

Characterisation of amorphous silica in air-oxidised Ti_3SiC_2 at 500–1000 °C using secondary-ion mass spectrometry, nuclear magnetic resonance and transmission electron microscopy

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ABSTRACT

In this paper we have described the use of secondary-ion mass spectrometry (SIMS), solid state ^{29}Si magic-angle-spinning (MAS) nuclear magnetic resonance (NMR) and transmission electron microscopy (TEM) to detect the existence of amorphous silica in Ti_3SiC_2 oxidised at 500–1000 °C. The formation of amorphous SiO_2 and growth of crystalline TiO_2 with temperature was monitored using dynamic SIMS and synchrotron radiation diffraction. A duplex structure with an outer TiO_2 -rich layer and an inner mixed layer of SiO_2 and TiO_2 was observed. Results of NMR and TEM verified 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.

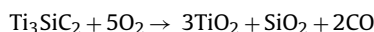
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1. Introduction

Ti_3SiC_2 is the first $\text{M}_{n+1}\text{AX}_n$ or MAX phase to have been extensively studied because of its unique metallic and ceramic properties. 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 oxidised layers to exhibit a duplex microstructure in the temperature range of 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 has remained 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 (tridymite or cristobalite) during Ti_3SiC_2 oxidation at temperature ≥ 1100 °C has been confirmed [11–17], the form or the nature of silica formed below 1100 °C is still unknown. Based on transmission electron microscopy (TEM) observations, Chen et al. [14] 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 [13] reported the existence of amorphous SiO_2 that sealed the cracks formed in the oxide layers. With the aid of TEM, Low and co-workers [17,18] also reported the existence of amorphous silica during the oxidation of Ti_3SiC_2 . According to Barsoum and El-Raghy [19], the oxide layers formed during low temperature oxidation consist of rutile and amorphous silica, but at temperatures greater than 1240 °C, cristobalite is formed. The presence of amorphous silica was also predicted by Okano et al. [20] to exist during the oxidation of Ti_3SiC_2 .

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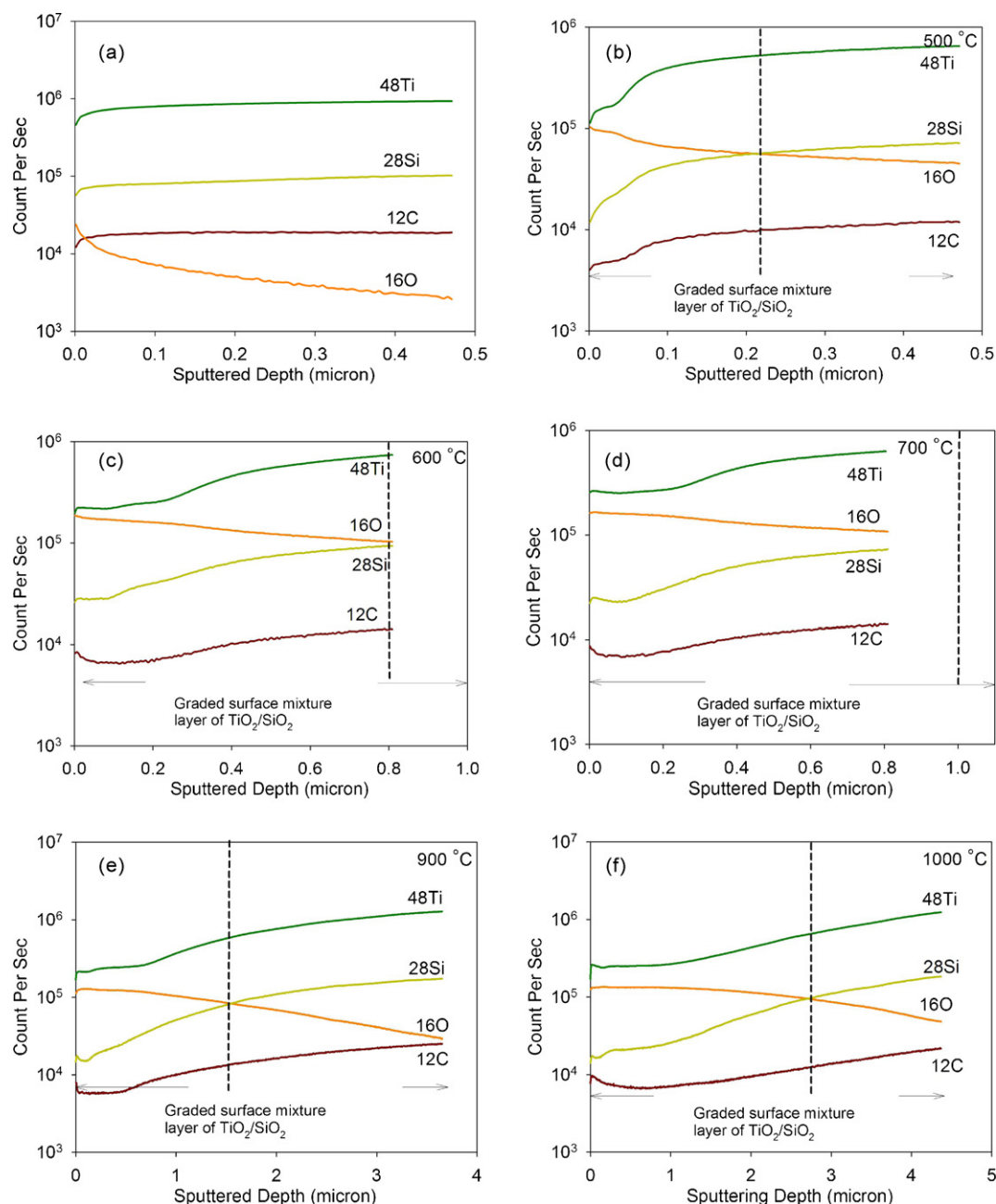


Fig. 1. SIMS depth profiles of (a) control sample and oxidised Ti_3SiC_2 at (b) 500, (c) 600, (d) 700, (e) 900 and (f) 1000 °C (dash line is the separation between outer layer of rich- TiO_2 and inner layer of mixture of TiO_2 and SiO_2).

In this paper, we have described 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 of 500–1000 °C. We have verified the existence of the elusive amorphous SiO_2 with the aid of transmission electron microscopy and solid state ^{29}Si magic-angle-spinning (MAS) nuclear magnetic resonance (NMR).

2. Experimental procedure

2.1. Sample preparation

Commercial hot-isostatically-pressed Ti_3SiC_2 (Maxthal[®]) supplied by Kanthal AB in Sweden, 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 six slices were each oxidised 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 six batches where each batch was oxidised in an air-ventilated furnace for 20 min at 500, 600, 700, 900, and 1000 °C, respectively.

2.2. Secondary-ion mass spectrometry

The near-surface compositions of the oxidised samples were analysed using a Cameca Ims-5f SIMS through the elemental monitoring of Ti, C, Si and C. 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 $250 \times 250 \mu\text{m}^2$. 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 $7.87 \mu\text{m s}^{-1}$ was determined and used to change the sputtering time to the sputtered depth.

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