Biomass-derived nano-laminated Ti$_3$SiC$_2$ MAX phase

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Carbide-based MAX phases, titanium silicon carbide (Ti$_3$SiC$_2$), were synthesized with Ti, Si, and C elements using a sintering process. Eggshell membranes, which have been generally dumped as domestic wastes, were used as carbon sources in starting materials. After a sintering process at 1500 °C, Ti$_3$SiC$_2$ phases were mainly formed with a few secondary phases such as TiSi$_2$ and TiC$_x$. The formation and extinction of secondary phases were influenced by the quantities of Si contents in starting materials, which also affected the peak shifts of the Ti$_3$SiC$_2$ phase in X-ray diffraction spectra. The possible mechanism of this phenomenon was proposed, and the thermoelectric properties of products were also investigated.

**Experimental**

Eggs were purchased from a nearby grocery store. Eggshell membranes were detached from eggs by soaking them in a hydrochloric acid (HCl, 9.9%) solution. After egg yolks and whites in eggs were removed, eggshell membranes were subjected to an ultra-sonication in ethanol (99.9%) solution for 30 min. They were sufficiently dried at 70 °C using an oven for 30 min.

After thermal annealing at 900 °C with a tube furnace for 1 h under an argon (99.999%) gas atmosphere, they were lightly ground in an agate mortar and pestle by hand. Then, a planetary milling was performed for 1 h at 300 rpm. As a result, a dark gray powder was obtained.

Ti (<45 μm, 99.98%), Si (325 mesh, 99%), and carbonized-eggshell membranes were mixed in a molar ratio of 3 : 1.2 : 2, 3 : 1.4 : 2, and 3 : 1.6 : 2. They were named as TS1.2C, TS1.4C, and TS1.6C, respectively. The mixing process was performed with 8 zirconia balls in a zirconia jar at 300 rpm using a planetary ball mill. The mixed powder weighing 1 g was placed in a graphite mold (10 φ) and then was pressed to form pellets using spark plasma sintering (SPS) equipment. The working pressure, temperature, and duration time were 50 MPa, 900 °C, and 5 min, respectively. The fabricated pellets were thermally annealed at 1500 °C using a tube furnace for 4 h in an argon (99.999%) gas atmosphere. After the annealing process with a heating rate of 4 °C min$^{-1}$, the furnace was slowly cooled to room temperature. The whole preparation process of the MAX phases is shown in Fig. 1(a).

The microstructural, morphological, and composition analyses of specimens were conducted using X-ray diffraction (XRD,
Malvern Panalytical, UK) and two scanning electron microscopess (SEM, JEOL, Japan/EMCRAFTS, Korea) equipped with energy dispersive spectroscopy (EDS), respectively. The density of the products was measured using the Archimede's method. Their thermoelectric properties were determined by temperature differential and four-probe methods using commercial equipment (RZ2000Li, Ozawa Science Co., Japan) in the temperature range from room temperature to about 590 °C under an Ar (99.999%) gas atmosphere.

As-exfoliated eggshell membranes have a net-liked shape, composed of many fibers with an average diameter of 1.36 μm (Fig. 1(b)). Several elements were found in the EDS mapping analyses: C (62.6 at%), N (19.6 at%), O (15.8 at%), and S (1.3 at%). When eggshell membranes were thermally treated at 900 °C, their weight was decreased to about 76%. The compositions also changed into C (88.6 at%), N (7.8 at%), and O (3.5 at%). In addition, the traces (less than 0.1 at%) such as Cl, S, and Ca were detected in all EDS analyses. These results were due to the thermal decomposition of organic components at high temperatures.

The carbonized eggshell membranes have broad XRD patterns (Fig. 1(d)), indicating that they were nearly amorphous or nano-crystalline. Fig. 1(e) shows the XRD pattern of the mixed-powders with Ti, Si, and carbonized eggshell membranes before the SPS process. All peaks were indexed with Si (ICSD no. 426975) and Ti (ICSD no. 192331) phases, not C-related crystalline peaks. The inner SEM images in Fig. 1(d) and (e) show the morphologies of as-carbonized eggshell membranes and mixed powders in each process.

Fig. 2 shows low-(inner images) and high-magnification SEM images of TS1.2C, TS1.4C, and TS1.6C after thermal annealing. The unique laminated morphologies of MAX phases are clearly observed in all products. Moreover, the yellow arrow in Fig. 2(b) presents that step growth of Ti₃SiC₂ was carried out.¹⁹,²⁰

To further verify the formation of Ti₃SiC₂ phases, XRD analyses were performed (Fig. 3). The XRD patterns show that Ti₃SiC₂ phases were mainly formed with secondary phases such as TiSi₂, Ti₅Si₃, and TiCₓ. The peaks were indexed with Ti₃SiC₂ (ICSD no. 25762), TiSi₂ (ICSD no. 96029), Ti₅Si₃ (ICSD no. 652424), and Ti₅.₇C₃.₇ (TiCₓ ICSD no. 18494). TSC, TS53, TS12, and TC in Fig. 3 indicate Ti₃SiC₂, Ti₅Si₃, TiSi₂, and TiCₓ phases, respectively. From the results of XRD analyses, the possible reaction mechanism during the sintering process is described as follows:²¹

\[
\begin{align*}
\text{Ti}(s) + x\text{C(s)} & \rightarrow \text{TiC}_x(s) \quad (1) \\
\text{Ti}(s) + y\text{Si(s)} & \rightarrow \text{Ti-Si}_{\text{rich}}(l) \quad (2) \\
\text{TiC}_x(s) + \text{Ti-Si}_{\text{rich}}(l) & \rightarrow \text{Ti}_3\text{SiC}_2(s) + \text{TiSi}_2(s) + \text{Ti}_5\text{Si}_3(s) + \text{TiC}_x(s) \quad (3)
\end{align*}
\]

