Thermodynamic and microstructural study of Ti<sub>2</sub>AlNb oxides at 800 °C

J. M. Xiang<sup>1</sup>, G. B. Mi<sup>2</sup>, S. J. Qu<sup>1</sup>, X. Huang<sup>2</sup>, Z. Chen<sup>1,3</sup>, A. H. Feng<sup>1</sup>, J. Shen<sup>1</sup> & D. L. Chen<sup>4</sup>

The high-temperature structural applications of Ti<sub>2</sub>AlNb-based alloys, such as in jet engines and gas turbines, inevitably require oxidation resistance. The objective of this study is to seek fundamental insight into the oxidation behavior of a Ti<sub>2</sub>AlNb-based alloy via detailed microstructural characterization of oxide scale and scale/substrate interface after oxidation at 800 °C using X-ray diffraction (XRD), scanning electron microscopy (SEM), electron probe microanalysis (EPMA), and transmission electron microscopy (TEM). The oxide scale exhibits a complex multi-layered structure consisting of (Al,Nb)-rich mixed oxide layer (I)/mixed oxide layer (II)/oxygen-rich layer (III)/substrate from the outside to inside, where the substrate is mainly composed of B2 and O-Ti<sub>2</sub>AlNb phases. High-resolution TEM examinations along with high-angle annular dark-field (HAADF) imaging reveal: (1) the co-existence of two types (α and δ) of Al<sub>2</sub>O<sub>3</sub> oxides in the outer scale, (2) the presence of metastable oxide products of TiO and Nb<sub>2</sub>O<sub>5</sub>, (3) an amorphous region near the scale/substrate interface including the formation of AlNb<sub>2</sub>, and (4) O-Ti<sub>2</sub>AlNb phase oxidized to form Nb<sub>2</sub>O<sub>5</sub>, TiO<sub>2</sub> and Al<sub>2</sub>O<sub>3</sub>.

Ti<sub>2</sub>AlNb-based alloy, sometimes referred to as orthorhombic alloy<sup>1,2</sup>, is a class of highly promising lightweight high-temperature materials. This type of alloy is considered to partially substitute the high-density (ρ = 8–8.5 g/cm<sup>3</sup>) Ni-based superalloys in the aerospace industry due to its low density, high strength, superior plasticity, high fracture toughness and excellent creep resistance at elevated temperatures<sup>3–7</sup>. In such applications, the operating temperatures could go beyond 600–650 °C<sup>10,11</sup>, leading to severe oxidation of the alloy surface<sup>12–14</sup>. There are three potential approaches to improve high-temperature oxidation resistance: alloying<sup>15–17</sup>, pre-oxidation<sup>18</sup>, and coating<sup>19–26</sup>. For example, Wang et al.<sup>27</sup> reported that a two-step voltage-controlled microarc oxidation (MAO) method can be used to produce ceramic coatings on a Ti<sub>2</sub>AlNb-based alloy. However, after a prolonged exposure to air at elevated temperatures, intermetallics exhibit oxygen-induced embrittlement characteristics such as low ductility and brittle fracture<sup>16,28,29</sup>. Thus, an understanding of high-temperature oxidation mechanisms is essential for improving the oxidation resistance of materials. In our previous study<sup>30</sup>, a Ti<sub>2</sub>AlNb-based alloy was observed to exhibit fairly good oxidation resistance below 750 °C. After reaching 800 °C, the oxidation resistance decreased dramatically. Thus, the oxidation behavior and mechanisms are investigated at a higher temperature of 800 °C in this study.

