



Detection of Amorphous Silica in Air-Oxidized Ti_3SiC_2 at 500–1000°C

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Abstract

In this paper we describe the use of secondary-ion mass spectrometry (SIMS) and nuclear magnetic resonance (NMR) to detect the existence of amorphous silica in Ti_3SiC_2 oxidised at 500-1000°C. The formation of an amorphous SiO_2 layer and its growth in thickness with temperature was monitored using dynamic SIMS. A duplex structure with an outer layer of TiO_2 and an inner mixture layer of SiO_2 and TiO_2 was observed. Results of NMR verify for the first time the direct evidence of amorphous silica formation during the oxidation of Ti_3SiC_2 at the temperature range 500-1000°C.

Keywords: SIMS, NMR, Ti_3SiC_2 , Amorphous silica, Oxidation

WYKRYWANIE AMORFICZNEJ KRZEMIONKI W Ti_3SiC_2 UTLENIANYM W 500–1000°C

W artykule opisano wykorzystanie spektroskopii masowej jonów wtórnych (SIMS) i magnetycznego rezonansu atomowego (NMR) do wykrywania amorficznej krzemionki w Ti_3SiC_2 utlenianym w 500–1000°C. Tworzenie się warstwy amorficznej krzemionki i wzrost jej grubości wraz z temperaturą monitorowany był za pomocą dynamicznej metody SIMS. Zaobserwowano budowę podwójną warstwy złożoną z warstwy zewnętrznej TiO_2 i wewnętrznej mieszanej warstwy SiO_2 i TiO_2 . Wyniki NMR potwierdzają po raz pierwszy bezpośredni dowód tworzenia się amorficznej krzemionki podczas utleniania Ti_3SiC_2 w temperaturach z przedziału 500-1000°C.

Słowa kluczowe: SIMS, NMR, Ti_3SiC_2 , krzemionka amorficzna, utlenianie

1. Introduction

Ti_3SiC_2 is a functional ceramic that exhibits the merits of both metals and ceramics. 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 [1-16]. This unique combination of properties makes Ti_3SiC_2 a potential candidate material for high temperature applications.

To date, the oxidation properties of Ti_3SiC_2 have been widely investigated. However, mixed and confusing results have been reported for the oxidation behaviour of Ti_3SiC_2 in air. For example, the oxidation resistance of Ti_3SiC_2 was reported by Li *et al.* [12] to be excellent at temperatures below 1100°C due to the formation of a protective SiO_2 surface layer. In addition, although the existence of a protective TiO_2 (rutile) has been confirmed by all the researchers [11-14], the presence of a protective SiO_2 film is much more elusive [4]. Li *et al.* [12] also reported the oxidized layers to exhibit a duplex microstructure in the temperature range 1000-1500°C with an outer layer of TiO_2 (rutile) and an inner mixture layer

of SiO_2 and TiO_2 . In a similar study, Barsoum *et al.* [10] also found the protective oxide scales to be layered with an inner mixture layer of silica (formed at ~1200°C) and TiO_2 , and an outer layer 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 Ti_3SiC_2 can be described as [12].

However, the nature and precise composition of the oxide layers formed during oxidation remain controversial, especially in relation to the presence of SiO_2 and the graded nature of the oxides formed. Although the existence of crystalline SiO_2 (cristobalite) during Ti_3SiC_2 oxidation at temperatures above 1200°C has been confirmed [11-14], the form or the nature of silica formed below 1200°C is still unknown. Based on transmission electron microscopy (TEM) observations, Chen *et al.* [13] reported the oxide layer formed to contain a mixture of amorphous SiO_2 and crystalline rutile at the very early stages of oxidation. Similarly, Zhang and co-workers [14] reported the existence of amorphous SiO_2 that sealed the cracks formed in the oxide layers. With the aid of TEM, Low

et al. [15–16] also reported the existence of amorphous silica during the oxidation of Ti_3SiC_2 . According to Barsoum and El-Raghy [17], the oxide layers formed during low temperature oxidation consist of rutile and amorphous silica, but at temperatures greater than 1240°C, cristobalite formed. The presence of amorphous silica was also predicted by Okano *et al.* [18] to exist during the oxidation of Ti_3SiC_2 .

In this paper, we describe the use of secondary-ion mass spectrometry (SIMS) to characterise the formation of amorphous silica during oxidation of Ti_3SiC_2 over the temperature range 500–1000°C. We verify the existence of the elusive amorphous SiO_2 with the aid of ^{29}Si nuclear magnetic resonance (NMR).

