

Oxidation Resistance and Electrical Conductivity of Ti_3SiC_2 with Thin Oxide Layer

Sung-Ik Hwang^{1,a}, Kyoung Ran Han^{2,b}, and Chang-Sam Kim^{1,c}

¹Battery Research Center, KIST, P. O. Box 131, Cheongryang, Seoul Korea

²Division of Materials Science and Technology, KIST, P.O. Box 131, Cheongryang, Seoul Korea

^acalmysi@kist.re.kr, ^bkrlim@kist.re.kr, ^ccskim@kist.re.kr

Abstract

Ti_3SiC_2 was coated with Al_2O_3 , MgO and SiO_2 respectively by sol-gel method and cured at 900 and 1200°C. The coated oxides did not react with Ti_3SiC_2 at 900°C but reacted with it to form TiC_x at 1200°C. The specimen coated with SiO_2 at 900°C formed a dense protecting layer and showed the best oxidation resistance at 800°C in air. However, the dense protecting layers did not form in Al_2O_3 and MgO coated specimens cured even at 900°C. MgO coated specimen showed the worst improvement in the oxidation resistance because the reactivity of MgO with Ti_3SiC_2 was highest. On the other hand, the electrical conductivities were measured in MgO and Al_2O_3 coated specimens to have TiC_x but could not be measured in the SiO_2 coated ones because of the nonconductive dense protected layers.

Keywords : Ti_3SiC_2 , TiC_x , Sol-Gel Coating, Oxidation Resistance, Electric Conductivity

1. Introduction

The characteristic of Ti_3SiC_2 which consists of nano-layered structure is to have both metallic and ceramic properties[1,2]. That is, this material shows the metallic properties such as outstanding electrical and thermal conductivities, good machinability, high thermal shock resistance, and significant plastic deformation even at room temperature. It also has the ceramic properties such as high melting temperature, good chemical stability, low thermal expansion coefficient, low density and high elastic constant. Its critical disadvantage is an easy oxidation at high temperature[3]. Therefore in this study Ti_3SiC_2 was coated with some oxides and the change of oxidation resistance and electrical conductivity was investigated.

2. Experimental and Results

In this experiment Ti, C and Si powders were used as starting materials and firstly TiC_x was synthesized to make Ti_3SiC_2 . Ti and C powders were mixed as a mole ratio of 3 to 2 and the mixture was pressed in the metal mould with 20 MPa for making a disk type green body. It was then heat-treated in the graphite vacuum furnace at 1550°C for 3 hrs under 10^{-1} torr. This synthesized TiC_x was crushed in specs mill and sieved through 325mesh screen. Then TiC_x and Si powders were mixed as a mole ratio of 3 to 1 and hot-pressed at 1550°C for 1.5hrs under 25MPa to make the dense sintered Ti_3SiC_2 . This Ti_3SiC_2 was cut into $10 \times 10 \times 3$ mm, dip-coated in Al_2O_3 , MgO and SiO_2 sol respectively and heat-treated at 900 and 1200°C for 1 hr in flowing Ar gas. The coated surface and crystal structure of samples were investigated with SEM and XRD, and the

electrical conductivity was measured with tester.

The weight increase of Ti_3SiC_2 occurs during high temperature oxidation under oxygen partial pressure. Although C in Ti_3SiC_2 reacts with O_2 and volatilizes as CO or CO_2 , TiO_2 and SiO_2 forms on the surface of Ti_3SiC_2 during oxidation resulting in weight gain. Fig. 1 shows the oxidation kinetics of oxide-coated Ti_3SiC_2 at 800°C in air. The increase of weight occurred nearly within 10 hrs the early stage of the oxidation. Uncoated specimen showed the largest weight gain, which is 3 times higher than that of SiO_2 -coated one to be cured at 900°C. It should be noticed that the SiO_2 -coated specimen to be cured at 900°C showed better oxidation resistance than that at 1200°C, whereas the Al_2O_3 - and MgO -coated specimens to be cured at 1200°C showed better oxidation resistance than that at 900°C. This means that there are different protecting routes for oxidation between the SiO_2 and the others.

Fig. 2 shows the XRD patterns of coated Ti_3SiC_2 specimens after curing. Ti_3SiC_2 and weak TiC_x peaks are detectable in the specimens cured at 900°C, but exaggerated TiC_x peaks appear in those cured at 1200°C. The intensity of TiC_x peaks is stronger than that of Ti_3SiC_2 in MgO and Al_2O_3 , which suggests that Ti_3SiC_2 reacts with MgO or Al_2O_3 to form TiC_x more actively than with SiO_2 . One interesting thing is the absence of any trace of silicon compounds in the XRD patterns. The Gibb's free energies of SiO (g) and SiO_2 are -227 and -642 kJ/mol at 1200°C, respectively. Therefore the Si should remain in the form of SiO_2 on the surface of Ti_3SiC_2 rather than volatile as SiO during curing. The formation of TiC_x on the surface is thought to improve the oxidation resistance slightly even though the reason is not clear yet.

