

Mapping of Elemental Composition in Air-Oxidized Ti₃SiC₂

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Available Online at: www.austceram.com/ACS-Journal-2008vol2.asp

Abstract

Depth-profiling of elemental composition at the near surface of air-oxidized Ti₃SiC₂ was studied by secondary ion mass spectrometry (SIMS). The duplex microstructure of oxides formed at air-oxidized Ti₃SiC₂ surface was observed which consisted of an outer uniform layer of rutile-TiO₂ and an inner graded layer of TiO₂ and SiO₂. The thickness of oxide scales increased with an increase in temperature. Ti₃SiC₂ is resistant to oxidation in air at up to 1100°C.

Keywords: SIMS, depth profile, oxidation, rutile, Ti₃SiC₂.

INTRODUCTION

Ti₃SiC₂ is known as a novel functional material, which exhibits the merit of both metals and ceramics. For example, like metals, it is readily machineable, thermally shock resistant, thermally and electrically conductive, and damage tolerant. Like ceramics, it is lightweight, high-temperature oxidation resistant, and elastically stiff [1-10].

To date, mixed and confusing results have been reported for the oxidation behaviour of Ti₃SiC₂ in air. For example, the oxidation resistance of Ti₃SiC₂ was reported by Li et al. [12] to be excellent at temperatures below 1100 °C due to the formation of a protective SiO₂ surface layer. However, oxidation of Ti₃SiC₂ was detected by Racault et al. [11] to commence as low as 400 °C through the formation of an anatase-like TiO₂ film that eventually transforms to rutile at 1050 °C. In addition, although the existence of a protective TiO₂ (rutile) has been confirmed by all the researchers, the presence of a protective SiO₂ film is much more elusive [4]. Li et al. [12] reported the oxidized layers to exhibit a duplex microstructure in the temperature range 1000-1500 °C with an outer layer of TiO₂ (rutile) and an inner layer consisting of SiO₂ and TiO₂. In a similar study, Barsoum et al. [10] also found the protective oxide scales that formed to be layered with the inner

layer comprised of silica (formed at ~1200 °C) and TiO₂ and the outer layer comprised of pure rutile (formed at ~900 °C). The growth of these oxide layers is both temperature and time-dependent and was thought to occur by the outward diffusion of titanium and carbon and the inward diffusion of

oxygen through surface pores or cracks. The overall oxidation reaction for Ti₃SiC₂ suggested by Li et al. [12] is:



However, the nature and precise composition of the oxide layers formed during oxidation remain controversial, especially in relation to the presence of SiO₂ and the graded nature of the oxides formed. In addition, the effects of temperature and time on the graded surface composition of TiC, TiO₂ and SiO₂ during oxidation of Ti₃SiC₂ are still unknown.

In this study, SIMS experiments were conducted to map the composition depth profiles of air-oxidized Ti₃SiC₂ at various temperatures. SIMS is a well-known technique for quantitative depth profiling and analysis of trace elements in solid materials, especially semiconductors and thin films. SIMS enables the detection of all elements with very high

sensitivity, in combination with high depth resolution and the possibility of depth profiling on small area ($< 100 \times 100 \mu\text{m}^2$) [14]. It has been reported that acquiring molecular MCs^+ secondary ions (M is the matrix or major element to be depth profiled) under Cs^+ bombardment results in significantly reduced matrix effects [14-15]. The enhanced elemental sensitivity of SIMS allows the detection of oxygen within the structure of the surface oxide layers. MCs^+ -SIMS is widely used for depth profiling of thin films and coatings. The graded oxide surface of Ti_3SiC_2 can be treated as an oxide coating for improved oxidation resistance of Ti_3SiC_2 . Thus, SIMS was chosen as the tool for surface analysis in this study.

EXPERIMENTAL

The Ti_3SiC_2 samples were fabricated using a procedure described elsewhere [1]. Essentially, powders of Ti, SiC and C were mixed in the proper molar ratio, cold pressed, and then hot-isostatically pressed at 1600°C for 4 h at a pressure of 40 MPa to produce dense Ti_3SiC_2 samples of grain size in the range of 10–30 μm and with less than 2 wt.% TiC as an impurity phase. Thin slices of ~ 3 mm thick were cut from a rectangular Ti_3SiC_2 bar ($15 \times 12 \times 50 \text{ mm}^3$). One of the slices was used as a control and the remaining slices were each oxidized in an air-ventilated furnace for 20 min at 800, 900, 1000, 1100 and 1200°C , respectively.

