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Ti-based ceramic composites derived from polymer pyrolysis

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Abstract

The formation and microstructure of the Ti-based ceramic composite derived from polymer pyrolysis in various atmosphere were investigated. Methylpolysiloxane was mixed with TiH_2 as a filler and pyrolyzed in nitrogen, argon and oxygen atmosphere at 1400–1600 °C. TiH_2 as active filler were reacted with atmospheric gas phase and pyrolytic products such as C and SiO_2. TiN, TiC, TiO_2 and Ti_5Si_3 were formed respectively depending on the atmospheric conditions used. Consequently, microcrystalline composites with the filler reaction products embedded in a silicon oxycarbide glass matrix were formed. Depending on the pyrolysis conditions, ceramic composites with a density of 85–88 TD% were obtained.

Keywords: Polymer pyrolysis; Composites; Nitrides; Silicides

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1. Introduction

Titanium-based composites are attracting attention because of their superior mechanical, chemical and thermal properties. Until now, a variety of Ti-based materials such as titanium nitride, -silicide and -carbide have been studied as potential materials for high temperature structural applications and for applications in the electronic industry. Especially, TiN has received the most attention because of its high hardness and high melting temperature, making it a useful material for coating cutting tools for obtaining improved hardness and wear resistance. In addition, its good electrical conductivity makes it an important electrically conducting ceramic for use in self-heating crucibles or as a conductor for electronic application.[1]

There are several methods reported for manufacturing Ti-based ceramic composites. For example, shaping and sintering of TiN ceramics have been carried out by conventional ceramic processing routes such as pressureless sintering (PLS), reaction sintering, hot pressing (HP) and self-propagating high temperature synthesis (SHS) for densification.[2] Also, Ti_5Si_3 for high temperature structural application has usually been fabricated by various methods, including arc melting of Ti and Si pieces, hot isostatic pressing or hot pressing of Ti_5Si_3 powders.[3] However, methods for the formation of Ti-based ceramics are accompanied with an expensive manufacturing cost due to the difficulty of shaping and sintering.

To solve these problems of a conventional ceramic process, the manufacturing of ceramic material preceramic silicon containing polymers such as polysilanes, -carbosilanes, -silazanes or -siloxanes has been recently been attained. Controlling of the molecular structure and composition of compound is highly attractive because of its potential to form new materials with nanostructured and molecular composites.[4–6] Additionally, preceramic polymers have good shaping and processing ability that may be easily changed to ceramic at low temperature. However, the formation of the defects, as pores and cracks can be caused by the tremendous shrinkage due to the density increase in the pyrolytic polymer–ceramic conversion.[7] To reduce shrinkage and porosity, it needs active filler materials, such as a carbide, silicide or nitride forming transition metal (Ti, Cr, V, etc.), which are then added to ceramic composites. The dispersion of active filler materials in the polymer precursor offers a possibility of reducing shrinkage and porosity[8–10] as well as producing Ti-based ceramic composites with various compositions. Therefore, a variety of Ti-based ceramic composites can be manufactured by reaction with atmospheric gas phase and pyrolytic product such as C and SiO_2 derived from polymer.

The aim of the study at hand is to manufacture the Ti-based ceramic composites by polymer pyrolysis in various atmospheres.

2. Experimental procedure

A methylsiloxane (MK, Wacker, Germany) with an average molecular weight of 9400 g/mol was chosen as the preceramic

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polymer precursor and TiH_2 was used as the active filler. Polymer/filler mixtures with an initial filler fraction of 40, 60 and 70 vol.% and a catalyst (aluminumacetyacetonate, $C_{15}H_{21}AlO_6$) of 2 wt.% of the total polymer amount were prepared by a dry ball milling method for 15 h. For shaping, the versatility of plastic shaping technologies for polymer can be used. The polymer-filler mixture powders were moulded with an axial pressure of 30 MPa at 230 °C for 45 min in metal die with a diameter of 20 mm. Pyrolysis was carried out in a vertical furnace at a temperature of 1400–1600 °C for a period of 4 h in N_2, Ar and O_2 gas atmospheres, respectively. To sufficiently remove the decomposition gases derived from polymer and filler, the compact was heated with a low heating rate of 0.5 °C/min up to final temperatures. The sintering density and theoretical density of the specimens were measured by the Archimedes method and Gas Pycnometer (Accupic 1330, Micrometrics, USA), respectively. The specimens were polished, using SiC sandpapers, down to 1 μm diamond finish. Phase composition was determined by X-ray diffraction using monochromated Cu Kα radiation. Microstructures of the specimens were examined by scanning electron microscopy (SEM; S-2150, Hitachi) followed etching the specimen by plasma ($CF_4 + O_2$).