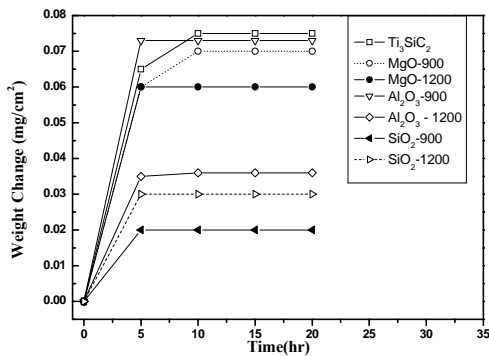


Fig. 1. Oxidation curves of Ti_3SiC_2 coated with Al_2O_3 , MgO and SiO_2 .

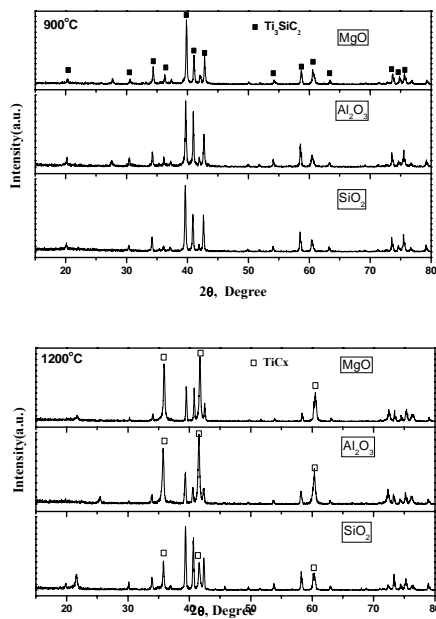
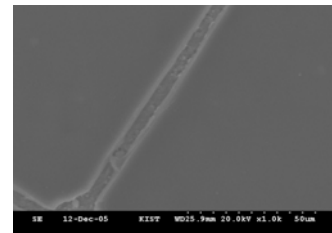
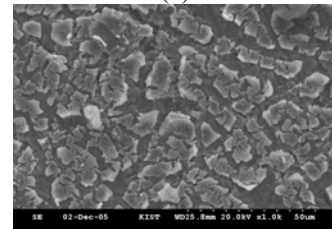


Fig. 2. XRD patterns of Ti_3SiC_2 coated with Al_2O_3 , MgO and SiO_2 at 900 and 1200°C.

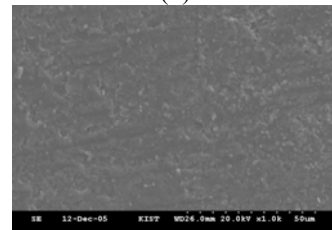
Fig. 3 shows the surface morphology of specimens coated with SiO_2 and cured at 900°C, Al_2O_3 and cured at 1200°C, and MgO and cured at 1200°C. A dense coated layer was observed in SiO_2 coated specimen, but a tortoiseshell-like layer with wide open area was formed in Al_2O_3 -coated one and no layer in MgO -coated one. It is clear that the dense layer of SiO_2 -coated Ti_3SiC_2 enhances the oxidation resistance. The poor improvement of MgO coated specimen is due to the lack of protecting layer. On the electrical conductivity point of view, however, the MgO - and Al_2O_3 -coated specimens showed higher conductivity than SiO_2 -coated ones.



(a)



(b)



(c)

Fig. 3. SEM micrographs of Ti_3SiC_2 surface coated with (a) SiO_2 at 900°C, (b) Al_2O_3 at 1200°C and (c) MgO at 1200°C.

3. Summary

Ti_3SiC_2 was coated with Al_2O_3 , MgO and SiO_2 by sol-gel method. All the oxides reacted with Ti_3SiC_2 to form TiC_x at 1200°C, while a dense layer was observed on the surface of SiO_2 -coated specimen to be cured at 900°C. The weight increase of SiO_2 -coated Ti_3SiC_2 was reduced to one third of uncoated one during oxidation at 800°C and the electrical conductivity was significantly lowered due to the dense nonconductive layer.

4. References

1. M. W. Barsoum, L. Farber and T. E. Raghy, Metall. mater. trans., **30A**, 1727(1999).
2. M. Radovic, M. W. Barsoum, T. E. Raghy, J. Seidenskicker and S. Widerhorn, Acta Mater., **48**, 453(2000).
3. D. B. Lee, J. H. Han, Y. D. Kim and S. W. Park, Mater. Sci. Forum, **510-511**, 422(2006).