2. Experimental procedure

Maxthal® Ti_3SiC_2 , supplied by Kanthal AB, was used in this study. For SIMS analysis, thin slices of ~3 mm thick were cut from the as-received Ti_3SiC_2 sample. One of these slices was used as a control and 6 slices were each oxidized in an air-ventilated furnace for 20 min at 500, 600, 700, 900, and 1000°C, respectively. The Ti_3SiC_2 sample was also ring-milled to obtain fine Ti_3SiC_2 powder for ^{29}Si NMR analysis. The powdered samples were then divided into 6 batches where each batch was oxidized in an air-ventilated furnace for 20 min at 500, 600, 700, 900, and 1000°C, respectively.

The near-surface compositions of the oxidized samples were analysed using a Cameca Ims-5f SIMS through the elemental monitoring of Ti, C, Si, O and TiC. A 5.5 keV impact-energy Cs^+ ion beam was employed. Typical beam currents ranged from 50 to 150 nA and the beam was scanned across areas of $250 \times 250 \mu m^2$. Oxidised samples were gold-coated prior to SIMS analysis. To optimize depth profiling, the intensity in all mass channels were first normalised to Cs^+ secondary ion count rates to minimise any ion yield related matrix effects, and to reduce any effect of variation in the primary ion beam current. The sputtering times were assumed to be directly proportional to the sputtered depth. With the aid of profilometry, a constant conversion factor of 7.87 $\mu m/s$ was determined and used to change the sputtering time to the sputtered depth.

High resolution solid state ^{29}Si magic-angle-spinning (MAS) nuclear magnetic resonance (NMR) spectra were acquired at ambient temperatures using an MSL-400 NMR spectrometer ($B_0 = 9.4$ T) operating at the ^{29}Si frequency of 79.48 MHz. Data of ^{29}Si MAS NMR were acquired using a Bruker 7-mm double-air-bearing probe with single pulse (Bloch decay) methods which utilised high-power 1H decoupling during data acquisition. The MAS frequencies implemented for these measurements were ~5 kHz. For these ^{29}Si MAS single pulse/ high-power 1H decoupling measurements, a single ^{29}Si $\pi/4$ pulse width of 2.5 μs and a pre-acquisition delay of 10 μs were used in conjunction with recycle delays of 30–60 s for quantitative ^{29}Si speciation analysis. All ^{29}Si MAS chemical shifts were externally referenced to tetramethylsilane (TMS) at $\delta = 0$ ppm via a high purity sample of kaolinite.

3. Results and discussion

Fig. 1 shows the variation of specific ion yields as a function of sputtering depth for the control sample and the

corresponding oxidized Ti_3SiC_2 at various temperatures. As would be expected, the composition within the control sample before oxidation was uniform as indicated by the flat curves of the Ti, Si and C ions.

Based on the results reported in the literatures [1–14] that a duplex structure with an outer layer of TiO_2 and an inner mixture layer of SiO_2 and TiO_2 formed during oxidation of Ti_3SiC_2 , the crossover point of 28Si and 16O shown in Fig. 1 can be assumed to be the boundary between the TiO_2 outer layer and inner mixture layer of SiO_2/TiO_2 . Based on the results of synchrotron radiation diffraction (Fig. 2), the TiO_2 formed at 500°C is anatase and its abundance increases only moderately at up to 800°C before it disappears completely. At 600°C, rutile also appears and its abundance increases rapidly with a further increase in temperature. No crystalline SiO_2 was detected at between 500–1000°C.

Compared to the control sample, the oxidized Ti_3SiC_2 samples show a relatively high count of 16O. This indicates the diffusion of oxygen into the sample at the near-surface and the subsequent oxidation at temperatures above 500°C. The elemental mass transportation and the thickening process of oxide scales formed are depicted by the SIMS depth profiles for oxidized Ti_3SiC_2 . As Ti_3SiC_2 is oxidized at 500°C, an outer layer of TiO_2 (~0.21 μm thick) forms at the surface. At the same time, an inner mixture layer of TiO_2 and SiO_2 also forms. As the temperature increases from 600 to 1000°C, the TiO_2 layer dramatically grows to 2.81 μm thick. This suggests that the growth of oxide layer occurs by the outward diffusion of Ti and the inward diffusion of O via surface pores or cracks [19]. The thickness of the measured outer TiO_2 layer as a function of temperature is summarised in Table 1.

Table 1. Variation of TiO_2 layer thickness as a function of temperature.