3. Results and discussion

Fig. 1 shows the thermogravimetric analysis (TGA) of the 100 vol.% polymer (a) and 60 vol.% polymer and 40 vol.% TiH_2 (b) up to 1000 °C in N_2 atmosphere. When 100 vol.% polymer was heated, the crosslinking was begun at 200 °C and then the weight loss was drastically occurred by release of H_2O and oligomers. The decomposition of the polysiloxane started above 400 °C and was almost completed at 800 °C, which resulted in additional weight loss by the evaporation of CH_4 gas.[8] An amorphous silicon oxycarbide glass was formed over 800 °C, followed by crystalline phases such as SiC, SiO_2 and C at higher temperature, so that there was no weight change. In the case of the powder with 40 vol.% TiH_2, the weight loss was happened by the decomposition of polymer and the dehydrogenation reaction from endothermic reaction of TiH_2 filler below 700 °C.[11] When the temperature was reached up to 700 °C, the abrupt weight gain was occurred because of the formation of TiN by the reaction of Ti and N_2 gas. The polymer–ceramic conversion and filler reaction can be summarized in following Eqs. (1) and (2).

$$(CH_3SiO_{1.5})_n(s) \xrightarrow{800^\circ C} \text{Si–O}_X\text{–C}_Y(s) + \text{gas} \xrightarrow{1200^\circ C} \text{SiC(s), SiO}_2\text{(s), C(s)} \tag{1}$$

$$TiH_2(s) \xrightarrow{600^\circ C} Ti(s) + 1/2N_2(g) + H_2(g) \xrightarrow{700^\circ C} TiN(s) \tag{2}$$

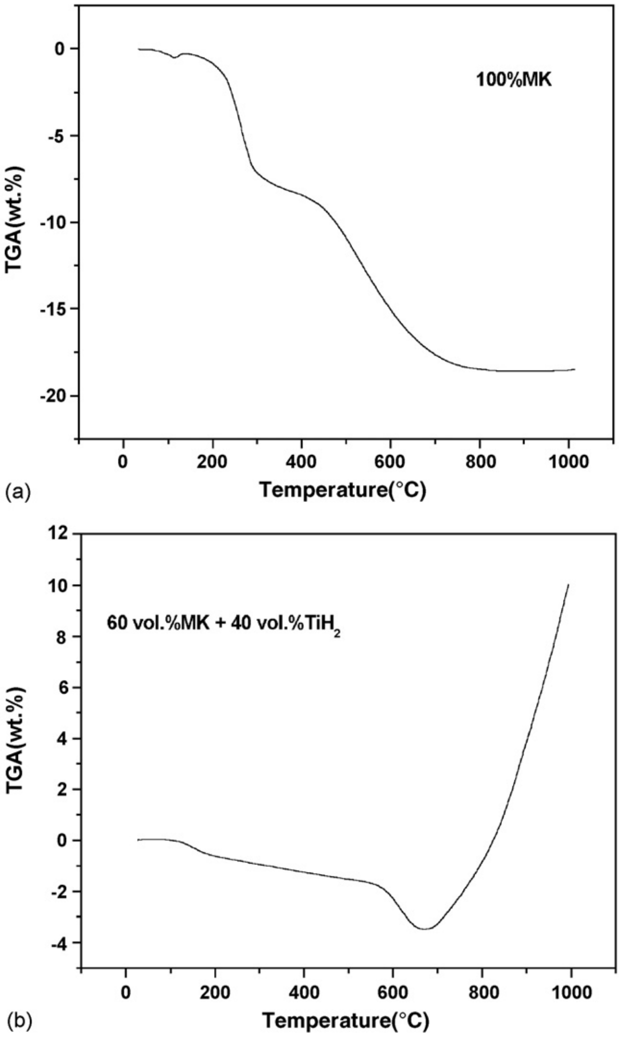

Fig. 1. Thermogravimetric analysis (TGA) up to 1000 °C in N_2 atmosphere: (a) polymer and (b) 60 vol.% polymer and 40 vol.% TiH_2.