The near-surface composition of the oxides formed at each temperature was analysed using a Cameca Ims5f SIMS through the elemental monitoring of Ti, C, Si, O and TiC. A Cs^+ ion beam of 5.5 keV impact energy was employed. Typical beam currents ranged from 50 to 150 nA and the beam was scanned across areas of $250 \times 250 \mu\text{m}^2$. MCs^+ secondary ions were accepted from a circular analysis area on the sample limited to a diameter of 55 μm by a combination of lens and aperture settings. Oxidised samples were gold-coated prior to SIMS analysis.

RESULT AND DISCUSSION

To optimize depth profiling, the ion count rates in all mass channels were first normalized to Cs^+ secondary ion count rates to minimize any ion yield related matrix effects, and to negate any effect of variations in the primary ion beam current. With the aid of profilometry, the sputtering times were converted into sputtered depths. Due to the different total sputtering time in each sample, the crater depth is slightly different; however, the sputter rate obtained was almost the same, because of the similar target material. For the ease of data analysis and

sample comparison, only the depth of ~ 2.4 micron from surface was considered in this work.

Figure 1 shows the variation of specific ion yields as a function of depth in the control sample. As would be expected, the composition with depth within the control sample before oxidation was quite uniform or homogeneous. As Ti_3SiC_2 was oxidized at 800°C (Fig. 2), an outer layer of rutile- TiO_2 formed ($\sim 1 \mu\text{m}$ thick) at the surface. At the same time, an inner layer of TiO_2 and SiO_2 also formed.

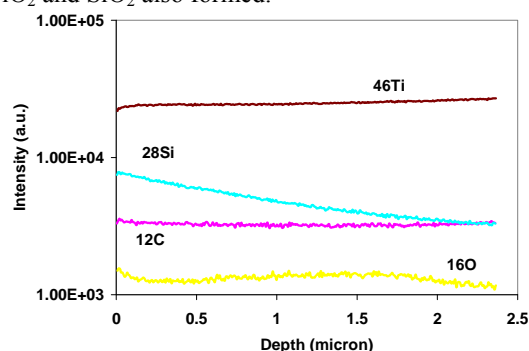


Fig. 1: Depth profile of control sample.

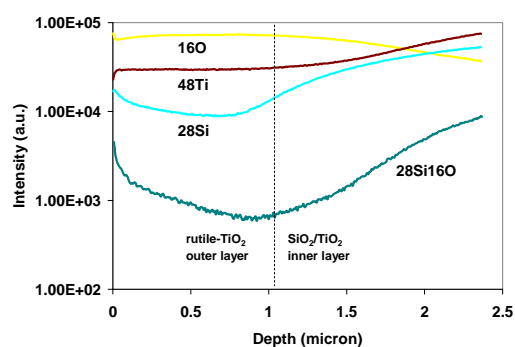


Fig. 2: Depth profile of oxidized Ti_3SiC_2 at 800°C

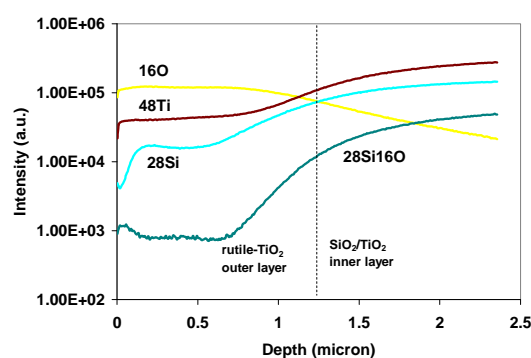


Fig. 3: Depth profile of oxidized Ti_3SiC_2 at 900°C

As the temperature increased to 900°C (Fig. 3), the rutile-TiO₂ grew to ~1.25 μm thick. This suggests that the growth of oxide layer occurred by the outward diffusion of Ti and C and the inward diffusion of O via surface pores or cracks. Thus, the formation of rutile-TiO₂ is both temperature and time-dependent. The growth of oxide scales was quite gradual from 800 to 1100°C but became very rapid at 1200°C where the rutile layer grew to more than 10 μm thick (Figs. 4-7). This suggests that Ti₃SiC₂ is resistant to oxidation in air at up to 1100°C and is not suitable for prolonged use at a temperature greater than 1100°C. Table 1 summarises the thickness of rutile layer formed at various temperatures.

