Microstructural Evolution During High-temperature Oxidation of
Spark Plasma Sintered Ti_2AlN Ceramics

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Abstract

Microstructures of Ti_2AlN ceramics synthesized and simultaneously consolidated from starting mixtures of Ti/Al/TiN powders by spark plasma sintering (SPS) were characterised using XRD, SEM, FIB and TEM. When sintered at 1300 °C, nearly single-phase Ti_2AlN ceramics with elongated ($\sim 22 \times 6 \times 6 \mu\text{m}$) grains were obtained. After sintering at 1200 °C and chemical etching, Ti_2AlN nanowhiskers (150-200 nm dia., 1-5 μm long) were exposed in pores coexisting with TiAl, TiN and Ti_2AlN grains. FIB-TEM studies revealed single-crystal Ti_2AlN nanowhiskers in a TiAl matrix with orientation relationship $[1\ 1\ -2\ 0]_{\text{H}} // [-1\ 0\ 1]_{\gamma}$, $(0\ 0\ 0\ 1)_{\text{H}} // (1\ 1\ 1)_{\gamma}$, $\gamma = \text{TiAl}$, $\text{H} = \text{Ti}_2\text{AlN}$. The nanowhiskers are believed to form by diffusion of TiN into TiAl during SPS and be exposed during the chemical etch.

Microstructural development during high-temperature oxidation of dense Ti_2AlN ceramics below 1200 °C involves gradual formation on the surface of layered microstructures containing anatase, rutile and $\alpha\text{-Al}_2\text{O}_3$. Above 1200 °C, more complex layered microstructures containing Al_2TiO_5 , rutile, $\alpha\text{-Al}_2\text{O}_3$ and continuous void layers form. After heating to 1100 °C and cooling to room temperature, planar defects are observed in surface TiO_2 grains identified as stacking faults bounded by partial dislocations. It is believed formation of planar defects releases thermal stresses that generate in TiO_2 grains, and arise from thermal expansion mismatch of the phases in the oxide scale. After heating to 1400 °C and cooling to room temperature, crack propagation in TiO_2 grains resulted from thermal expansion mismatch of phases in the oxide scale, the high anisotropy of thermal expansion in Al_2TiO_5 and volume changes associated with reactions during Ti_2AlN oxidation. An oxidation mechanism for Ti_2AlN ceramics is proposed, which involves initial reaction with atmospheric oxygen to form oxide phases, demixing of the mixed oxide phases, and void formation due to the Kirkendall effect and gaseous NO_x release. Oxidation of Ti_2AlN to 1200 °C is limited, while above which this temperature the oxide scale grows rapidly and Ti_2AlN ceramics undergo heavy oxidation.

Keywords

Microstructure; Oxidation; MAX phases

1. Introduction

Ti₂AlN belongs to a novel class of layered ternary compounds with the general formula of M_{n+1}AX_n (n=1-3), termed MAX phases (space group P6₃/mmc) where M is a transition metal, A is a IIIA or IVA element and X is C or N. It combines many of the best attributes of ceramics and metals [1-4]: like a metal, it is readily machinable, thermal-shock resistant, thermally and electrically conductive and damage tolerant; like a ceramic, it is lightweight (4.30 g cm⁻³), refractory, and elastically stiff. This unique combination makes Ti₂AlN a promising candidate for many high temperature applications [5-7]. Recently, Ti₂AlN demonstrated a high tolerance to 100 keV Ar²⁺ ion irradiation damage induced by nuclear elastic interactions [8]. Due to its exceptional thermal and mechanical properties, Ti₂AlN has attracted attention for potential application as a structural material in nuclear reactors.

Compared to other MAX-phases such as Ti₃SiC₂, Ti₂AlC and Ti₃AlC₂, Ti₂AlN has been the subject of relatively few investigations. This is partly attributed to the difficulty of synthesizing single-phase bulk material because of the narrow stability region of Ti₂AlN in the ternary Al-N-Ti system [9, 10]. The most common fabrication method for bulk Ti₂AlN is hot pressing (HP) from either a powder mixture of Ti and AlN [11] or of Ti, TiN and Al [12]. In addition, single-crystal Ti₂AlN thin films have been prepared by reactive magnetron sputtering [13, 14]. Spark plasma sintering (SPS), by which ceramics can be rapidly sintered at relatively low temperature and over short times, providing fine grains (~μm) and high performance, is competitive with these methods.

Understanding the formation of MAX-phase microstructures is crucial to their application because MAX-phases always coexist with phase such as M-A intermetallics, M-X or A-X binary compounds which are intermediate products of their synthesis [9-12]. This paper examines the relation between processing and fired microstructures in Ti₂AlN ceramics made by SPS and characterised using a range of advanced microscopy techniques.

All materials operating at high temperatures in air have to endure oxidation from O₂. However, the oxidation mechanism of Ti₂AlN, which may limit its high temperature application, has been little investigated and is not fully understood. A generalized model [15] for oxidation of the

ternary compounds $Ti_{n+1}AlX_n$ ($n=1-3$ and X is C and/or N) has been proposed, based on oxidation via inward diffusion of oxygen and outward diffusion of Al^{3+} and Ti^{4+} ions through a rutile-based solid solution $(Ti_{1-y}Al_y)O_{2-y/2}$ where $y < 0.05$. However, Ti_2AlN was not included in the experimental studies [16] by the same authors. Their basic assumption is the presence and demixing of the $(Ti_{1-y}Al_y)O_{2-y/2}$ layer. The results presented in this paper demonstrate that this phase was not observed in microstructural investigation of oxidised SPS Ti_2AlN . Furthermore, their three-stage oxidation model, which is based on the above assumption, is not consistent with our observations. Our parallel study of the oxidation mechanism of another MAX-phase, with similar chemical composition to Ti_2AlN , i.e. Ti_2AlC [17], revealed many different characteristics to Ti_2AlN which will be discussed further in this paper.

Generally, the oxidation resistance of high-temperature ceramics and alloys depends on formation of a protective surface oxide. In an ideal case, the oxide layer is highly stable, slow growing, free from pores or cracks, adherent and coherent [18]. In many cases, $\alpha-Al_2O_3$ provides an oxide which comes close to satisfying these requirements. The slow growth rate is related to its highly stoichiometric structure and the low diffusion coefficients of Al^{3+} and O^{2-} in $\alpha-Al_2O_3$. The oxidation resistance of high-temperature materials is thus strongly related to the composition and microstructure of oxide scales formed on them during high-temperature oxidation.