Fig. 2 shows the weight change (a) and shrinkage (b) of the specimens pyrolyzed at various temperatures in N_2 atmosphere. Weight gain (a) was increased with subsequent increasing of the filler content due to the larger formation of TiN phase. The weight gain of the specimens with over 60 vol.% TiH_2 reacted at 1400 °C were higher than that of at 1600 °C. It was considered that Si–O–C matrix derived from polymer was changed to gaseous species such as CO(g) and SiO(g) by the carbothermal reduction above 1500 °C.[12]

$$\begin{aligned} &Si(s) + SiO_2(s) \rightarrow 2SiO(g) \\ &SiC(s) + 2SiO_2(s) \rightarrow CO(g) + 3SiO(g) \end{aligned} \tag{3}$$

However, the weight gain of the specimen with 40 vol.% TiH_2 at 1400 °C was lower than that of at 1600 °C due to the formation of Ti_5Si_3 phase as shown in Fig. 3(a), which accompanied with the decomposition of Si–O–C matrix phase. After pyrolysis at 1400 and 1600 °C, the densities of the specimens were almost same, ranging from 85 to 88 TD%. With increase of the filler content, shrinkage (b) is gradually decreased even though the almost same relative density. The reducing of shrinkage with the increase of filler content was resulted from increasing TiN content as reaction product. It is considered that the volume increase during the reaction of Ti with decomposition product of the polymer or reaction gas atmosphere compensates the polymer shrinkage. The XRD analysis of the specimens pyrolyzed at various temperatures for 4 h in N_2 atmosphere is shown in Fig. 3. In the specimen with 40 vol.% TiH_2 pyrolyzed at 1400 °C (a),

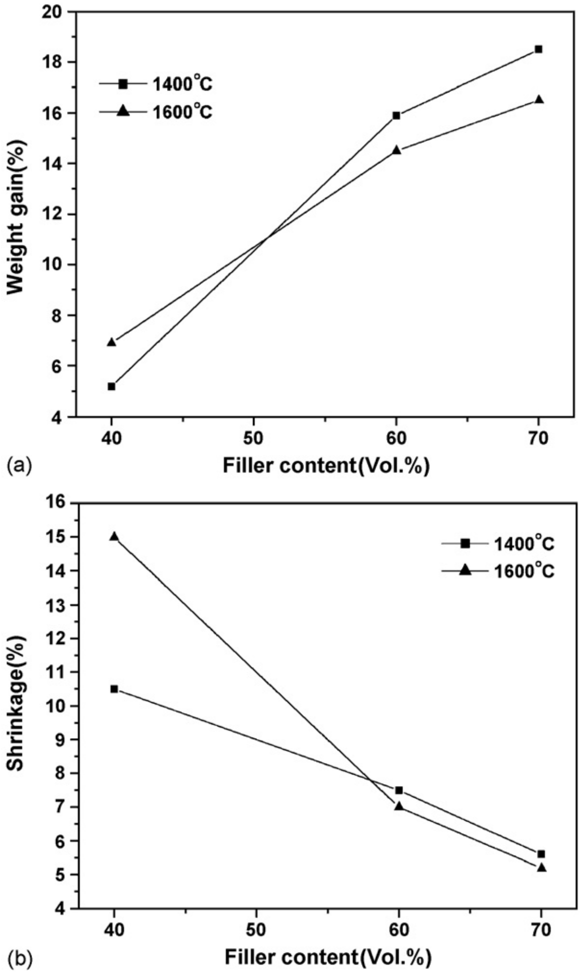

Fig. 2. The weight change (a) and shrinkage (b) of the specimens pyrolyzed at various temperatures in N_2 atmosphere.

