Chemical constitutes of common ceramics as substrate are shown in Table 1 and the craft of glaze film of antibacterial ceramics surface is shown in Fig. 1. Antibacterial ceramics was made through adding the composite phosphate containing rare earths.

Antibacterial bone china was formed through adding about 3% rare earth composite phosphate antibacterial materials in present production ingredients after sintering. The results show that the surface quality of sanitary wares can be improved by doping ceramic glaze with rare earth composite phosphate antibacterial materials which has no obvious influence on main crystalline phase, and the antibacterial rate is 99.7%[5].

Table 1 Chemical constitutes of common ceramics

Chemical constitutes	Na_2O	K_2O	Li_2O	CaO	SrO	B_2O_3	Al_2O_3	SiO_2
$w/\%$	2.94	4.49	0.80	6.0	7.6	3.0	19.4	55.77

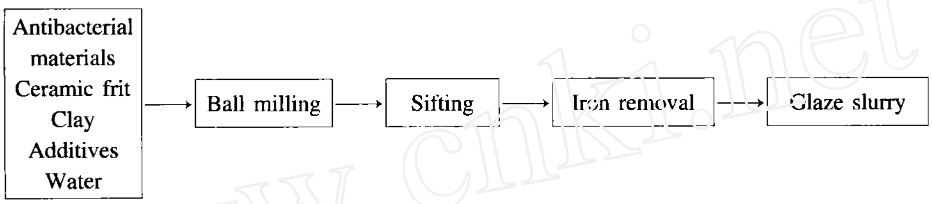

Fig. 1 Preparation of glaze slurry

1.2 Experiments and instrument

Topography of fracture surface was measured by SEM.

Morphology of antibacterial ceramic and common ceramic was measured by CSPM-3400. Image *XY* size of Figs. 3(a) and 3(b) is 20 μm × 20 μm, and *Z* range of Figs. 3(a) and 3(b) is 22.06 nm and 70 nm, respectively.

Nanoindentation experiments were carried out using a Nano Indenter XP® nanomechanical testing instrument (MTS Inc., USA) because the depth of antibacterial ceramic layer is about 0.5 mm, which has the property of film. The contact load and depth of penetration into the sample are continuously monitored. The reduced modulus, contact depth, and hardness data are determined from the load vs. displacement curves using the technique introduced by Oliver and Pharr[6]. Four points and five points were taken in the nanoindentation of common ceramic and antibacterial bone china, respectively.

2 Results and Discussion

2.1 Characterization of fracture surface

Figs. 2(a) and (b) show the fracture surface of common bone china and antibacterial bone china, respectively. Fig. 2 shows that needle-like crystalline appears in the glaze layer of common ceramic, which is pointed out by arrow, but the microstructure of antibacterial ceramic with nanoparticles of rare earth is uniform, compact and has no needle-like crystalline. Topography of fracture surface indicates that nanoparticles of rare earth can suppress grain growth, decrease the possibility of one dimensional growth and refine the graze, which can enhance the nanochanical property of antibacterial ceramic.

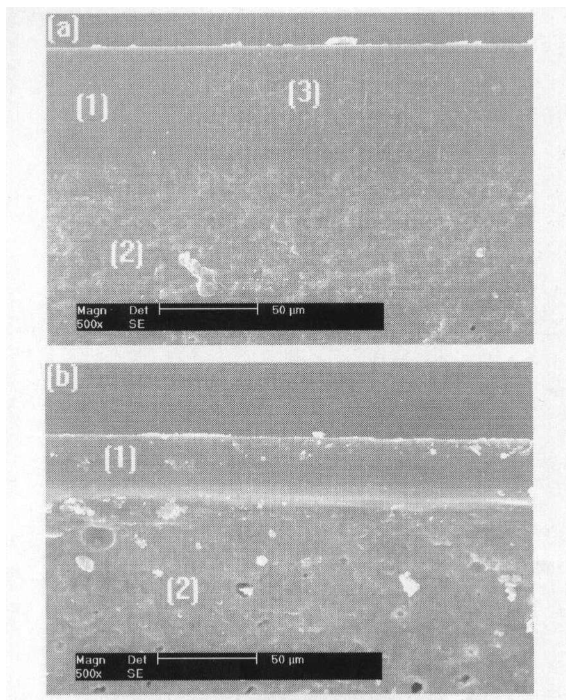

Fig. 2 SEM fracture surface appearance with and without antibacterial materials
(a) Common ceramic; (b) Antibacterial ceramic
(1) Glaze layer; (2) Green body; (3) Needle-like crystal

2.2 Characterization of surface topography

Figs. 3(a) and (b) show the morphology of common bone china and antibacterial bone china, respectively. Results show that the adding of nanoparticles of rare earth decreases the melting point of glaze layer and insoluble particles, which is beneficial for the emission of produced gas in the sintering process of green body. Gas produced in the sintering process releases in the liquid of glaze layer as a kind of bubble. Surface of bubble breakage was formed by the pits which have not been filled by liquid in time in the course of cooling and are seen in Fig. 3. Covalent bonging was formed by the melted ceramic particles and rare earth nanoparticles, which refine microstructure and enhance the nanomechanical property. However, common ceramic has higher melting point and less melted solid at the same sintering temperature, bubbles produced in the green body leak among bigger particles of glaze layer and don't form the pits in the surface but leave a lot of outgrowth in the surface of glaze layer, which is shown in Fig. 3(b).

