Mechanical Properties of $\text{CaSiO}_3/\text{Ti}_3\text{SiC}_2$ Composites and Hydroxyapatite Forming Ability in Simulated Body Fluid

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$\text{CaSiO}_3/\text{Ti}_3\text{SiC}_2$ composites with different Ti_3SiC_2 volume fractions were fabricated by spark plasma sintering. The mechanical properties and hydroxyapatite formation ability in simulated body fluid were investigated. The results showed that no reaction occurred between the CaSiO_3 and Ti_3SiC_2 , and mechanical properties were improved significantly with the increase of the Ti_3SiC_2 volume fraction. Bending strength and fracture toughness reached 271 ± 12 MPa and 2.47 ± 0.17 MPa·m^{1/2} respectively, with the addition of 30 vol% Ti_3SiC_2 . However, bioactivity is reduced due to the presence of large amount of Ti_3SiC_2 . In order to retain the enough bioactivity, the Ti_3SiC_2 volume fraction should not be above 30%. [doi:10.2320/matertrans.MRA2008064]

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1. Introduction

It is well established that many man-made materials such as bioactive ceramics, bioglass, hydroxyapatite and glass ceramic can bond directly to the living bone,¹⁻⁴ and so be expected to be used as artificial bone. CaSiO_3 (CS) is one of these materials which show superior bioactivity. Studies have shown that pure CS powders induced formation of a hydroxyapatite (HAp) layer on their surface after soaking in simulated body fluid (SBF) or in human saliva.^{5,6} Siriphannon *et al.* have found that the rate of HAp formation on pure CS ceramic surface was faster than that on the biocompatible A/W glass ceramics and some other bioactive glass ceramics.^{7,8} Thus, CS ceramic is expected to be a good implant material. However, the bending strength and fracture toughness of cortical bone are 50–150 MPa and 2–12 MPa·m^{1/2}, respectively,⁹ but the CS ceramic shows poor sintering ability (relative density below 90) and mechanical properties (bending strength lower than 70 MPa),^{7,8,10-12} which restrict it from the practical application. Thus, synthesis of CS based composites may be a solution.

Ti_3SiC_2 (TSC) has recently received considerable attention because it combines the merits of metals and ceramics.¹³⁻¹⁶ It has damage tolerance like metals and high specific stiffness like ceramics. Besides, it's self-lubricable and readily machinable owing to its special sandwich structure. These imply its inexhaustible potential of practical application. Gao and Miyamoto have also shown that TSC exhibits good biocompatibility, no biotoxicity, and high corrosion resistance in 0.9% NaCl solution, suggesting the possibility of bioinert ceramics and implying the application on the biomaterials.¹⁷

In the present work, CS/TSC composites containing up to 30 vol% TSC were prepared by spark plasma sintering (SPS). Both the mechanical properties and bioactivity of the different composites were investigated.

2. Experimental

2.1 Samples preparation

Pure CS powders were synthesized through a chemical precipitation method. Calcium nitrate ($\text{Ca}(\text{NO}_3)_2 \cdot 4\text{H}_2\text{O}$) and sodium silicate ($\text{Na}_2\text{SiO}_3 \cdot 9\text{H}_2\text{O}$) using reagent grade (Sinopharm Chemical Reagent Co., Ltd, China) were dissolved in deionized water respectively to obtain solution with same concentration. The obtained Na_2SiO_3 solution was added into $\text{Ca}(\text{NO}_3)_2$ solution dropwise over 40 to 60 minutes while stirring to produce a white precipitate. The precipitate was filtered, then washed three times with deionized water and finally washed by ethanol. The powder was dried at 80°C, and then calcined at 800°C for 2 h.

Bulk TSC was fabricated directly from Ti, C and Si powders via SPS. The raw material used in this work were 99% pure Ti powder (10 μm), 99.9% pure C powder (1.6 μm), 99% pure Si powder (2 μm) and 99% pure Al powder (45 μm). Ti, C and Si powders were mixed with a small amount of Al powder (lower than 1 mass% in the mixed powders), Al was used as reaction accelerator to improve the rate of reaction. In order to identify the purity of TSC quantitatively, we had adopted the following two equation to calibrate the dependence of relative intensity $I_{\text{TC}(200)}/I_{\text{TSC}(104)}$ of TC main peak (41.988°) to TSC main peak (39.548°).¹⁸⁾

$$W_{\text{TSC}} = \frac{1.80}{1.80 + I_{\text{TC}(200)}/I_{\text{TSC}(104)}} \quad (1)$$

$$W_{\text{TC}} = \frac{I_{\text{TC}(200)}/I_{\text{TSC}(104)}}{1.80 + I_{\text{TC}(200)}/I_{\text{TSC}(104)}} \quad (2)$$

Herein, W_{TSC} and W_{TC} represent the weight percentages of TSC and TC phases, respectively. $I_{\text{TC}(200)}/I_{\text{TSC}(104)}$ represents the integrated intensity ratio of TC to TSC main peaks and can be obtained from the XRD results of the samples. The effect of Al on the equations can be disregarded because the content of Al was quite low. The purity of TSC in the samples was calculated in this way, it can be seen the TSC content reach the value of 93 mass%. The bulk TSC was then crushed into powder.