The goal of this research is to understand the oxidation mechanism of Ti_2AlN by investigating the fundamental nature of the microstructural evolution of the oxide scale during high-temperature oxidation. Based on these microstructural observations, an oxidation mechanism for Ti_2AlN ceramics is proposed.

2. Experimental

Commercially-available Ti (99.5% pure, $< 45 \mu m$), Al (99.5% pure, $< 45 \mu m$), and TiN (99.7% pure, $< 10 \mu m$) powders were used as raw materials to synthesize Ti_2AlN by SPS. All powders were purchased from Alfa Aesar (a Johnson Matthey Company, Heysham, Lancashire, UK). The powders with a designed composition (Ti: 1.1Al: TiN) were mixed in a glove box under Ar

atmosphere to avoid oxidation. Mixtures were then milled for 24 h with addition of ethanol (>99.7% pure) using Al₂O₃ grinding media (99.5% pure, purchased from Dynamic Ceramic Ltd, Crewe, Cheshire, UK). After milling, powders were dried in a rotary evaporator under vacuum. For the SPS, powders were placed into 2 cm dia. graphite crucibles, sintered in vacuum for 10 min at 1200 °C and 1300 °C by using a SPS system (HPD 25/1, FCT Systeme, Rauenstein, Germany). Temperature was measured using 2 pyrometers and 4 thermocouples. The samples were heated at a rate of 80 °C /min at a pressure of 30 MPa. Synthesized samples were 20 mm in diameter and 5-6 mm in thickness.

Bulk density was measured using the Archimedes method in water. Phases present were characterized using an X-ray diffractometer (Philips PW1700, Eindhoven, The Netherlands) with Cu-K_α radiation. JADE software (Materials Data Inc., Livermore, CA, US) was used to refine the lattice parameters from XRD peaks. Quantitative analysis was carried out using the Reference Intensity Ratio (RIR) method [19, 20]. International Centre for Diffraction Data (ICDD) used are Ti₂AlN (5.3, JCPDS 65-3496), TiAl (5.53, JCPDS 65-0428), TiAl₃ (4.99, JCPDS 65-2667), and TiN (4.07, JCPDS 01-087-0628). Errors of quantitative analysis were determined by repeating calculations 3 times for parallel samples. Microstructures of as-sintered samples were investigated using a field emission gun scanning electron microscope (FEGSEM, Gemini LEO 1525, Oberkochen, Germany) operated in secondary electron imaging (SEI) and backscattered electron imaging (BEI) modes, coupled with energy-dispersive spectroscopy (EDS) for chemical analysis (Oxford Instruments INCA, Oxford, UK, using an ultra-thin window (UTW) detector which is capable of detecting light elements with atomic numbers Z>4). Before FEGSEM, the samples were etched using HF+HNO₃+H₂O (1:1:1) [12] for less than 20s, and then observed in reflected light in an optical microscope (OM). The grain size was statistically measured for over 145 grains using Adobe Photoshop software.

Ti₂AlN samples (SPS for 10 min at 1300 °C) for oxidation experiments were cut by diamond saw to about 4×4×4 mm in size. The surfaces were ground to 1200 grit, polished to 1 μm, followed by degreasing in acetone. During oxidation experiments, samples were placed on a Pt crucible and heated to temperature at 20 °C/min in an open hearth furnace. Isothermal oxidation runs were performed for 1h from 900-1400 °C in air before samples were removed and air cooled.

Thermogravimetry (TG) experiments were performed in a thermal analyzer (Netzsch STA 449F1, Netzsch Instruments, Aldridge, UK) by heating the Ti_2AlN samples (approximately $3.5 \times 3.5 \times 3.5$ mm in size) from ambient temperature to 1400°C at a rate of $20^\circ\text{C min}^{-1}$ in a flowing air atmosphere. Samples used for TG were prepared in an identical manner as those for oxidation tests to understand the phase evolution associated with Ti_2AlN oxidation. Differential thermogravimetry (DTG) curves were derived from the TG curves.

Microstructures of oxide scales on Ti_2AlN samples were characterized *post mortem* at room temperature (i.e. on samples heated to the oxidation temperature and cooled). Phases present in the oxide scale were characterized using an X-ray diffractometer (Philips PW1700, Eindhoven, The Netherlands) with Cu-K_α radiation. Quantitative analysis was carried out using the RIR method. ICDD data used include Ti_2AlN (5.3, JCPDS 65-3496), $\alpha\text{-Al}_2\text{O}_3$ (0.87, JCPDS 01-088-0826), anatase (4.89, JCPDS 01-073-1764), rutile (3.45, JCPDS 01-073-1765) and Al_2TiO_5 (1.54, JCPDS 01-081-0030). Errors in quantitative analysis were determined by repeating calculations for 3 times for parallel samples. Surface and cross-section microstructures were investigated using a FEGSEM (Gemini LEO 1525, Oberkochen, Germany) operated with SEI, coupled with EDS for chemical analysis. Samples for FEGSEM were unetched, and were chromium coated to avoid electrical charging, because the electrical conductivity of oxidation products (e.g. TiO_2 and Al_2O_3) is low.

100 nm-thick sections for transmission electron microscopy (TEM) were prepared using the *in situ* lift-out technique on a dual-beam focused ion beam (FIB) instrument (FEI Helios 650 NanoLab, FEI Company, Acht, Eindhoven, The Netherlands) and imaged using SEI and secondary ion imaging. During FIB section preparation, a Pt protection layer was deposited to protect the feature of interest from Ga^+ milling, and then a cross-section containing the feature of interest was lifted-out and attached to a support grid that fits in 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 dark-field (DF) imaging and selected area electron diffraction (SAED) crystallographic analysis (operated using a double-tilt holder). Diffraction patterns were solved using the SingleCrystal software (CrystalMaker

Software Ltd., Yarnton, Oxfordshire, UK). In addition, EDS chemical analysis in the JEM 2000 was performed using an UTW detector (Oxford Instruments INCA, Oxford, UK).

