行政院國家科學委員會專題研究計畫成果報告

生態陶瓷韌化材料的研發
Development of eco-ceramic reinforcements for ceramic matrix composites

計畫編號：NSC91-2216-E-002-030

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一. 摘要

本研究開發出一種具孔隙分佈梯度的多晶板材，此板材一面為完全緻密的 SiO_2 表面層，其餘大多數為鈣氧化物，板材中的孔隙量隨距離 SiO_2 層愈遠愈多，此板材為層狀結構，層與層間為一多孔隙層，此板材最大直徑可達 10mm，厚度為 20-40μm，本研究是以魚鱗作為板材的模版。

魚鱗的微結構是一種層狀結構，其中 40%-80%為有機蛋白，其餘為陶瓷，以魚鱗作為模版，本研究開發出多孔層狀氧化鈣板材。製程設計為先以 sol-gel 方式在魚鱗上披覆上一層均勻的 SiO_2 膠體，之後在 1000°C 至 1400°C 及控制氣氛下鍛燒，如此可製造出具孔隙分佈梯度的層狀韌板材。

此多晶材料有可能作為韌化其他脆性材料的韌化材。

關鍵字：生態陶瓷、魚鱗、複合陶瓷、溶膠/凝膠製程、二氧化矽、氫氧基磷灰石

Abstract

In the present study, we developed a new polycrystalline platelet. The platelet is porous with gradient distribution. One side of the platelet is a dense SiO_2 layer. Other phase in the platelet is mainly calcium oxide. The amount of pores increases with the increase of the distance from SiO_2 layer. The macro-structure of the calcium oxide is a mutli-layered structure, many porous are inside it. The largest diameter of this platelet is 10mm, the thickness is 20-40μm. In the present study, fish scale is used as template.

The macro-structure of fish scale is a layered one. There is 40% to 80% organic protein, the rest is ceramic. We applied fish scale as template to prepare porous layered platelet by using a novel process. The process mainly composes of two stages, silica coating and reaction sintering. First stage, the acid and alkaline solutions were used to apply SiO_2 coating onto fish scale with the sol-gel process. Second stage, the coated fish scale is fired within the temperature range from 1000°C to 1400°C in a well-controlled atmosphere. Pores are still existed after firing, the pores distributes gradiently within the platelet.

This polycrystalline platelet can be used as the reinforcement material for other materials.

Keywords: eco-ceramic、fish scale、ceramic-matrix composite、sol-gel process、silica、hydroxyapatite

二. 緣由及目的

In the present study, we are going to use fish scale as the template to form ceramic reinforcement. The objective is to mimic the macrostructure and microstructure of fish scale. The woodceramics are under development for some time already. Woodceramics have the advantages of stiffness, corrosion, friction resistance and electromagnetic shielding ability. These features of woodceramics have made wood an attractive template for making special porous ceramics. These ceramics can be used as filters, absorbent, catalyst supports, light ceramics, and electromagnetic shielding material [1-4]. However, the use of other biological systems as template attracts much less attention. In the present study, the scale of Mullet fish (Mugli cephalus) is used as template, a thin SiO_2 is first coated onto the scale by using the sol-gel process [5-9]. Calcium oxide platelet with porosity gradient is produced after high temperature treatment.

三. 實驗步驟

The flow diagram for the processing and analysis techniques used in the present study is shown in Fig. 1. In short, the morphology and microstructure of the fish scale are observed carefully. Then, a thin layer silica is coated onto the surface of fish scale by using a sol-gel technique. The microstructures of the un-coated and coated fish scales after firing in air from 900C to 1400C were then observed.

四. 結果

The scales of mullet were used in the present study. Fig. 2 shows the morphology of the fish scale we used in the present study. Grooves can be found on the surface of the scale. Fig. 3 shows the cross-section of the scale. Fig. 4 shows the cross-section of the fish scale after firing at 900C in air. The organic within the scale was removed completely after firing. However, the replica of the original fish scale is preserved. From Fig. 3 and Fig. 4, the upper surface is mainly composing of a ceramic-rich layer (bony layer). Laminated structure was observed below the bony layer. There are abound 60% organic in the fish scale, cracks can thus observed after firing in air.

Fig. 5 shows the morphology of silica particles prepared by the sol-gel process. The structure of the silica after sol-gel process is mainly microcrystallized and/or amorphous.