Temperature [°C]	500	600	700	900	1000
Thickness [μm]	0.21	0.80	1.00	1.67	2.81

From the SIMS results, it is also evident that the intensity of Si increases with an increase in sputtering time or depth which indicates the existence of an inner Si-rich region during the oxidation of Ti_3SiC_2 (Fig. 1). The Si-rich region implies the existence of inner mixture layer of TiO_2 and silica. As previously mentioned, results from synchrotron radiation diffraction showed no presence of crystalline silica in oxidized Ti_3SiC_2 at 500–1000°C (Fig. 2). This suggests that the silica formed in this temperature range is glassy or amorphous which concurs with the predictions previously made by other researchers [17–18].

In order to verify the claimed existence of amorphous SiO_2 , ^{29}Si MAS NMR was employed to ascertain the bonding nature of the silica formed during oxidation of Ti_3SiC_2 at 500, 600, 700, 900, and 1000°C (Fig. 3). As to be expected and in the absence of oxidation, the NMR spectrum (not shown) of as-received Ti_3SiC_2 showed no silica signal. This is expected because the strongly paramagnetic Ti^{3+} centres will lead to profound broadening resulting in the parent structure beyond observation. In contrast, the ^{29}Si spectra of the oxidised samples show only the semi-condensed/condensed silica phase that has separated from the parent Ti_3SiC_2 upon oxidation. It is worth-noting here that the Ti_3SiC_2 ^{29}Si resonance(s)