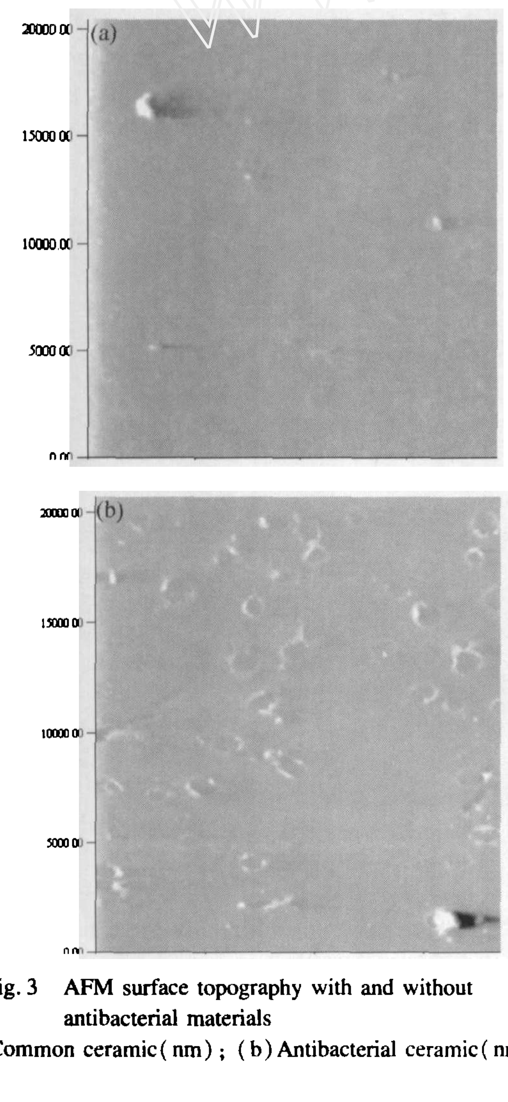

Fig. 3 AFM surface topography with and without antibacterial materials
(a) Common ceramic(nm); (b) Antibacterial ceramic(nm)

2.3 Nanomechanical property of materials

Load vs. displacement curves on four points of common ceramic and five points of antibacterial ceramic were shown in Figs. 4(a) and (b). It is observed that values of all points of common ceramic and antibacterial ceramic have ideal repeatability and reliability. Data drawn in Figs. 5 ~ 7 is the average value of sample points because of the excellent repeatability of sample.

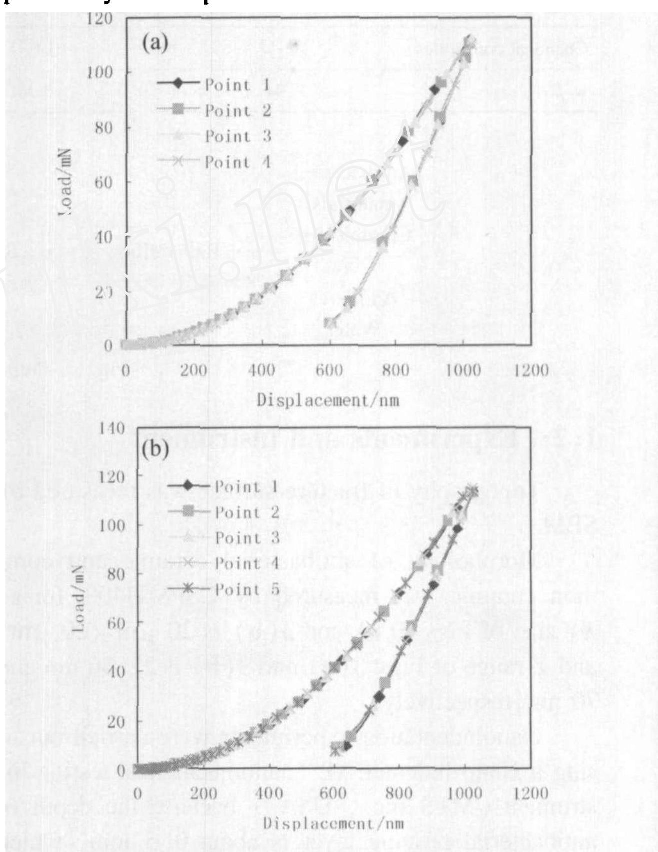

Fig. 4 Load vs. displacement curves on sample points
(a) Common ceramic; (b) Antibacterial ceramic

Elastic vs. displacement curves were got by continuous stiffness measurement CSM. Elastic modulus curves of common ceramic and antibacterial ceramic has stable tendency more than 80 nm, which is basically parallel with horizontal axis. The cross phenomenon of elastic modulus curves of common ceramic and antibacterial ceramic appears between 80 ~ 500 nm, but elastic modulus of antibacterial ceramic is more than that of common ceramic between 500 ~ 1000 nm.