Fig. 6 shows the top surface of the silica-coated fish scale. The coated fish scale was fired in air at 900C. The top surface was fully covered by the silica. The cross-section of the coated fish scale shows that the thickness of SiO2 is around 2 μm. The macro-structure of the scale was maintained after firing except that many cracks were present.

五 結論

Several conclusions can be drawn from the present study.

1. The organic protein in fish scale is about 65wt%. The organic distribution is not uniform, the amount of organic increases with the increase of the distance from the back surface.
2. After firing in air, the surface layer is dense and the inner part is porous. The inner grains are about submicron-sized before heating at 1100^0C. The grains coarsen significantly after heating above 1300^0C. There are many pores near the back surface; though the top surface is dense.
3. Dense SiO_2 coating can be applied onto fish scale by using a sol-gel process.
4. The bonding between the residual ceramic in the fish scale and SiO_2 is relatively strong.
5. The carbon in the fish scale is too low to form silicon carbide.

六. 參考文獻

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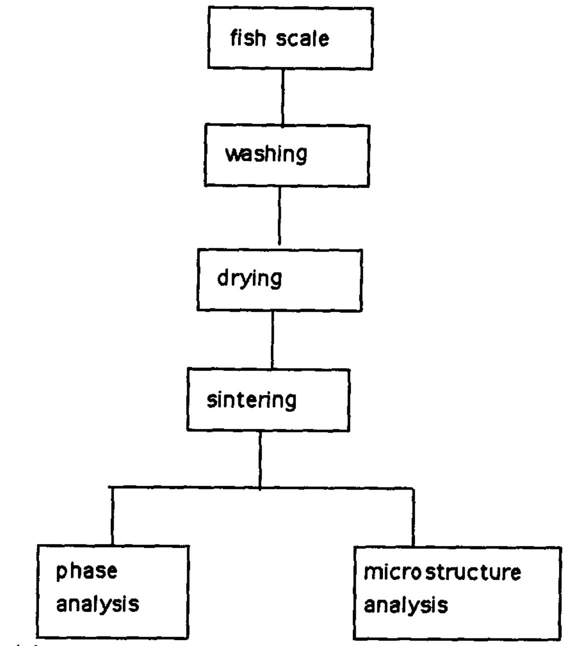
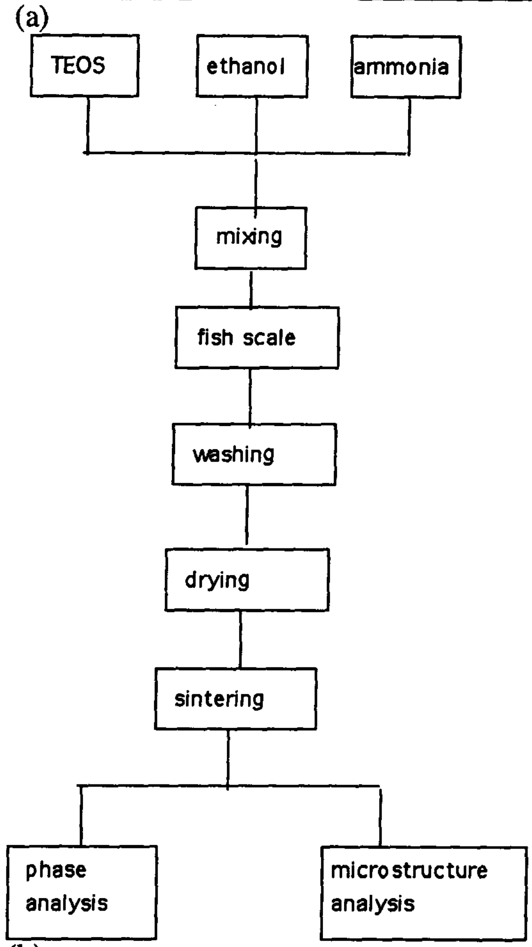
七. 圖形



(a)



(b)

Fig. 1, Flow diagram to illustrate the experimental procedures used in the present study.

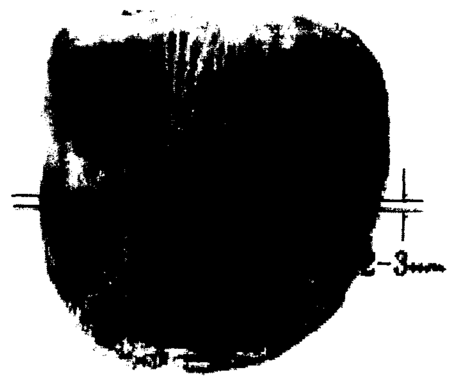


Fig. 2, The morphology of the fish scale from mullet.