3. Results and Discussion

3.1 Nanowhisker-containing microstructures

Figure 1 shows XRD from Ti_2AlN ceramics sintered at 1200 and 1300 °C by SPS. Samples were obtained from a mixture of Ti +Al +1.1Ti N (in molar ratio) raw materials sintered at 1200 and 1300 °C for 10 min, respectively, under a pressure of 30 MPa. Quantitative analysis (Table 1) reveals that the crystalline phases present in the samples sintered at 1200 °C are Ti_2AlN , TiAl and TiN. As the temperature was increased to 1300 °C, Ti_2AlN became the dominant crystalline phase (96.6 wt%) with 2.7 wt% TiN and 0.7 wt% TiAl_3 . This XRD analysis suggests the following reactions are possible during SPS [9, 10, 12]:

Al melts at approximately 660 °C (reaction 1) while reaction between Ti and Al forms Ti-Al intermetallics such as TiAl and TiAl_3 [9, 10, 12] at approximately 700-900 °C. Formation of Ti-Al intermetallics has also been found during synthesis of layered ternary ceramics such as Ti_2AlC [21] and Ti_3AlC_2 [22]. It is also possible that Ti_2AlN forms by reactions between TiN and Ti-Al intermetallics [12].

The density of bulk Ti_2AlN samples sintered at 1300 °C was 4.26 g cm^{-3} , which is 99.0 % of the theoretical value of 4.30 g cm^{-3} . The crystal structure of Ti_2AlN is hexagonal (space group: $\text{P6}_3/\text{mmc}$). Based on this structure, the lattice parameters of Ti_2AlN were refined to $a = 0.2980 \text{ nm}$

and $c = 1.3573$ nm, respectively, which agrees reasonably well with theoretical values ($a = 0.2994$ nm and $c = 1.3610$ nm, given in JCPDS 65-3496 for Ti_2AlN).

OM (Figure 2a) and SEM (Figure 2b) of the etched Ti_2AlN samples sintered at 1300°C revealed typical elongated grains (typically $22 \times 6 \times 6 \mu\text{m}$) with an average aspect ratio of 3.7. EDS analysis suggested that the atomic ratio of Ti to Al is about 2:1 in all grains, indicating they are Ti_2AlN .

For comparison, microstructures of samples sintered at 1200°C were also investigated. Unetched samples contained pores (Figure 3a). After etching, Ti_2AlN nanowhiskers (approximately 10 vol. %) are present in the pores (Figure 3b), while EDS suggested the phases in pores beneath nanowhiskers are most likely TiAl. The high magnification image (Figure 3c) of these Ti_2AlN nanowhiskers revealed that they are 150-200 nm dia. and 1-5 μm long. In addition, TiN grains appear in the Ti_2AlN matrix with different contrast (Figure 3d). EDS analysis confirms that these grains contain no Al, with the atomic ratio of Ti to N being close to 1:1.

BF-TEM images from the Ti-Al-N sample sintered at 1200°C reveal straight (Figure 4a) and bent Ti_2AlN nanowhisker (Figure 4b) morphologies in a TiAl matrix. EDS revealed the atomic ratio of Ti to Al is close to 1:1 for the TiAl matrix, while it is close to 2:1 in the nanowhiskers. SAED patterns from a matrix region A (Figure 4c) in Figure 4a index as TiAl $[-1\ 0\ 1]$. Overlapping SAED patterns were recorded from region B (Figure 4d) containing the nanowhisker. An indexed SAED pattern for region B is shown in Figure 4e. The orientation relationship between Ti_2AlN nanowhiskers and TiAl matrix is:

$$(0\ 0\ 0\ 1)_H // (1\ 1\ 1)_\gamma, [1\ 1\ -2\ 0]_H // [-1\ 0\ 1]_\gamma, H=\text{Ti}_2\text{AlN}, \gamma=\text{TiAl}$$

This relationship is consistent with previous work on nitride precipitates in L10-ordered TiAl [23]. The nanowhiskers lie parallel to the $(0\ 0\ 0\ 1)$ planes. In addition, SAED revealed the Ti_2AlN nanowhiskers are single-crystal.

3.2 Nanowhisker formation mechanism

A 4-step mechanism (Figure 5) for formation of Ti_2AlN nanowhiskers is suggested based on these microstructural observations.

At room temperature, a mixture of Ti+Al+1.1TiN (in molar ratio) particles were used as starting materials for SPS (Figure 5). During SPS, TiAl intermetallic formed by reaction between Ti and Al at approximately 700-900 °C (Equation 2) [9, 10, 12] (Figure 5). At 1200 °C, Ti₂AlN formed by reaction between TiN and the TiAl intermetallic (Equation 4) [12]. There are two routes for Ti₂AlN formation: TiN diffusing into TiAl forming Ti₂AlN nanowhiskers, and Ti₂AlN grains forming around TiN particles (Figure 5). After heating 10 min at 1200 °C, as more Ti₂AlN formed, the final microstructures evolved in which TiAl and TiN are distributed in a Ti₂AlN matrix and Ti₂AlN nanowhiskers embedded in isolated regions of TiAl (Figure 5). Etching using HF+HNO₃+H₂O (1:1:1) solution removes TiAl exposing Ti₂AlN nanowhiskers (Figure 3c). It appears the chemical etch preferentially attacked the TiAl, over the Ti₂AlN [1, 24].

The whisker shape is related to a preferred growth direction. It has been suggested that MAX-phases, such as Ti₂AlN, Ti₂AlC and Ti₃AlC₂ [21, 25], undergo a preferential growth, i.e. each layer grows fast and expands quickly on the (0 0 0 1) basal plane and all the layers are successively stacked along the normal direction identical to the c-axis (i.e. [0 0 0 1]) in the hexagonal structure. In the layered structure of MAX-phases, close-packed layers of M layers are interleaved with layers of pure group A-elements, with X atoms located in octahedral M atom coordination. The c axis is much larger than the a axis (e.g. Ti₂AlN, a = 0.2994 nm and c = 1.3610 nm). Along the c axis the M-A bonds are weaker than the M-M bonds in the (0 0 0 1) basal plane [21, 25]. Therefore, the growth rate in the direction parallel to the c-axis should be lower than those in other directions. Under equilibrium conditions, the MAX-phase grains appear as hexagonal plates in which the hexagonal surfaces are parallel to the (0 0 0 1) planes [25]. However, SPS is a nonequilibrium process due to use of pulsed electrical current combined with rapid heating and the application of pressure to achieve rapid sintering [26]. In this case, the growth of Ti₂AlN nanowhiskers in TiAl occurs preferentially along the (0 0 0 1) planes, but is also influenced by other factors, such as the concentration gradient of TiN, grain boundaries and dislocations in TiAl. The nucleation and growth of nanowhiskers is caused by diffusion of TiN into TiAl, and TiN diffuses more quickly along the grain boundaries and dislocations in TiAl. As a result, the growth direction of Ti₂AlN nanowhiskers is relatively random, and they are sometimes bent (Figure 3b, 3c and 4b).