According to the quantities of Si contents in the starting materials, the XRD patterns of secondary phases were slightly changed. When Si contents were increased, the intensities of TiSi₂ and TiCₓ peaks were increased and decreased, respectively (Fig. 3(b)). It is known that excess Si is needed for the increase of
the newly-formed Ti$_3$SiC$_2$ phase because the melted Si can partially be evaporated during the fabrication process at high temperatures.\textsuperscript{21} Inset of Fig. 3(a) presents the intensity variations of the main peak of the Ti$_3$SiC$_2$ phase at about $39^\circ$. When Si content is increased, it shows a tendency to increase the intensities of the products. This phenomenon was also found for the second peak (at about $42.7^\circ$) of the Ti$_3$SiC$_2$ phase. The reason may be that excess Si induces the formation of both Ti$_3$SiC$_2$ and Ti-based secondary phases, such as TiSi$_2$. In addition, we found one interesting pattern in enlarged XRD peaks in Fig. 3(b). The peaks of the Ti$_3$SiC$_2$ phase were shifted to the higher position with the increase in Si contents (Fig. 4), while the peaks of secondary phases were not changed. This indicates that the lattice constants and the size of the unit cells were decreased. To the best of our knowledge, no research has been reported about this phenomenon in MAX phases. Generally, the shrinkage of unit cells occurs when small atoms are doped into their interstitial sites. The out-diffusion by a low melting point Si and the weak Ti–Si bonding in Ti$_3$SiC$_2$ (ref. 22) may create Si vacancies. Hence, the unit cell of Ti$_3$SiC$_2$ could decrease because excess Si atoms may occupy the site of Si vacancies (inset of Fig. 4).

The densities of the products are shown in Fig. 5(a), and that of TS1.6C was the highest; TS1.2C (4.134 g cm$^{-3}$), TS1.4C (4.115 g cm$^{-3}$), and TS1.6C (4.151 g cm$^{-3}$). These values were lower than the theoretical value (4.50 g cm$^{-3}$) of Ti$_3$SiC$_2$,\textsuperscript{21} while higher than those (3.792–3.836 g cm$^{-3}$) of our previous reports obtained by an arc melting process.\textsuperscript{19} Fig. 5(b) shows the thermoelectric properties of TS1.2C, TS1.4C, and TS1.6C in the temperature range of $\sim$590 °C. The electrical conductivity of TS1.2C ($1.564 \times 10^6$ $\Omega$ m) was the lowest at room temperature, while those of TS1.4C ($2.012 \times 10^6$ $\Omega$ m$^{-1}$) and TS1.6C ($1.995 \times 10^6$ $\Omega$ m$^{-1}$) were similar. This result may be due to the different electrical resistivities of secondary phases such as TiC (70 $\mu$Ω cm)$^{23}$ and TiSi$_2$ (10 $\mu$Ω cm).\textsuperscript{24,25} As can be seen in Fig. 3, the XRD intensities of TiC and TiSi$_2$ phases gradually decreased and increased, respectively, with increasing Si contents. When TiSi$_2$ phases with low resistivity compared with TiC phases were formed, the electrical conductivities of the products were improved. When the temperature was increased,
their electrical conductivities gradually decreased: TS1.2C (6.274 × 10^5 Ω^−1 m^−1), TS1.4C (7.814 × 10^5 Ω^−1 m^−1), and TS1.6C (7.532 × 10^5 Ω^−1 m^−1) at 590 °C. This presents that the products have temperature-dependent behavior of metals. In general, a thermoelectric ZT value is used to present the performance of thermoelectric materials: 

\[ ZT = \frac{\alpha^2 T \sigma}{k} \]

(α, Seebeck coefficient; T, absolute temperature; σ, electrical conductivity; k, thermal conductivity). This equation shows that the electrical and thermal conductivities are inversely proportional to each other. The Seebeck coefficients of TS1.2C, TS1.4C, and TS1.6C are 6.422–10.981 μVK^−1, 6.277–9.643 μVK^−1, and 5.778–9.543 μVK^−1, respectively (inset of Fig. 5(b)). These values are negative in the temperature range of ~590 °C, which indicates that the products were n-type.

Conclusions

Eggshell membranes with a net-like shape were used as carbon sources for fabricating the Ti3SiC2 phase. After thermal treatment at 900 °C, they were pulverized and mixed with Ti and Si powders. The mixed powders were condensed by an SPS process. Ti3SiC2 phases were successfully fabricated by thermal annealing using a tube furnace at 1500 °C. When Si contents were increased, TiSi2 and TiC phases were formed and disappeared, respectively. The peak shift of Ti3SiC2 phases to a higher angle was observed in XRD analyses. The electrical conductivities of TS1.2C, TS1.4C, and TS1.6C were 1.564 × 10^6 to 6.274 × 10^5 Ω^−1 m^−1, 2.012 × 10^6 to 7.814 × 10^5 Ω^−1 m^−1, and 1.995 × 10^6 to 7.532 × 10^5 Ω^−1 m^−1, respectively. Their Seebeck coefficients were negative and inversely proportional to the electrical conductivities: TS1.2C (6.422–10.981 μVK^−1), TS1.4C (6.277–9.643 μVK^−1), and TS1.6C (5.778–9.543 μVK^−1).

Author contributions

C. Nou performed the fabrication and process of MAX phase and analyses of the products; B. G. Kim gave ideas for this study; B. G. Kim, S. Y. Suk, and S. M. Choi planned the experiment; B. G. Kim and S. M. Choi wrote the manuscript; All authors have given approval to the final version of the manuscript.

Conflicts of interest

There are no conflicts of interest to declare.

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