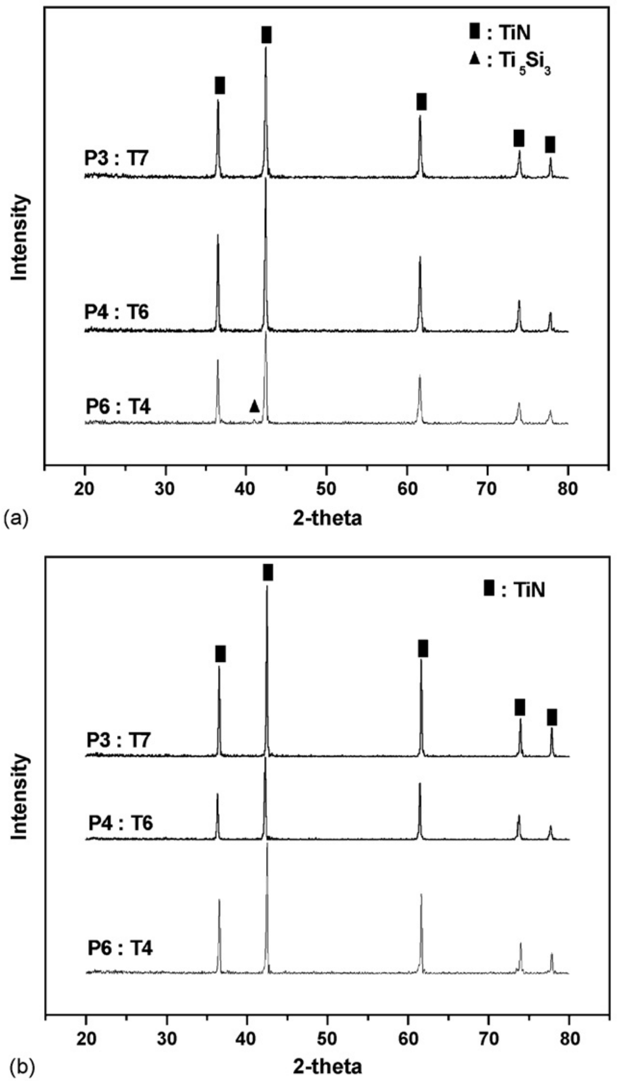

Fig. 3. XRD patterns of the specimens pyrolyzed at 1400 °C (a) and 1600 °C (b) for 4 h in N_2 atmosphere.

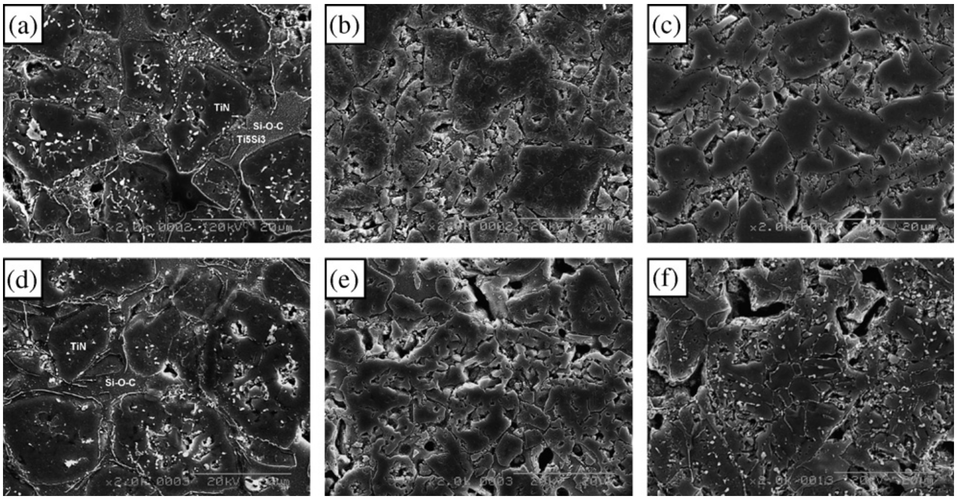

Fig. 4. SEM microphotographs of the specimens pyrolyzed at 1400 °C (a–c) and 1600 °C (d–f) for 4 h in N_2 atmosphere; 40 vol.% TiH_2 (a and d), 60 vol.% TiH_2 (b and e) and 70 vol.% TiH_2 (c and f).