This first observation of Ti₂AlN nanowhiskers has significant implications for MAX-phase nanostructures. MAX whiskers may have some unique properties, for example they may have higher tensile strength and be more resistant to chemical attack (including oxidation) compared with bulk materials because they are single crystal and single phase.

3.3 Phase evolution during Ti₂AlN oxidation

Figure 6 shows XRD of Ti₂AlN (sintered for 10 min at 1300 °C) after oxidation at 900-1400 °C in air for 1 h. The phase composition of the oxide scale detected via XRD is summarized in Table 2. The phase evolution of oxidation products: anatase (TiO₂), rutile (TiO₂), α-Al₂O₃, and Al₂TiO₅ can clearly be seen.

The intensity of diffraction peaks associated with Ti₂AlN decreases with increasing oxidation temperature and these peaks could not be identified in the oxide scale after heating to temperatures higher than 1100 °C, suggesting that Ti₂AlN is oxidized at temperatures from 900 to 1400 °C. With increasing oxidation temperature, α-Al₂O₃ and the two polymorphs of TiO₂, anatase and rutile, form in the oxide scale formed at or above 900 °C. After oxidation from 1000 to 1400 °C, the weight percentages of α-Al₂O₃ and rutile are higher than the other phases (Table 2), suggesting that they are the main phases of the oxide scale. Anatase peak heights decrease in samples heated from 900 to 1100 °C and could not be identified after oxidation above 1100 °C. Compared with anatase, rutile is a more stable polymorph of TiO₂ at high temperature [27]. Therefore, anatase gradually transformed to rutile with increasing temperature, and at 1200 °C, all anatase has been transformed to rutile in the oxide scale. Al₂TiO₅ arises in the oxide scale after oxidation at 1200 °C. Al₂TiO₅ formed by reaction between TiO₂ and Al₂O₃ [28, 29]:

where ΔV is volume change and Δm mass change on reaction. Concomitant with the presence of Al₂TiO₅, is a decline in the weight % of rutile after oxidation at 1200 °C (from 87.8% to 67.4%) compared with that after 1100 °C, implying formation of Al₂TiO₅ consumes some rutile (TiO₂).

TG and the corresponding DTG curves for Ti₂AlN are shown in Figure 7. TG reveals significant mass increase starting from near 1000 °C, suggesting that significant oxidation

products were formed at temperatures >1000 °C. Below this temperature, the sample mass increased slowly. DTG peaks occurred at 1040, 1209 and 1379 °C. XRD revealed that after oxidation at 1000 °C, the TiO₂ (rutile) content in the oxide scale was much greater than at 900 °C (Table 2), indicating the 1040 °C DTG peak is likely associated with formation of a large amount of TiO₂ (rutile). XRD revealed that Al₂TiO₅ arises in the oxide scale after oxidation at 1200 °C, suggesting that the 1209 °C DTG peak corresponds to Al₂TiO₅ formation. The 1379 °C DTG peak is likely associated with the further extensive oxidation of Ti₂AlN, supported by the crack formation in surface TiO₂ grains after oxidation at 1400 °C (Figure 8f) providing channels for rapid ingress of oxygen to the body, leading to heavy oxidation (discussed further later).

Based on the above analysis, the oxidation of Ti₂AlN occurs via the reactions:

In equations 6 and 7, NO_x (x=1-2) refers to the gaseous oxidation products of Ti₂AlN.

3.4 Microstructural evolution during Ti₂AlN oxidation

To further understand the microstructural evolution of the oxide scale on Ti₂AlN, both plan views and cross-sections of samples after oxidation at 900-1400 °C were investigated.

Typical plan view surface morphologies of the oxide scales formed at different temperatures are shown in Figure 8. The surface morphologies formed on Ti₂AlN changed along with the composition at different temperatures. After oxidation at 900 °C (Figure 8a), small nano-scale (<0.2 μm) grains were formed on the Ti₂AlN surface. The size of these grains is beyond the resolution limit of EDS in the SEM (typically 1 μm³ in volume) and so EDS analysis of their composition was inconclusive although later TEM analysis (Figure 10b) confirms they are a mixture of TiO₂ and α-Al₂O₃. After oxidation at 1000 and 1100 °C (Figure 8b and 8c), EDS indicated the grains (2-10 μm after 1000 °C; 3-15 μm after 1100 °C) were TiO₂, which suggests

that at these temperatures the surface of the oxide scale on Ti_2AlN is covered predominantly with TiO_2 . In addition, after oxidation at 1100 °C, planar defects occur in the TiO_2 grains. TEM characterization of the planar defects will be shown later. After oxidation at 1200 °C (Figure 8d), fine ($<1\mu\text{m}$) grains have developed along the edges of large (5-15 μm) TiO_2 grains. After oxidation at 1300 °C (Figure 8e), small ($<2\mu\text{m}$) globular grains have developed along the edges of the large (5-20 μm) TiO_2 grains. EDS analysis revealed that the Ti/Al atomic ratio of these small grains is close to 1:2. Combined with the results of phase analysis of the sample oxidized at 1200 and 1300 °C (Table 2), these small grains are most likely Al_2TiO_5 . In addition, at these temperatures, the planar defects can still be seen in the TiO_2 grains although fewer in number. After oxidation at 1400 °C (Figure 8f), small (2-5 μm) globular Al_2TiO_5 grains were formed along the edges of large (10-50 μm) TiO_2 grains. The planar defects in TiO_2 grains, which were present after oxidation from 1100 to 1300 °C, are no longer present after oxidation at 1400 °C. In addition, cracks were developed in TiO_2 grains (Figure 8f).

