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# TEM study of the early stages of $Ti_2AlC$ oxidation at 900 °C

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The cross-sectional microstructure on $Ti_2AlC$ oxidized for 1 h at 900 °C was investigated using focused ion beam/transmission electron microscopy. An Al-depleted intermediate layer formed between the oxide scale and the substrate that consisted of nonstoichiometric $Ti_2Al_xC$ nanocrystallites. The oxide scale consisted of a $TiO_2$-rich outer layer and an $Al_2O_3$-rich inner layer. $Ti_2AlC$ has been theoretically predicted to preserve its crystal structure down to a sub-stoichiometry of $Ti_2Al_{0.5}C$, and such a $Ti_2Al_xC$ phase was observed in this study.

*Keywords:* MAX phases; Oxidation; Microstructure; Ti2AlC

$Ti_2AlC$ is a promising material for various high-temperature applications, such as electrical heating elements [1], hot corrosion-resistant coatings [2], high-temperature electrodes [3] and cladding materials in lead-cooled fast nuclear reactors [4]. $Ti_2AlC$ is a typical MAX phase [3,5] in the family of ternary compounds, with general formula $M_{n+1}AX_n$, where M is a transition metal, A is a group IIIA or IVA element, X is C or N, and $n$ is from 1 to 3.

A major difficulty with non-oxide ceramics such as MAX phases is their tendency to oxidize in air. Understanding the oxidation behaviour of $Ti_2AlC$ is critical for its application at elevated temperature in oxidizing atmospheres, and is also essential for the control of crack healing ability via surface oxidation [6,7]. The oxidation behaviour of $Ti_2AlC$ has been investigated under isothermal conditions at high temperatures (1000–2000 °C) [8–10] and at intermediate temperatures (500–1000 °C) [11]. Parabolic oxidation kinetics have been observed by various researchers, and the growth of oxide scale on $Ti_2AlC$ is believed to be caused by inward diffusion of $O^{2-}$ and outward diffusion of $Al^{3+}$ and $Ti^{4+}$ [12,13]. The high-temperature oxidation resistance of $Ti_2AlC$ involves selective oxidation of Al, leading to formation of continuous and protective $Al_2O_3$-rich scales [8–10,14]. After isothermal oxidation from 1100 to 1300 °C, a dense and continuous inner $\alpha$-$Al_2O_3$ layer and a discontinuous outer $TiO_2$ layer are formed [8–10]. At 1400 °C, a mixed outer layer of $TiO_2$ and $Al_2TiO_5$ and a cracked $\alpha$-$Al_2O_3$ inner layer are formed [8,14]. The cracked oxide scale provides channels for rapid ingress of oxygen to the body, leading to heavy oxidation above 1400 °C [8].

There has been disagreement over the detail of the intermediate-temperature oxidation behaviour of $Ti_2AlC$, particularly that at 900 °C [8,15,16]. In our previous publication [8], X-ray diffraction (XRD), secondary electron imaging (SEI) and energy-dispersive spectroscopy (EDS) in a scanning electron microscope revealed that rutile $TiO_2$ was mainly present after 1 h of oxidation at 900 °C in air. Based on cross-sectional focused ion beam (FIB)/scanning electron microscopy (SEM) observation and thermodynamic arguments, Yang et al. [15] argue that a continuous $Al_2O_3$ layer (~250 nm thick) forms in the oxide scale on $Ti_2AlC$ after 1 h of oxidation at 900 °C along with some large $TiO_2$ grains dispersed in the $Al_2O_3$ scale. Wang and Zhou [11] investigated the isothermal oxidation behaviour of $Ti_2AlC$ at 500–900 °C by XRD, Raman spectroscopy and SEM, identifying transitional polymorphs of $Al_2O_3$ ($\gamma$-, $\delta$-, $\theta$- and $\alpha$-) and $TiO_2$ (anatase and rutile) in the oxide scale. After 20 h of oxidation at 900 °C in air, the oxide scale formed is rutile $TiO_2$ and $\alpha$-$Al_2O_3$ [11]. Reasons for these different observations likely include different as-made ceramic microstructures (such as grain size, porosity and impurity contents), and different oxidation temperatures and times used. These results

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do, however, demonstrate that the $Ti_2AlC$ oxidation behaviour at 900 °C is not fully understood. In all these studies, the oxide scale formed at 900 °C is thin (<1 μm) and nanosized grains are formed on the surface [8,11,15]. To fully understand the early stages of $Ti_2AlC$ oxidation at 900 °C, cross-sectional transmission electron microscopy (TEM), EDS and electron diffraction are necessary since only TEM investigations can provide all the structural, phase and crystallographic information of the materials down to atomistic levels [17]. The current work presents a detailed FIB/TEM examination of cross-sectional microstructures on $Ti_2AlC$ oxidized for 1 h at 900 °C.

