

폴리머 열분해에 의한 TiN/Ti<sub>5</sub>Si<sub>3</sub> 복합재료의 고온산화High Temperature Oxidation of TiN/Ti<sub>5</sub>Si<sub>3</sub> Composites Prepared by Polymer Pyrolysis

Dong-Bok Lee\*, Thuan Dinh Nguyen

School of Advanced Materials Science &amp; Engineering, Sungkyunkwan University

**1. Introduction**

Ceramics are usually processed by powder metallurgical routes, but the high sintering temperature, low diffusion rate, low sintered density, and difficulty in fabricating near-net shape are major drawbacks in many cases. Hence, the pyrolysis of organometallic pre-ceramic polymers to manufacture ceramics shows a great promise for producing improved ceramics and resultant expanded, new ceramic applications, because ceramic composites with high melting points can be processed easily to a near net shape. However, density difference and consequent shrinkage that occur during conversion of the low density polymer to the high density ceramic residue are still major concerns. These can be effectively overcome by incorporating reactive fillers in the preceramic polymers, which lead to reduction in shrinkage and porosity in the matrix by expansion due to carburization reaction during pyrolysis.

In this study, the TiN/Ti<sub>5</sub>Si<sub>3</sub> bulk composites were newly fabricated by pyrolyzing Si-containing pre-ceramic polymer and TiH<sub>2</sub> powders, and their high temperature oxidation behavior was investigated.

**2. Experimental**

Into the polymer powders of methylpolysilsesquioxane, TiH<sub>2</sub> powders were added as a filler. Then, the mixed powders were dry ball milled for 15 h using Si<sub>3</sub>N<sub>4</sub> balls, sieved to > 400 mesh, and warm pressed at 230°C for 45 min under 30 MPa to make 20 mm pellet. Since methylpolysilsesquioxane decomposes and converts to ceramic from about 450°C by pyrolysis, and TiH<sub>2</sub> liberates hydrogen from about 600~650°C, the pellet was preheated to 850°C with a rate of 0.5°C/min under 1 atm of N<sub>2</sub>, heated at 1~2°C/min up to the final temperature of 1600°C, and held at this temperature for 4 hr under 20 atm of an Ar atmosphere for gas pressure pyrolysis. Silicon in the polymer and N<sub>2</sub>(g) in the gas reacted with Ti in TiH<sub>2</sub>(s) to make the TiN/Ti<sub>5</sub>Si<sub>3</sub> composites.

The oxidation tests on the prepared specimens were carried out in air at the temperatures of 400 and 1000~1300°C up to 2040 hr. The weight gain during oxidation was monitored continuously as a function of time using a thermogravimetric analyzer (TGA). The oxidized specimens were investigated by the use of scanning electron microscope (SEM), X-ray diffractometer (XRD), and electron probe microanalyzer (EPMA).

### 3. Conclusion

From the Si-containing pre-ceramic polymer and  $TiH_2$  powders, new composites that consisted primarily of a TiN matrix containing dispersed  $Ti_5Si_3$  intermetallic phases were synthesized. The TiN/ $Ti_5Si_3$  composites were oxidized mainly by the oxidation of the TiN matrix in the temperature range of 700 and 900°C in air for up to 120 hr. The  $Ti_5Si_3$  intermetallic phase was not oxidized. The oxidation was preceded by the outward diffusion of nitrogen and Ti ions, and the inward diffusion of oxygen ions, to form a  $TiO_2$  layer on the surface.

Table I. Physical Properties of the TiN/ $Ti_5Si_3$  Composites

	TiN/ $Ti_5Si_3$	Remark
Vickers hardness (GPa)	18	bulk TiN=9, $Ti_5Si_3$ =20
3-point flexural strength(MPa)	270	
Fracture strength ( $MPm^{1/2}$ )	3.5	
Electrical conductivity ( $\Omega^{-1}m^{-1}$ ) at 25°C	6102-6211	bulk TiN=7692

### References

1. S. Yajima, J. Hayashi, M. Omori, and K. Okmura, Nature 262, 683 (1976).
2. R. W. Rice, Am. Ceram. Soc. Bull. 62, 889 (1983).