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TSC powder and CS powder were mixed in 10%, 20%, 30% volume fraction of TSC, and milled for 24 h in alcohol medium. After drying, the mixed powder was sieved to pass 120 meshes. The dried powder was compacted into a graphite mold of 20 mm diameter and sintered with SPS equipment (Dr Sinter 2040, Sumitomo Coal Mining Co., Ltd., Tokyo, Japan), which was carried out at 1050–1150°C in vacuum (<6 Pa) under a pressure of 50 MPa. The heating rate was controlled in the range of 100–200°C/min, and the dwelling time was 5 min.

2.2 Characterization

The sintered specimens were ground to remove the graphite layer. The bulk density of sintered samples was measured by the Archimede's method. Phase compositions were determined by XRD (D/max 2200 PC, Rigaku, Tokyo, Japan). After being polished, the microstructures of the specimens were observed by scanning electron microscopy (SEM; Model JSM-6700F, JEOL, Tokyo, Japan).

The bending strength were measured with a universal testing machine (Model 1195, Instron, Canton, MA) using a three-point test method. The specimens were sliced into test bars with the dimensions of 2 mm × 3 mm × 18 mm with surface polished by 0.5 μm diamond powders were used, and the three-point bending test was carried out at room temperature with a span of 12 mm and crosshead rate of 0.5 mm/min. Six measurement runs were carried out to determine the average value.

Vickers hardness (Hv) of the polished samples was measured using a hardness tester (Tukon 2100B, Wolpert-Wilson Instrument, Aachen, Deutschland) by the Vickers indentation technique. The indentation parameters were made using a 5 kg load with a dwell of 15 s. Fracture toughness were then determined through using the following equation:¹⁹⁾

$$K_{IC} = 0.0937 \left(\frac{H_V P}{4L} \right)^{1/2} \quad (3)$$

where P is the applied indentation load, L is the crack length.

In order to evaluate the bioactivity of sintered ceramic, the composites were soaked in SBF which was prepared according to the method developed by T. Kokubo *et al.*²⁰⁾ The ion concentrations of the SBF were similar to those in human blood plasma. The soaking periods were 1, 3, 7, 14, 21 days and SBF was renewed every day. The temperature was maintained at 36.5°C. After soaking, the samples were cleaned by deionized water and dried at room temperature. The new phase formed on the surface was analyzed by XRD, and the surface morphologies were observed by field emission scanning electron microscopy (FE-SEM, Model JSM-6700F, JEOL, Tokyo, Japan).

3. Results and Discussions

3.1 Microstructure

On preparation with SPS, the TSC/CS composite materials can be fully densified at a lower temperature (<1200°C) and within a very short time (5 min). Therefore, the relative densities of all of the specimens obtained with SPS were higher than 97% of the theoretical density.

Fig. 1 X-ray diffraction pattern of CaSiO₃/Ti₃SiC₂ composite with 30 vol% Ti₃SiC₂.

Figure 1 shows XRD pattern of polished surface for the composite with 30 vol% TSC. The XRD result indicates that no phases other than TSC, CS and TiC were present in the composite, which demonstrated that there was no reaction occurred between TSC and CS during the sintering. But the CS phase has completely changed into high temperature phase (α -CS).

Figure 2 shows the SEM micrographs of the fracture surfaces of samples with different TSC volume fractions. When the TSC volume fraction is under 20%, the fracture surfaces were smooth and no particles can be observed, which indicated the transgranular fracture mechanics. But particles can be observed from some part of the surface of the 30 vol% TSC sample, which means the fracture mechanics changed to intergranular fracture. The laminated particles were TSC particles, which are about 10 μm in length, the small granular particles are CS particles, which is about 1–2 μm in length.

3.2 Mechanical properties

The bending strength and fracture toughness of composites are plotted as a function of TSC volume fraction in Fig. 3. It can be seen that the strength of the composites is almost linear correlated with the addition of TSC. The strength of the sample with the addition of 10 vol% TSC was only 116 ± 5 MPa, but when the TSC content reach to 30 vol%, the strength had increased up to 271 ± 12 MPa.

The fracture toughness of the composites had also improved considerably by the addition of TSC following a linear relationship. A maximum fracture toughness of 2.47 ± 0.17 MPa·m^{1/2} was achieved for the composite with 30 vol% TSC.