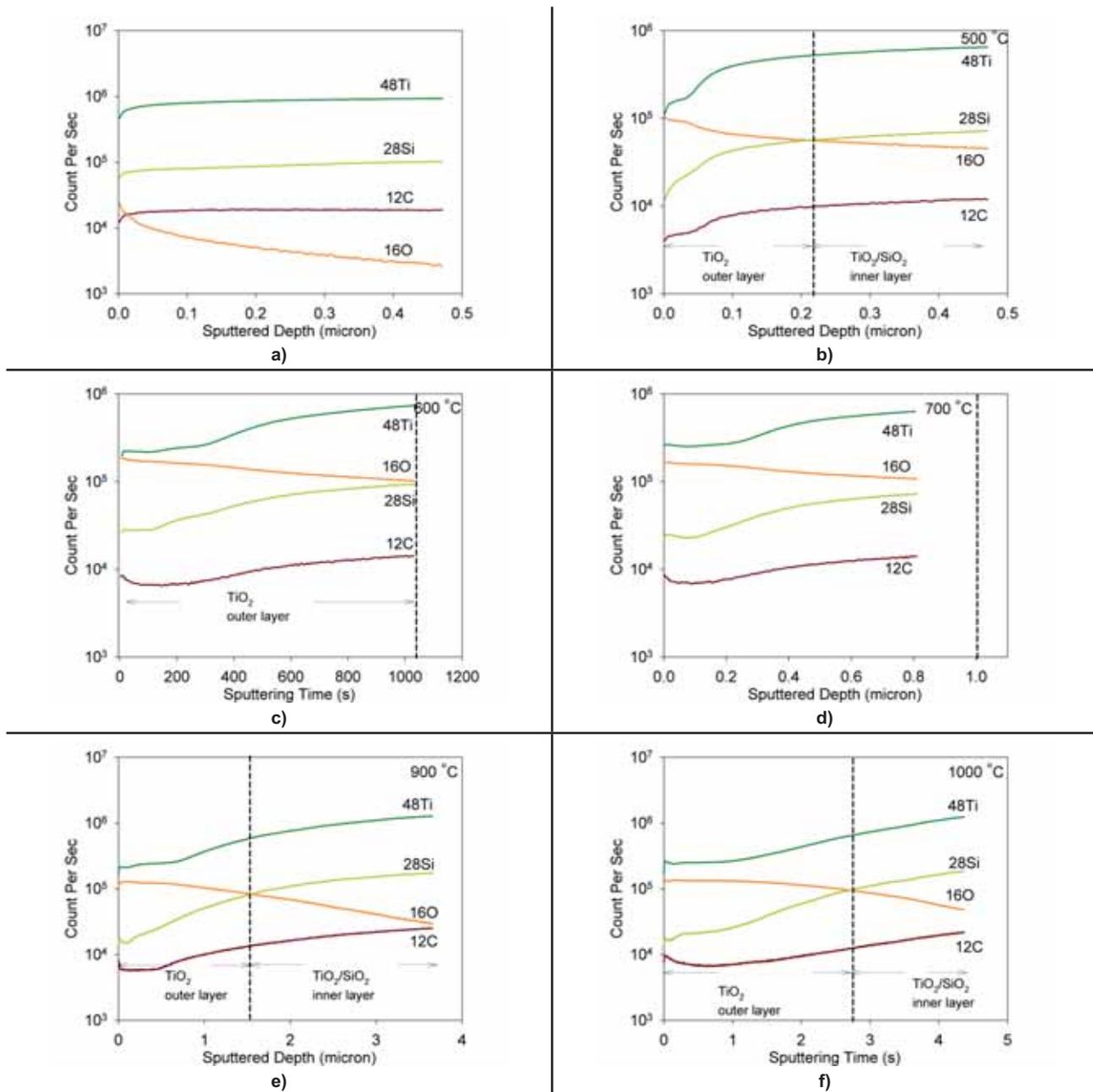


Fig. 1. SIMS depth profiles of a) control sample, and oxidized Ti_3SiC_2 at: b) 500°C, c) 600°C, d) 700°C, e) 900°C, and f) 1000°C.

would appear much closer to 0 ppm (*i.e.* further downfield) than that observed from the silica phase at \sim 112 ppm [20]. The spectrum of Q^2 represents the structures with chains of tetrahedral, Q^3 are sheet silicates and Q^4 are framework silicates. The observed NMR chemical shift peaks are what is expected for amorphous condensed Q^4 silica. It is thus evident that the results of ^{29}Si MAS NMR shown in Fig. 3 provide confirmation of the existence of amorphous silica during the oxidation of Ti_3SiC_2 at \leq 1000°C. The implication of this evidence is wide-ranging for the oxidation of MAX phases. It can be postulated that similar amorphous phases (*e.g.* Al_2O_3 , GeO_2 , SnO_2 , *etc.*) are likely to exist during oxidation of other ternary carbides such as Ti_3AlC_2 , Ti_3GeC_2 , and Ti_2SnC .

4. Conclusions

The composition depth profiles and the growth of oxide layers formed during oxidation of Ti_3SiC_2 in the temperature range 500–1000°C have been characterised by dynamic

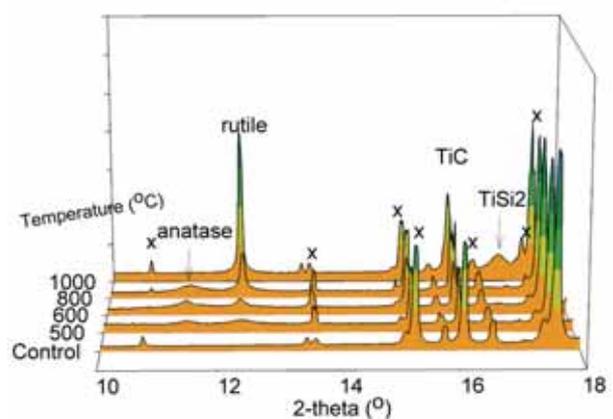


Fig. 2. Synchrotron radiation diffraction patterns for oxidized Ti_3SiC_2 at 500–1000°C.

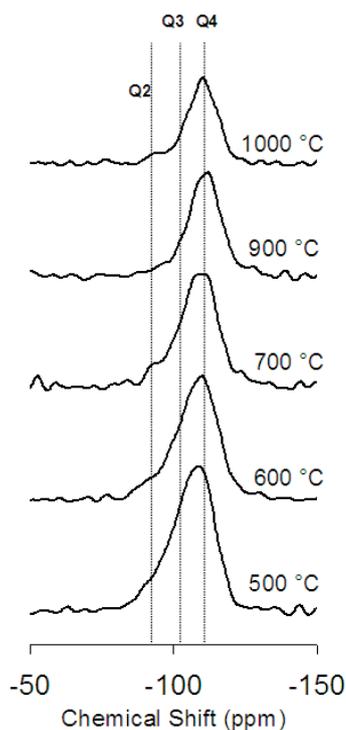


Fig. 3. ^{29}Si MAS NMR spectra of oxidized Ti_3SiC_2 at 500°C, 600°C, 700°C, 900°C, and 1000°C.

SIMS. A duplex structure with an outer layer of TiO_2 and an inner mixture layer of SiO_2 and TiO_2 was observed at temperature as low as 500°C. The existence of amorphous silica in oxidised Ti_3SiC_2 at the temperature range studied has been verified by ^{29}Si -NMR measurements.

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