Fig. 6 shows hardness vs. displacement curves of CSM. It is observed that hardness curve is above than that of common ceramic at the same displacement. Two curves have the stable tendency after 100 nm, which is basically parallel with horizontal axis.

Researches show that common ceramic and antibacterial ceramic have stable hardness and elastic modulus with the method of CSM.

It is shown that the antibacterial ceramic has higher modulus and hardness than those of common ceramic when at the same displacement and force, respectively, which can be seen from the displacement vs. force curves in Fig. 7. Table 2 shows the data of nanomechanical property about the apex of force vs. displacement curves. It is seen in Table 3 that the modulus and hardness of antibacterial ceramic is 74.397 GPa and 8.134 GPa, respectively. Furthermore, the standard deviation of modulus of antibacterial ceramic is lower than that of common ceramic, that is to say that modulus of antibacterial ceramic has higher stability. While the standard deviation of antibacterial and common ceramic is likely and has the same stability. Modulus and hardness of film of the antibacterial ceramic containing rare earth increases by 4.4% and 1.6%. Fig. 7 shows that loading curves have obvious nonlinear character under 700 nm but linear character between 700 ~ 1000 nm, and linear character is observed in unloading curves which can be simulated as two lines and has a cross-point at 700 nm. Furthermore, about 600 nm plastic deformation took place after unloading when the loading displacement is about 1000 nm.

Table 2 Mechanics property of some point in nanoindentation loading-unloading curve

Sample	Indentation depth/nm	Load/mN	Young's modulus/GPa	Hardness/GPa
Antibacterial ceramic	894.5039	90.80404	73.66553	8.729886
Common ceramic	896.5505	89.05085	71.35014	8.588385

Table 3 Nanomechanics property comparison between antibacterial ceramic and common ceramic

Samples	Young's modulus/GPa	Standard deviation	Hardness/GPa	Standard deviation
Antibacterial ceramic	74.397	0.431	8.134	0.092
Common ceramic	71.253	0.822	8.003	0.09

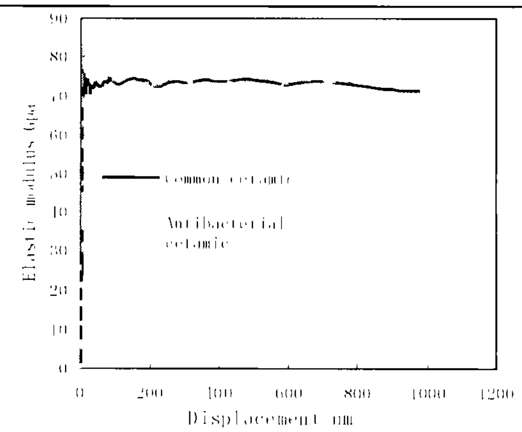

Fig. 5 Elastic modulus vs. displacement curves

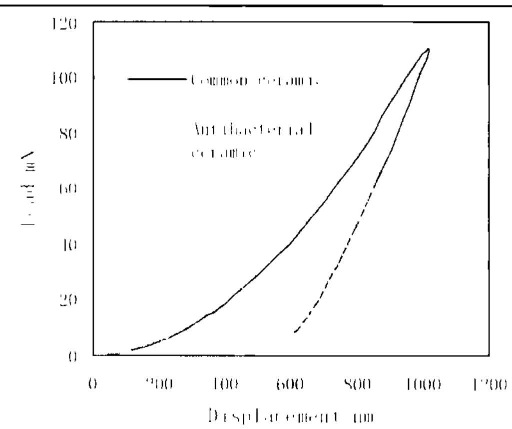

Fig. 7 Nanoindentation loading-unloading curves with and without antibacterial materials

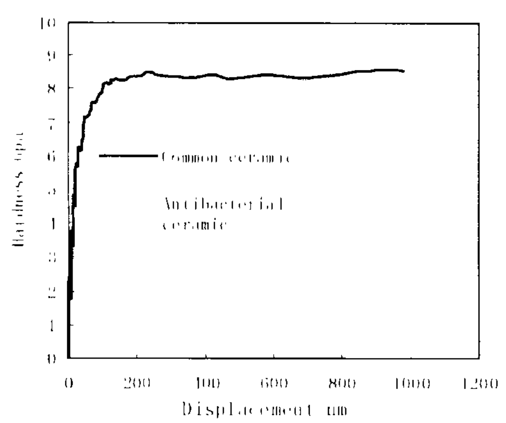

Fig. 6 Hardness vs. displacement curves

3 Conclusion

Microstructure of common and antibacterial bone china was characterized and the relationship between the mechanism and nanomechanical property was presented in this study. Elastic modulus and hardness, which is measured by nanoindenter, is 74.397 and 8.134 GPa, respectively. Research indicates that antibacterial ceramic not only has excellent antibacterial property, but also has the better mechanical property, which has a broad prospect in the engineering field.

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