Figure 4 illustrates the microstructure and indentation-induced crack propagation of a polished surface of the composite with 20 vol% TSC. The bright phase is TSC and the dark matrix is CS. The presence of crack deflection mechanism in the composite can be observed, which would play an important role in absorbing crack propagating energy during fracture and reinforcing fracture toughness.

Compare to the mechanical properties of pure α -CS (bending strength 65 ± 5 MPa, fracture toughness 0.5 ± 0.2 MPa·m^{1/2}) sintered via SPS, we can see that after adding TSC, the mechanical properties improved significantly, which may be attributed to the toughening effect on the

Fig. 2 SEM micrographs of the fracture surfaces of samples with different Ti_3SiC_2 volume fractions. The upper left corner of each is a higher magnification photo. (a) 10 vol% Ti_3SiC_2 ; (b) 20 vol% Ti_3SiC_2 ; (c) 30 vol% Ti_3SiC_2 .

Fig. 3 Effect of Ti_3SiC_2 content on the bending strength and fracture toughness of $\text{CaSiO}_3/\text{Ti}_3\text{SiC}_2$ composites.

Fig. 4 SEM micrograph of the indentation-induced crack propagation on a polished surface showing the crack deflection mechanism.

matrix by the TSC phase. But previous report also showed that the mechanical properties of β -CS were much better than α -CS because the rapid grain growth,²¹⁾ so if the β -CS phase can be retained in the composites, the mechanical properties may be improved more significantly.

Because the conversion between the two phases was controlled by both sintering temperature and dwelling time, so if the sintering temperature can be lower, the composites with β -CS may be attained. The sintering temperature may be reduced by using fine powder (especially the TSC powder) as the starting material and thus the mechanical properties may be enhanced much more.

3.3 SBF tests

Figure 5 shows the XRD patterns of the composites soaked for different periods. For the sample 1 (10 vol% TSC content), after soaking for 3 days, the peaks of CaSiO_3 became weaker, the broad diffraction peaks ($2\theta = 26$ and 32°) of HAp can be

observed after soaking for 7 days. The main peaks of HAp became more pronounced with prolonged immersion time due to the growth of the crystalline HAp. The peaks of CaSiO_3 disappeared completely after 14 days and the peaks of TSC became weaker, meanwhile, the peaks of HAp became stronger, which means the HAp grow more and almost covered the whole surface. The alike appearance and strengthen of the HAp peaks can also be observed from the XRD patterns of sample 2 (20 vol% TSC content). For sample 3 (30 vol% TSC content), weak HAp diffraction peaks appeared after soaking for 14 days, but HAp peaks didn't significantly become stronger with additional soaking. And the TSC diffraction peaks were still quite strong, which means HAp may only formed on some part of the surface and cannot grow to cover the whole surface.

The XRD patterns of samples soaked for different days with different TSC volume fraction attend composites revealed that when the volume fraction of TSC increases,

Fig. 5 X-ray diffraction pattern of composite with different Ti_3SiC_2 volume fractions soaked for different periods. (a) 10 vol% Ti_3SiC_2 ; (b) 20 vol% Ti_3SiC_2 ; (c) 30 vol% Ti_3SiC_2 .

Fig. 6 SEM photographs of the surface of Composites with 20 vol% Ti_3SiC_2 soaked in SBF for different days. (a) 3 days; (b) 7 days; (c) 14 days; (d) 21 days; (e) 14 days ($\times 1000$).

the bioactivity weaken, and when the TSC content reaches 30%, the composites is nearly bioinert. So the TSC content should be controlled blow 30% if high bioactivity is required.

In order to investigate the growth behavior of the HAp, the surface morphologies of the 20 vol% TSC samples soaked for different periods were observed by SEM and are showed in Fig. 6. After soaking for 3 days, the surface became coarse, but no HAp particles can be observed. After 7 days, HAp particles can be observed on some low-lying part of the surface. Soaked for 14 days, Silkworm-like HAp particles can be observed clearly, from a higher magnification photo. We can see that there was a HAp layer covered the whole surface, meanwhile, cracks can be observed due to desiccation and dehydration. The HAp layer grew denser with additional soaking. After soaking for 21 days, HAp particles grew bigger, and can be observed more significantly, the diameter of the particles was about 100 nm and length was 200–300 nm.

4. Conclusions

CaSiO₃/Ti₃SiC₂ composites with different Ti₃SiC₂ volume fractions were successfully fabricated at a low temperature and short dwelling time of 5 min via SPS. The maximum bending strength and fracture toughness of 271 ± 12 MPa and 2.47 ± 0.17 MPa·m^{1/2} were achieved for the 30 vol% TSC sample. SBF soaking results revealed that when the volume fraction of TSC is blow 30%, the composites showed good bioactivity with a larger growth rate of HAp layer on its surface. Controlling the TSC content, composites with both good mechanical properties and good bioactivity may be achieved and might be potential candidate as bioactive implant materials.

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