Typical cross-sections of the scales formed on Ti_2AlN surfaces after oxidation from 900 to 1400 °C are presented in Figure 9. After oxidation at 900 °C (Figure 9a), the oxide scale microstructure consisted of an outer dense layer (1-2 μm thick) and an inner porous layer (1-2 μm thick). FIB sectioning was performed on samples oxidized at 900 °C to characterize the oxide scale microstructure. BF images of the inner porous layer and the outer dense layer are shown in Figure 10. In the porous layer (Figure 10a) loose angular TiO_2 grains ($\sim 100\text{ nm}$ in size) were predominant and EDS indicated that no Al is present in this layer. In the dense layer (Figure 10b) angular TiO_2 grains ($<100\text{ nm}$) were distributed in a dense $\alpha\text{-Al}_2\text{O}_3$ grain ($<100\text{ nm}$) matrix.

After oxidation at 1000 (Figure 9b) and 1100 °C, the outermost layer was dense TiO_2 (6-7 μm thick at 1000 °C and 8-12 μm thick at 1100 °C), over dense $\alpha\text{-Al}_2\text{O}_3$ (6-7 μm thick at 1000 °C and 6-8 μm at 1100 °C). The outer dense layer at 900 °C, which was a mixture of TiO_2 and $\alpha\text{-Al}_2\text{O}_3$, has demixed into TiO_2 and $\alpha\text{-Al}_2\text{O}_3$ layers at 1000 and 1100 °C. The innermost porous layer (10-12 μm thick at 1000 °C, 24-28 μm at 1100 °C) was a mixture of TiO_2 and $\alpha\text{-Al}_2\text{O}_3$ and the Ti/Al atomic ratio is close to 2:1. An enlarged view of the porous layer in Figure 9b is shown in Figure 9c in which TiO_2 appears light and $\alpha\text{-Al}_2\text{O}_3$ appears dark. A number of pores (submicron, arrowed in Figure 9c) are distributed uniformly in $\alpha\text{-Al}_2\text{O}_3$, and their origin needs discussion. The fact that

the pores were distributed uniformly in α -Al₂O₃ indicates the Al³⁺ anions likely dissolve in the oxide scale and diffuse outward to precipitate as α -Al₂O₃ (at the higher oxygen potential side) in the dense α -Al₂O₃ layer (Figure 9c). The rapid outward diffusion of Al³⁺, which cannot be balanced by inward diffusion of O²⁻, requires a countercurrent vacancy flux resulting from the Kirkendall effect [30-32]. The vacancies accumulate and when the saturation level is exceeded, the vacancies coalesce and condense as voids. Barsoum *et.al* [15, 16] observed similar pores in Ti₂AlN_{0.5}C_{0.5} samples oxidized at 1100 °C for 2 and 16h, and suggested the origin of pores is the continual outward diffusion of the Al³⁺ ions as a result of demixing of a (Ti_{1-y}Al_y)O_{2-y/2} layer. However, the (Ti_{1-y}Al_y)O_{2-y/2} layer was not found in microstructural observation of oxidation of Ti₂AlN. In this case, the pores are likely developed by void formation due to the Kirkendall effect. Similar void formation resulting from the Kirkendall effect has been observed during high temperature oxidation of e.g. β -TiAl [32] and Ni₃Al containing yttrium [30]. Another possibility is that the pores are caused by the release of gaseous oxidation products (NO_x in this case), as observed during high temperature oxidation of Ti₃AlC₂ [33] and Ti₂SnC [34]. Once they are formed, these pores provide channels for the rapid ingress of oxygen causing rapid growth of the oxide scale.

After oxidation at 1200 °C (Figure 9d), the outmost dense layer was a mixture of TiO₂, α -Al₂O₃ and Al₂TiO₅ (25-50 μ m thick) and the Ti/Al atomic ratio is close to 2:1. A continuous void layer (12-50 μ m thick) formed below the dense layer. As discussed above, the void layer is likely developed due to the Kirkendall effect and gaseous NO_x release. The inner porous layer was a mixture of TiO₂, α -Al₂O₃ and Al₂TiO₅ (105-120 μ m thick) and the Ti/Al atomic ratio is close to 1:1.

After oxidation at 1300 °C (Figure 9e), the outmost dense layer was a mixture of TiO₂, α -Al₂O₃, and Al₂TiO₅ (15-35 μ m thick) and the Ti/Al atomic ratio is close to 2:1. A continuous void layer (35-45 μ m thick) formed below the dense layer. Below the void layer was a porous layer which was a mixture of TiO₂, α -Al₂O₃ and Al₂TiO₅ (~100 μ m thick) and the Ti/Al atomic ratio is close to 1:1. A second continuous void layer (~10 μ m thick) formed below the porous layer. Below the second void layer was a porous layer which was a mixture of TiO₂, α -Al₂O₃, and Al₂TiO₅ (50-55 μ m thick) and in which the Ti/Al atomic ratio is close to 1:1. The inner layer adjacent the Ti₂AlN substrate was a porous 5-10 μ m thick TiO₂ layer.

After oxidation at 1400 °C (Figure 9f), the outmost dense layer was a mixture of TiO_2 and Al_2TiO_5 (40-55 μm thick). EDS analysis showed that this layer is enriched in Ti. A continuous (<30 μm thick) void layer formed below the dense layer. Below the void layer was a porous $\alpha\text{-Al}_2\text{O}_3$ layer (100-140 μm thick). A second void layer (<30 μm thick) formed below the $\alpha\text{-Al}_2\text{O}_3$ layer. Below the second void layer was a porous TiO_2 layer (150-190 μm thick). A third void layer (10-40 μm thick) formed below the TiO_2 layer. Below the third void layer is another porous layer (30-60 μm thick), which was a mixture of TiO_2 , $\alpha\text{-Al}_2\text{O}_3$ and Al_2TiO_5 . A porous TiO_2 layer (120-140 μm thick) formed adjacent the Ti_2AlN substrate.

3.5 Planar defects and cracks

After oxidation at 1100 and 1300 °C, surface TiO_2 (rutile) grains contain planar defects (Figure 8c and e). FIB sectioning was performed for samples oxidized at 1100 °C to further understand the nature and formation mechanism of these planar defects. Planar defects were observed and identified as stacking faults.