Table 1: Variation of thickness of rutile-TiO₂ layer as a function of temperature

Temperature (°C)	800	900	1000	1100	1200
Thickness of TiO ₂ layer (μm)	1.1	1.25	1.5	1.78	>10

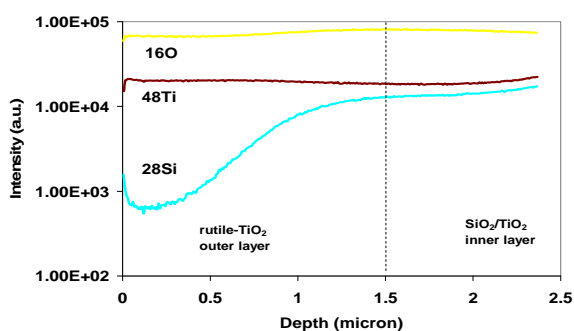


Fig. 4: Depth profile of oxidized Ti₃SiC₂ at 1000 °C

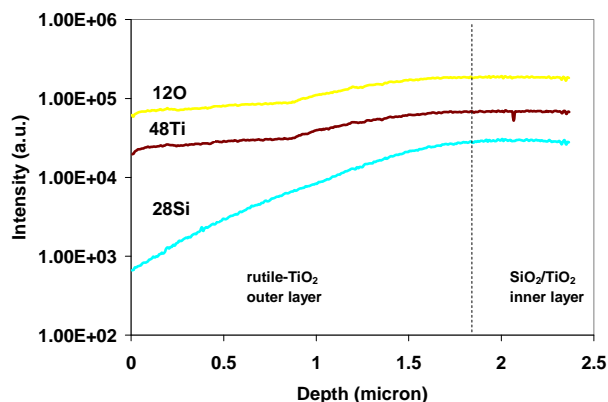


Fig. 5: Depth profile of oxidized Ti₃SiC₂ at 1100 °C

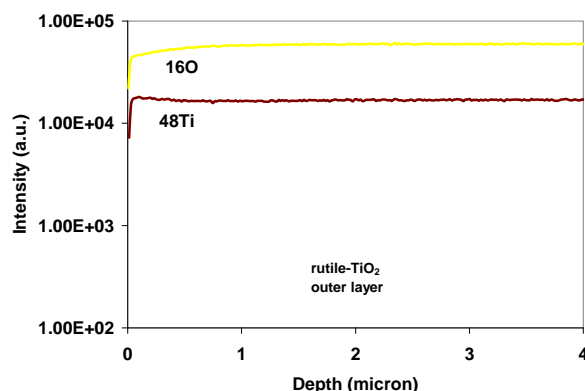


Fig. 6: Depth profile of oxidized Ti₃SiC₂ at 1200 °C.

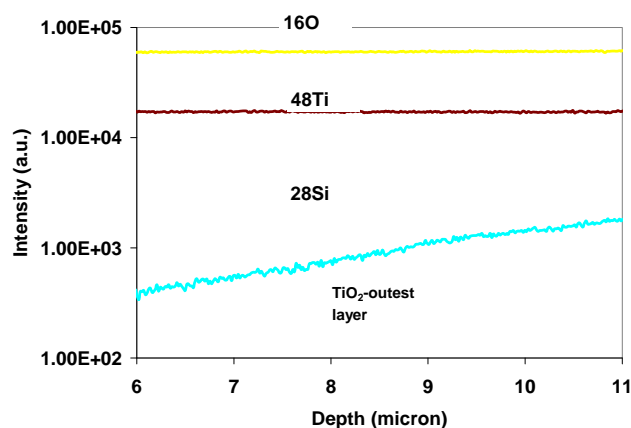


Fig. 7: Variation of secondary ions intensities at deeper surface of oxidized Ti₃SiC₂ at 1200 °C

It is interesting to note that the composition of rutile layer formed at the near surface of Ti₃SiC₂ is relatively uniform, homogeneous or continuous with depth. In contrast, the composition of the inner layer shows a distinct graded distribution of SiO₂ and TiO₂ which may indicate that this layer is porous and discontinuous [13].

CONCLUSIONS

The composition depth profiles at the near-surface of air-oxidized Ti₃SiC₂ at the temperature range 800-1200°C have been analysed by secondary ion mass spectrometry (SIMS). Ti₃SiC₂ is resistant to oxidation at up to 1100°C. The oxides formed following oxidation consist of an outer homogeneous and continuous layer of rutile-TiO₂ and an inner layer of SiO₂ and TiO₂ which is discontinuous and graded in composition. The thickness of oxide layers is both temperature- and time-dependent.

ACKNOWLEDGEMENT

This work is funded by an ARC Discovery-Project grant (DP0664586) and an ARC Linkage-International grant (LX0774743). The collection of SIMS data was conducted at ANSTO with financial support from AINSE (05/106 & 06247).

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