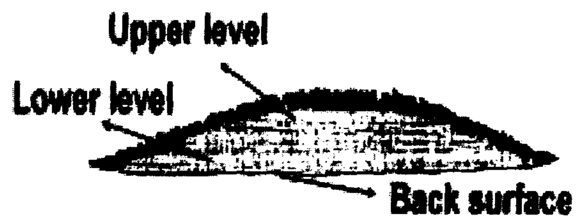


Fig. 3, Cross-section of the fish scale used in the present study.

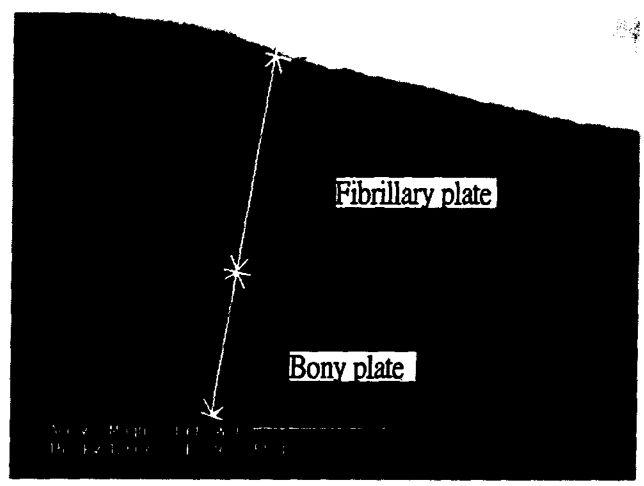
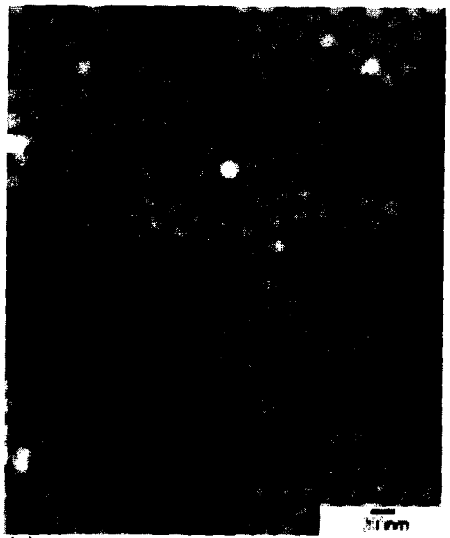


Fig. 4, Cross-section of the fish scale after firing at 900C in air.



(a)

(b)

Fig. 5, (a) TEM micrograph of the SiO2 prepared in the present study. (b) The corresponding diffraction pattern.

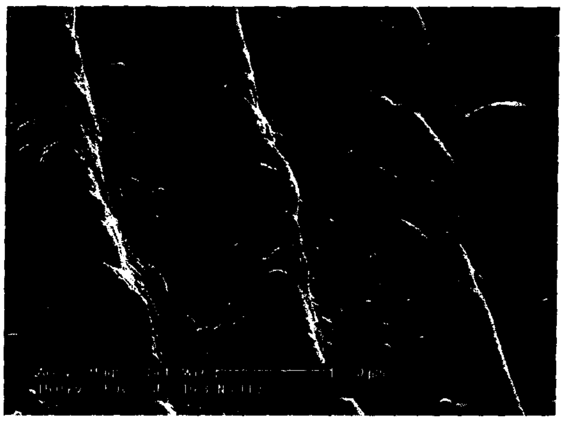


Fig. 6, SEM micrograph of the SiO2-coated fish scale. The coated scale was fired at 1100C in air before observation.

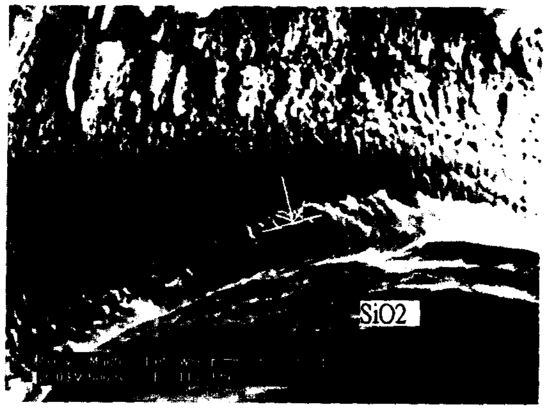


Fig. 7, Cross-section of the SiO2-coated fish scale after firing at 900C in air.