Figure 11a, b and c show BF, DF and SAED of stacking faults in TiO_2 grains. Alternating bright and dark fringes are observed and the visibility of fringes decreases towards the centre of the fault. The symmetrical nature of the BF image and the asymmetrical nature of the DF image, due to anomalous absorption effects, are clearly visible [35, 36] confirming these are stacking faults. In addition, these stacking faults are bounded by partial dislocations (arrows in Figure 11a) lying inside the grain. Apart from stacking faults, TEM revealed angular Al_2O_3 precipitates (<0.5 μm) occasionally formed at TiO_2 grain boundaries (Figure 12). Their presence at TiO_2 grain boundaries indicates that they are most likely formed by outward grain-boundary diffusion of Al^{3+} and inward grain-boundary diffusion of O^{2-} .

The formation of planar defects can release large thermal stresses in TiO_2 grains. During the oxide scale growth on the Ti_2AlN surface, thermal stresses (arising from thermal expansion coefficient (TEC) mismatch of the phases in the oxide scale) gradually accumulate in TiO_2 grains. The TEC of these phases are: Ti_2AlN ($\alpha_a = (8.6 \pm 0.2) \times 10^{-6} \text{ K}^{-1}$, $\alpha_c = (7.0 \pm 0.5) \times 10^{-6} \text{ K}^{-1}$, 297-1573K) [11], rutile ($\alpha_a = 9.2 \times 10^{-6} \text{ K}^{-1}$, $\alpha_c = 7.1 \times 10^{-6} \text{ K}^{-1}$), $\alpha\text{-Al}_2\text{O}_3$ ($\alpha_a = 7.9 \times 10^{-6} \text{ K}^{-1}$, $\alpha_c = 8.8 \times 10^{-6} \text{ K}^{-1}$),

and Al_2TiO_5 ($\alpha_a = 10.9 \times 10^{-6} \text{ K}^{-1}$, $\alpha_b = 20.5 \times 10^{-6} \text{ K}^{-1}$, $\alpha_c = -2.7 \times 10^{-6} \text{ K}^{-1}$, 0-1273 K) [37]. The large TEC anisotropy in Al_2TiO_5 grains is particularly significant. Hasselman assumed that in a solid body constrained in all directions and uniformly cooled through a temperature difference ΔT , the triaxial thermal stress can be given by [38, 39]

$$\sigma = \frac{\alpha \Delta T E}{1 - 2\nu} \quad (8)$$

where α is the average thermal expansion coefficient for the temperature range involved, E is Young's modulus, ν is Poisson's ratio. After oxidation at 1100 and 1300 °C and cooling to room temperature, stacking faults were formed, partly releasing the thermal stresses. After oxidation at 1400 °C and cooling to room temperature, cracks were developed (Figure 8f) in TiO_2 grains, which can release additional thermal stress. When the thermal stresses are greater than the strength of rutile TiO_2 , they will result in crack propagation and failure of the component. Planar defects were no longer present in TiO_2 grains at 1400 °C, and they were probably annealed out.

Crack formation after 1400 °C may have three origins [17]. Firstly, thermal expansion mismatch of phases in the oxide scale causes the cracks during rapid cooling. Secondly, the high anisotropy of thermal expansion in Al_2TiO_5 is known to trigger spontaneous microcracking upon cooling when a critical size is exceeded [40, 41]. The Al_2TiO_5 grain size observed is about 2-5 μm (Figure

8f), much larger than the critical size ($d_{crit} = k \frac{G_{c,gb}}{Y(\Delta\alpha\Delta T)^2} = 0.4 \mu\text{m}$, where k is a constant, $G_{c,gb}$

is the grain boundary fracture toughness, Y is Young's modulus, $\Delta\alpha$ is the maximum anisotropy of the thermal expansion coefficient, and ΔT is the temperature difference [40, 41]). Thirdly, the volume changes (ΔV) associated with the reactions during Ti_2AlN oxidation are large (see Equations 5-7). Stress generated by formation of reaction products with larger volumes than the reactants can cause cracks to form [42].

3.6 The oxidation mechanism

Base on the above analysis, the evolution of the oxide scale during high temperature oxidation of Ti_2AlN is as shown schematically in Figure 13. At temperatures below 1200 °C, layered

microstructures formed on the Ti_2AlN surfaces containing anatase, rutile, and $\alpha\text{-Al}_2\text{O}_3$. At oxidation temperature higher than 1200 °C, more complex layered microstructures formed. Two major characteristics of the oxide scales at temperatures higher than 1200 °C are: first, continuous void layers formed due to the Kirkendall effect and gaseous NO_x release; second, Al_2TiO_5 was present, which formed by reaction of TiO_2 and $\alpha\text{-Al}_2\text{O}_3$ (Equation 5).

The oxidation resistance of high-temperature ceramics is dependent on the formation of a protective surface oxide. In an ideal case, the oxide layer should be highly stable, slow growing, free from pores or cracks, adherent and coherent [18]. $\alpha\text{-Al}_2\text{O}_3$ is an oxide which comes close to satisfying these requirements. In the case of Ti_2AlN , the dense layer formed on the surfaces of Ti_2AlN would be more protective than porous layers. After oxidation at 1000-1100 °C (Figure 9d), a dense and continuous $\alpha\text{-Al}_2\text{O}_3$ layer formed, which is protective. However, after oxidation at 1200 °C (Figure 9e), no continuous $\alpha\text{-Al}_2\text{O}_3$ layer formed, in addition a continuous void layer formed in the oxide scale. Therefore, the oxidation resistance of Ti_2AlN is up to 1200 °C. On the other hand, the thickness of oxide scale as a function of oxidation temperature is plotted in Figure 14. An obvious inflection in the thickness of oxide scale occurred when the oxidation temperature becomes higher than 1100 °C. The thickness of oxide scale grew quickly after 1100 °C, which means that Ti_2AlN would undergo heavy oxidation. This result also reveals that the oxidation resistance of Ti_2AlN ceramics is up to 1200 °C. In addition, at 1400 °C the large TEC mismatch of $\text{TiO}_2\text{-Al}_2\text{TiO}_5$ and the TEC anisotropy in Al_2TiO_5 grains causes cracks in surface TiO_2 grains (Figure 8f) providing channels for rapid ingress of oxygen to the body, leading to extensive heavy oxidation above 1400 °C (corresponding to DTG peak at 1379 °C, Figure 7).