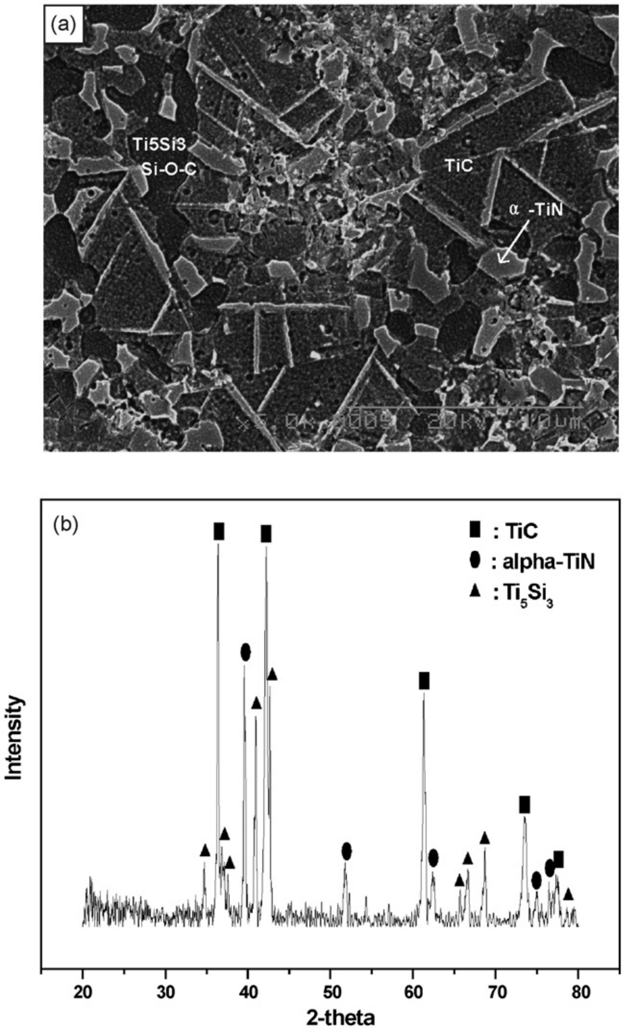

Fig. 5. SEM microphotographs (a) and XRD analysis (b) of the specimen with 60 vol.% TiH_2 pyrolyzed at 1400 °C for 4 h in Ar atmosphere.

Ti_5Si_3 phases were simultaneously formed due to the existence of the abundant Si component, which can be reacted with Ti, in polymer-derived Si–O–C matrix phase. However, Ti_5Si_3 phases were not observed in the specimen pyrolyzed at 1600 °C. The content of Si in the specimen could be reduced by the carbothermal reduction occurred above 1500 °C. With the increase of the filler content, the only TiN phase was formed.

Fig. 4 shows the SEM microphotographs of the specimens reacted at 1400 and 1600 °C for 4 h under N_2 atmosphere. The microstructure of the specimen with 40 vol.% TiH_2 at 1400 °C mainly consisted of TiN particles of 5–20 μm in size and nano-sized Ti_5Si_3 particles which were embedded in a polymer-derived Si–O–C glass matrix. However, Ti_5Si_3 particles were not found in the specimen pyrolyzed at 1600 °C. With increasing of the filler content, the particle size of TiN was gradually decreased.

Fig. 5 shows the SEM microphotographs (a) and XRD analysis (b) of the specimen with 60 vol.% TiH_2 pyrolyzed at 1400 °C for 4 h in Ar atmosphere. The microstructures of the specimen were composed of the faceted TiC particles, the very fine Ti_5Si_3 particles embedded in the Si–O–C glass matrix (dark) derived from polymer and small amount of TiN. During the pyrolysis of the specimen in Ar atmosphere, TiC and Ti_5Si_3 were formed by reaction of Ti with Si and C from solid and/or gaseous decomposition products of the polymer. In addition, the small amount of TiN phase was also observed. It was considered that TiN could be originated from the influence of a remaining N_2 gas as impurity in the furnace.