$Ti_2AlC$ samples were prepared by uniaxial hot-pressing Ti, Al and graphite starting materials at 1400 °C for 1 h at 30 MPa in flowing Ar [18], and were supplied by Prof. Yanchun Zhou (Shenyang National Laboratory for Materials Science, Chinese Academy of Sciences). The as-received samples are predominantly single-phase $Ti_2AlC$ ceramics as determined by XRD analysis, with densities of $4.10\ g\ cm^{-3}$ (99.8% theoretical) measured by the Archimedes method. The size of the lamellar grains in the $Ti_2AlC$ ceramics is ~50–100 μm long, ~3–10 μm thick and ~10–20 μm wide. $Ti_2AlC$ samples for oxidation experiments were cut by diamond saw to a size of $\sim 4 \times 4 \times 4\ mm^3$. The surfaces were ground to 1200 grit and polished to 1 μm, followed by degreasing in acetone. During oxidation experiments, samples were placed on a Pt crucible and heated to temperature at a rate of $20\ °C\ min^{-1}$ in an open hearth furnace. Isothermal oxidation runs were performed for 1 h at 900 °C in air before samples were removed and air cooled. Sections, 100 nm thick, were then prepared for TEM using the in situ lift-out technique on a dual-beam FIB instrument (FEI Helios 600 NanoLab, FEI Company, Acht, Eindhoven, The Netherlands). During FIB section preparation, a Pt protective layer was deposited to protect the feature of interest from $Ga^+$ milling, then a cross-section was in situ lifted-out and attached to a support grid that fits into a TEM specimen holder. TEM was carried out with an electron microscope operated at 200 kV (JEM 2000FX, JEOL Ltd., Tokyo, Japan) and a high-resolution electron microscope operated at 200 kV (JEM 2010, JEOL Ltd., Tokyo, Japan). Microstructures were examined in the TEM using bright-field (BF) and selected area electron diffraction (SAED) crystallographic analysis (operated using a double-tilt holder). The aperture size used for the selected area diffraction patterns is 200–300 nm. The diffraction patterns were solved using the SingleCrystal software (CrystalMaker Software Ltd., Yarnton, Oxfordshire, UK). EDS chemical analysis in the JEM 2000 was performed using an ultrathin window detector (Oxford Instruments INCA, Oxford, UK). An electron-beam probe of <10 nm diameter was obtained in this instrument for EDS chemical analysis.

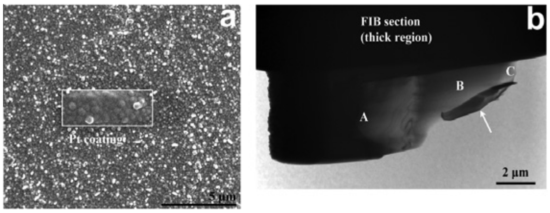

**Figure 1.** (a) Plan view of the surface morphology (SEI taken from FIB) of $Ti_2AlC$ oxidized for 1 h at 900 °C. The rectangular frame indicates the region where a Pt protective layer was deposited and then the cross-sectional lamina was lifted out. (b) Low-magnification BF-TEM image showing a cross-section of $Ti_2AlC$ oxidized for 1 h at 900 °C. A: $Ti_2AlC$ substrate; B: intermediate layer; C: oxide scale. The arrowed region is a thin bent layer caused by $Ga^+$ milling during FIB.

Figure 1a shows typical plan view surface morphology of the oxide scale formed after 1 h of oxidation at 900 °C. The EDS analysis indicates that the small (<1 μm) grains were composed of titanium and aluminium oxides. The rectangular frame in Figure 1a shows the region where a Pt protective layer was deposited and then the cross-sectional lamina was in situ lifted-out for TEM observations. Figure 1b is a low-magnification BF-TEM image of the cross-section of $Ti_2AlC$ oxidized for 1 h at 900 °C. The arrowed region in Figure 1b is a thin bent layer caused by $Ga^+$ milling during FIB. As revealed by EDS and SAED, the cross-section consisted of three parts (from the left to right): $Ti_2AlC$ substrate (A), intermediate layer (B) and oxide scale (C).

An enlarged view of the A/B interface is shown in Figure 2a. A SAED pattern from A (Fig. 2b) indexed as $Ti_2AlC$ [0001]. A ring pattern from B (Fig. 2c) also indexed as polycrystalline $Ti_2AlC$ structure (space group *P6₃/mmc*, ICDD 29-0095). EDS from A (not shown) suggests that the Ti/Al ratio is close to 2. EDS from B (not shown), however, indicates that it is close to 4. The combined SAED and EDS results indicate the intermediate layer B is likely to be nonstoichiometric $Ti_2Al_xC$ ($x < 1$). High-resolution TEM (HRTEM; Fig. 2d) revealed nanocrystallites (<20 nm) distributed in the intermediate layer B. A typical fringe periodicity is 1.30 nm (arrowed in Fig. 2d), coinciding with the the-

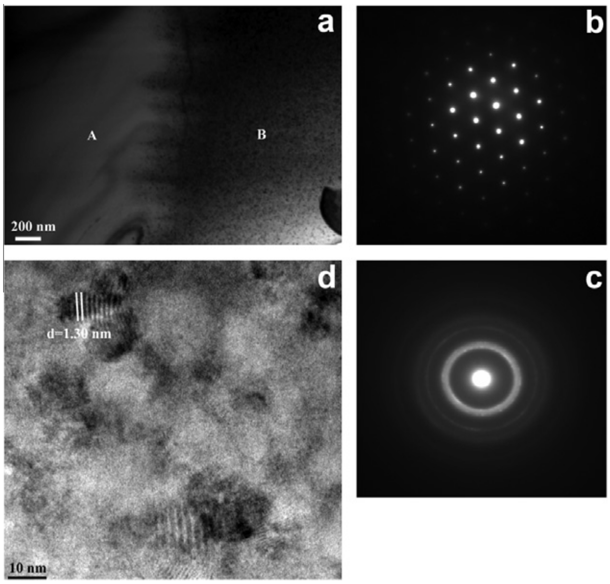

**Figure 2.** (a) An enlarged view of the A/B interface in Figure 1b. A: $Ti_2AlC$ substrate; B: intermediate layer. (b) SAED pattern from A, indexed as $Ti_2AlC$ [0001]. (c) SAED pattern from B, indexed as polycrystalline $Ti_2Al_xC$. (d) HRTEM image of intermediate layer B, revealing $Ti_2Al_xC$ nanocrystallites (<20 nm).