The oxidation mechanism of another MAX-phase which has similar chemical composition with Ti_2AlN , i.e. Ti_2AlC , was studied recently [17]. It was proposed that the evolution of the oxide scale during the high temperature oxidation of Ti_2AlC is as follows: at 900 °C, TiO_2 is formed on the surface of Ti_2AlC by inward diffusion of O^{2-} and outward diffusion of Ti^{4+} from Ti_2AlC ; at 1000 °C, $\alpha\text{-Al}_2\text{O}_3$ begins to be formed by inward diffusion of O^{2-} and outward diffusion of Al^{3+} from Ti_2AlC ; from 1100-1300 °C, an outer discontinuous TiO_2 layer and an inner dense and continuous $\alpha\text{-Al}_2\text{O}_3$ layer were formed; at 1400 °C, a mixed outer layer of TiO_2 and Al_2TiO_5 and a cracked $\alpha\text{-Al}_2\text{O}_3$ inner layer were formed. The major differences between the oxidation

mechanisms of Ti_2AlN and Ti_2AlC are: first, at relatively low temperature (900 °C) the oxide scale on the surface of Ti_2AlN becomes partly porous (Figure 9a) and at relatively low temperature (1200 °C) a continuous void layer is formed (Figure 9d), while in the case of Ti_2AlC , the oxide scale has no porosity or void layers from 900-1300 °C and only becomes cracked after oxidation above 1400 °C. This result implies that the oxide scale on the surface of Ti_2AlC is more stable than that on Ti_2AlN . Second, a continuous inner layer of $\alpha\text{-Al}_2\text{O}_3$ is formed on the surface of Ti_2AlC after oxidation at 1100-1300 °C, whereas the $\alpha\text{-Al}_2\text{O}_3$ layer is formed on Ti_2AlN at 1000-1100 °C. Because $\alpha\text{-Al}_2\text{O}_3$ is protective, this explains why the oxidation resistance of Ti_2AlC (up to 1400 °C) is better than that of Ti_2AlN (up to 1200 °C). The reasons for such a significant difference between the oxidation mechanisms of Ti_2AlC and Ti_2AlN are not clear, but it is likely that carbon oxides (CO/CO_2 , gaseous oxidation products of Ti_2AlC) and nitrogen oxides (NO_x , gaseous oxidation products of Ti_2AlN) play different roles in the formation of the oxide scales. It is generally known that the alumina densification is through diffusion of oxygen via the oxygen vacancies in Al_2O_3 [42, 43]. In reducing atmospheres (H_2 or CO) [42, 44, 45], mass transfer through diffusion of oxygen becomes easy due to the formation of oxygen vacancies. The defect chemistry for the formation of oxygen vacancies ($V_{\text{O}}^{\bullet\bullet}$) can be expressed as [43]:

According to Equation 9, reducing atmospheres (such as CO) would promote formation of oxygen vacancies, and consequently enhance the densification of as-formed Al_2O_3 (oxidation products of Ti_2AlC) through diffusion of oxygen via the oxygen vacancies in Al_2O_3 . A continuous and protective Al_2O_3 layer can thus be formed on the surface of Ti_2AlC . However, the gaseous oxidation products of Ti_2AlN , NO_x , have no positive effects on the densification of as-formed Al_2O_3 , in addition the release of NO_x gas causes pores in the oxide layers which provide channels for rapid ingress of oxygen leading to further oxidation. Therefore, the different gaseous oxidation products likely cause the observed microstructural difference between the oxide scales of Ti_2AlN and Ti_2AlC .

4. Conclusions

- (1) Ti_2AlN ceramics sintered by SPS at 1300 °C from a starting mixture of Ti/Al/TiN powders are nearly single-phase with elongated grains.
- (2) The microstructure of unetched Ti_2AlN ceramics sintered at 1200 °C contained TiN, TiAl, and pores. Chemical etching removed TiAl exposing Ti_2AlN nanowhiskers (150-200 nm dia., 1-5 μm long) in the pores. FIB-TEM studies revealed Ti_2AlN nanowhiskers are single-crystal in a TiAl matrix. The orientation relationship between the Ti_2AlN nanowhiskers and TiAl is $[1\ 1\ -2\ 0]_{\text{H}} // [-1\ 0\ 1]_{\gamma}$, $(0\ 0\ 0\ 1)_{\text{H}} // (1\ 1\ 1)_{\gamma}$, $\gamma = \text{TiAl}$, $\text{H} = \text{Ti}_2\text{AlN}$.
- (3) A formation mechanism of the Ti_2AlN nanowhiskers is proposed. The nucleation and growth of nanowhiskers is caused by diffusion of TiN into TiAl during SPS. The whisker shape is related to preferred growth parallel to the Ti_2AlN $\{0\ 0\ 0\ 1\}$ planes, and the growth direction is relatively random, likely influenced by the concentration gradient of TiN, grain boundaries and dislocations in TiAl.
- (4) Microstructural development during high-temperature oxidation of Ti_2AlN has been investigated. Below 1300 °C, layered microstructures containing anatase, rutile and $\alpha\text{-Al}_2\text{O}_3$ were gradually formed. Above 1200 °C, more complex layered microstructures containing Al_2TiO_5 , rutile, $\alpha\text{-Al}_2\text{O}_3$ and continuous void layers were formed. The porous layers and the void layers are likely developed by void formation due to the Kirkendall effect and gaseous NO_x release.
- (5) After heating to 1100 °C and cooling to room temperature, planar defects in surface TiO_2 grains were identified as stacking faults bounded by partial dislocations. The formation of planar defects is believed to be related to thermal stresses generated in TiO_2 grains, arising from thermal expansion mismatch of the phases in the oxide scale. The planar defects were annealed out by 1400 °C.
- (6) After heating to 1400°C and cooling to room temperature, the large TEC mismatch of $\text{TiO}_2\text{-Al}_2\text{TiO}_5$, and the TEC anisotropy in Al_2TiO_5 grains, along with the large volume changes associated with the reactions resulted in cracks in TiO_2 grains, providing channels for rapid ingress of oxygen to the body, leading to extensive heavy oxidation

above 1400 °C.

- (7) An oxidation mechanism for Ti_2AlN ceramics is proposed, which attributes the formation of microstructures to phase evolution with the increasing temperature, demixing of the mixed oxide phases, and void formation due to the Kirkendall effect and gaseous NO_x release. The oxidation of Ti_2AlN is limited up to 1200 °C, above which the thickness of oxide scale grows quickly and Ti_2AlN ceramics undergo heavy oxidation.