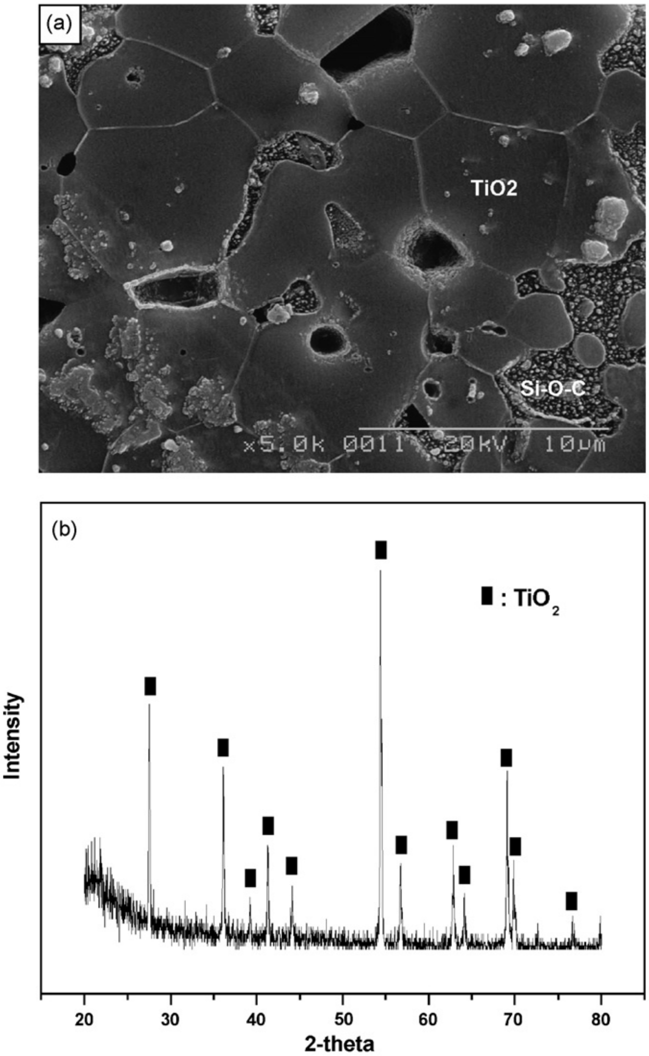

Fig. 6. SEM microstructure (a) and XRD analysis (b) of the specimen with 60 vol.% TiH_2 pyrolyzed at 1400 °C for 4 h in O_2 atmosphere.

Fig. 6 shows the microstructure (a) and XRD analysis (b) of the specimen with 60 vol.% TiH_2 at 1400 °C for 4 h in air. The pyrolyzed composites were composed of the TiO_2 particles of 3–8 μm in size with a clear boundary and an amorphous Si–O–C matrix. In the XRD diffraction patterns, Ti reacted with atmospheric oxygen and rutile TiO_2 can be formed.

4. Conclusion

Ti-based ceramic composites were synthesized by polymer pyrolysis of TiH_2-filled methylpolysiloxane in various atmospheres. When the specimen was pyrolyzed in N_2 atmosphere at 1400 and 1600 °C, Ti-based ceramic composites composed with TiN, Ti_5Si_3 and Si–O–C glass with a density of 85–88

TD% were obtained. Based on XRD analysis, the mainly TiN phases were formed in the specimens except the specimen with 40 vol.% TiH_2 pyrolyzed at 1400 °C. The microstructures of the specimens pyrolyzed at 1400 °C in N_2 atmosphere were composed of silicon oxycarbide matrix, TiN and Ti_5Si_3. However, Ti_5Si_3 phases could not be discerned in specimens pyrolyzed at 1600 °C. The phases of the specimen with 60 vol.% TiH_2 at 1400 °C in Ar and that in O_2 atmosphere were TiC, alpha-TiN (hcp), Ti_5Si_3 and TiO_2 (rutile), respectively.

Acknowledgement

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