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Table 1. Phase composition after SPS at 1200 and 1300 °C.

Sintering temperature (°C)	Crystal structure and weight fraction of each phase (wt %)				Density (g/cm ³) (% theoretical)
	Ti ₂ AlN	TiN	TiAl	TiAl ₃	
	(Hexagonal, P6 ₃ /mmc)	(Cubic, Fm-3m)	(Tetragonal, P4/mmm)	(Tetragonal, I4/mmm)	
1300	96.6 ± 0.4	2.7 ± 0.4	0	0.7 ± 0	4.24 ± 0.02 (99.0)
1200	71.7 ± 0.3	16.6 ± 0.2	11.7 ± 0.2	0	3.86 ± 0.02 (89.8)

Table 2. Phase composition of oxide scale after oxidation of Ti_2AlN from 900 to 1400 °C.

Oxidation temperature (°C)	Crystal structure and weight % of each phase				
	Ti_2AlN (Hexagonal, $\text{P6}_3/\text{mmc}$)	Anatase (Tetragonal, $\text{I4}_1/\text{amd}$)	Rutile (Tetragonal, $\text{P4}_2/\text{mmn}$)	$\alpha\text{-Al}_2\text{O}_3$ (Rhombonedral, R-3c)	Al_2TiO_5 (Orthorhombic, Cmcm)
900	47.5 ± 1.0	4.4 ± 0.2	23.0 ± 0.4	25.1 ± 0.4	0
1000	1.4 ± 0.2	1.7 ± 0.2	79.0 ± 1.2	17.9 ± 0.2	0
1100	0.7 ± 0.1	1.2 ± 0.1	87.8 ± 1.6	10.3 ± 0.2	0
1200	0	0	67.4 ± 1.0	22.6 ± 0.6	10.0 ± 0.4
1300	0	0	74.0 ± 1.2	16.4 ± 0.2	9.6 ± 0.2
1400	0	0	65.0 ± 1.0	27.6 ± 0.4	7.4 ± 0.2

Figure Captions

Figure 1. XRD of Ti-Al-N prepared by SPS at 1200 and 1300 °C. Miller indices (h k l) are shown.

Figure 2. (a) Optical micrograph and (b) SEI image of etched Ti₂AlN sintered at 1300 °C by SPS. Elongated grains are predominantly Ti₂AlN.

Figure 3. SEI image of a) unetched and b) etched Ti-Al-N sintered at 1200 °C by SPS. (c) High magnification image of the Ti₂AlN nanowhiskers. (d) BEI image of the same sample, showing TiN grains in Ti₂AlN matrix.

Figure 4. BF-TEM images of a) straight and b) bent Ti₂AlN nanowhiskers in a TiAl matrix. The TEM sections were from Ti-Al-N sintered at 1200 °C. (c) SAED pattern from a matrix region A in a), indexed as TiAl [-1 0 1]. (d) Overlapping SAED patterns from region B in a) containing the nanowhisker. (e) Indexed schematic for (d). $d^*(1\ 1\ 1)_\gamma/d^*(0\ 0\ 0\ 1)_H = 4.30\text{ nm}^{-1}/0.737\text{ nm}^{-1} \approx 6$. $d^*(1\ 1\ 1)_\gamma$ is the reciprocal lattice distance of (1 1 1) plane of TiAl. $d^*(0\ 0\ 0\ 1)_H$ is the reciprocal lattice distance of (0 0 0 1) plane of Ti₂AlN.

Figure 5. A proposed mechanism for Ti₂AlN nanowhisker formation: step 1, at room temperature, a mixture of Ti+Al+TiN particles; step 2, 700-900 °C, TiAl intermetallics formed by reaction between Ti and Al; step 3, at 1200 °C, Ti₂AlN whiskers formed by diffusion of TiN into TiAl, and Ti₂AlN formed around TiN particles by reaction between TiAl and TiN; step 4, after 10 min at 1200 °C, TiAl and TiN distributed in the Ti₂AlN matrix and Ti₂AlN whiskers scattered in TiAl, forming the final microstructure. Etching removes TiAl exposing Ti₂AlN nanowhiskers (Figure 3b). The whisker shape is explained by preferred growth (see 3.2).

Figure 6. XRD after oxidation of Ti₂AlN at temperatures from 900 to 1400 °C in air for 1 h.

Oxidation products: anatase, rutile, α -Al₂O₃ and Al₂TiO₅ are shown.

Figure 7. TG-DTG curves recorded during heating of Ti₂AlN to 1400 °C at a rate of 20 °C min⁻¹ in flowing air.

Figure 8. Typical surface morphology (SEI images) of Ti₂AlN oxidized at (a) 900 °C, (b) 1000 °C,

(c) 1100 °C, (d) 1200 °C, (e) 1300 °C and (f) 1400 °C.

Figure 9. Cross-section SEI images of Ti_2AlN oxidized at (a) 900 °C, (b) 1000 °C, (d) 1200 °C, (e) 1300 °C and (f) 1400 °C. (c) An enlarged view of the porous $\text{TiO}_2\text{-Al}_2\text{O}_3$ mixed layer in b), indicating the presence of submicron pores (arrowed).

Figure 10. BF images of (a) the porous TiO_2 layer and (b) the dense $\text{Al}_2\text{O}_3\text{-TiO}_2$ mixed layer in figure 9a. In a) loose angular TiO_2 grains (~100 nm) are predominant; in b) angular TiO_2 grains (<100 nm) are distributed in a dense Al_2O_3 grain (<100 nm) matrix.

Figure 11. BF (a) and DF (b) images of the stacking faults in TiO_2 grains for samples oxidized at 1100 °C, recorded with $g=1\ -1\ 0$ along the rutile $[1\ 1\ 3]$ zone axis. Arrows in a) indicate partial dislocations. (c) Corresponding SAED patterns along the rutile $[1\ 1\ 3]$ zone axis.

Figure 12. BF image of an alumina precipitate on TiO_2 grain boundaries (indicated by arrows) for sample oxidized at 1100 °C.

Figure 13. Schematic illustration of oxide scale formation during high-temperature oxidation of Ti_2AlN .

Figure 14. Ti_2AlN oxide scale thickness as a function of oxidation temperature.

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