Mass transfer is known to be the essence of oxidation reaction. During the high-temperature oxidation of a Ti<sub>2</sub>AlNb-based alloy, O and N elements diffuse inward, whereas Al, Ti and Nb elements diffuse outward. Among the many elements that can improve the oxidation resistance, such as Al, Nb, Mo, Si, Zr, etc., Al and Nb are the most important elements<sup>31</sup>. While Al atoms and O atoms are able to generate a continuous and dense Al<sub>2</sub>O<sub>3</sub> protective layer on the alloy surface and thus improve the oxidation resistance of alloys, this is not the case in Ti<sub>2</sub>AlNb-based alloys. The Gibbs free energy of Al<sub>2</sub>O<sub>3</sub> and TiO<sub>2</sub> is so similar that both oxides are produced almost simultaneously<sup>32</sup>. The addition of the element Nb can improve the oxidation resistance of the alloy: Nb substitutes for Ti in TiO<sub>2</sub> as a cation with a valence of 5, while no Nb is present in Al<sub>2</sub>O<sub>3</sub><sup>33–37</sup>. The doping of Nb in TiO<sub>2</sub> grains reduces oxygen vacancy and Ti cations, which impedes the mass transfer in TiO<sub>2</sub><sup>38–40</sup>. Lu et al.<sup>35</sup> observed the substitution of Ti by Nb via high-resolution transmission electron microscopy (HRTEM) Z-contrast imaging, as
X-ray, Person symbol: cP2), and weighed. It should be noted that the Ti2AlNb-based alloy was observed to exhibit a fairly good oxidation resistance below 750 °C, while its oxidation resistance decreased considerably above 800 °C. Thus, the oxidation resistance below 750 °C, while its oxidation resistance decreased considerably above 800 °C. Thus, the oxidation behavior, and structure, have been investigated12,21,38–41. Leyens and Gedanitz12 studied the mass gain and oxidation rate of a Ti-22Al-25Nb alloy in air between 650 °C and 800 °C, and reported a fairly good oxidation resistance at 650 °C up to 4000 hours and at 700 °C up to 500 hours, whereas at 800 °C “breakaway” oxidation occurred after about 100 hours. Wang et al.21 observed layers of TiO2 and a small amount of AlNbO4 with needle-like TiO2 crystals present all over the surface. Ralison et al.38,39 reported a multi-layered scale (TiO2 + AlNbO4/(eventually Ta, Mo) – rich AlNbO4) along with an oxygen-affected zone in a Ti-27Al-15Nb alloy at 800 °C in air, and Al2O3/(TiO2 + AlNbO4)/Ta-rich Al2O3/oxygen-affected zone in a Ti-27Al-10Nb alloy at the same temperature of 800 °C. Some cracks were present in the multi-layered scale. Zheng et al.30 studied the oxidation behavior of a Ti-22Al-25Nb alloy at 800 °C for 300 hours and observed the formation of a mixed oxide scale on the alloy surface, which was predominantly composed of TiO2, AlNbO4, and Nb2O5.

These studies revealed a complex scale structure containing oxidation products of Al2O3, TiO2, Nb2O5, AlNbO4, etc., with an outer layer consisting mainly of TiO2. When the content of the element Nb is high enough, Nb2O5 or AlNbO4 would be present, however, they are prone to spall-off and are unfavorable to the oxidation resistance. As for the structure of inner oxide layer, Malecka41 observed that it consists of an Al-rich layer and Ti, Al (Nb, Mo, V)-rich zone. Li et al.42 reported that it has such a structure: TiO2-rich layer/AlNbO4-rich layer/TiO2-rich layer/AlNbO4-rich layer/oxygen and a nitride-enriched zone. Leyens43 reported that when the temperature is above 900 °C there exists a nitrogen-enriched layer underneath the oxide scale, i.e., a nitride-containing layer. However, the questions remain as to how the oxide scale containing various oxides is formed; in what form (crystalline or amorphous) the substance/scale interface region would be; and if different types of Al2O3 can be co-existent in the oxidation of Ti2AlNb-based alloys. The objective of the present study is to address these questions via detailed microstructural examinations using different advanced techniques along with thermodynamic calculations.

**Materials and Methods**

The selected material is as-cast Ti2AlNb alloy with a nominal composition of Ti-22Al-20Nb-2V-1Mo-0.25Si (in at.%). The alloy ingot was cut into small plates with a size of 8 × 8 × 3 mm by electro-discharge machining. The surface of the samples was ground with sandpaper from grit #400 to #1200, ultrasonically cleaned in acetone for 15 mins. The dimensions were measured using a Vernier caliper and the samples were weighted using an analytical balance with an accuracy of 0.00001 g. During the isothermal oxidation in air at 800 °C, the samples were taken out of the furnace at intervals of 1, 3, 6, 12, 24, 36, 50, 62, 74, 86, and 100 h, cooled to room temperature and weighed. It should be noted that the Ti2AlNb-based alloy was observed to exhibit a fairly good oxidation resistance below 750 °C, while its oxidation resistance decreased considerably above 800 °C. Thus, the oxidation behavior and mechanism are studied in detail at 800 °C in the present investigation. The time of oxidation experiments was selected according to the standard HB5258-2000 of aerospace sector in China, where a duration of 100 hours is suggested to be sufficient. Also, if the oxidation time was too long, the oxide layer would peel off, causing difficulties for the study of the oxide scale.

A stereoscope was used to observe the grain sizes. XRD (Rigaku D/Max-2550) with a Cu Kα radiation (λ = 1.5418 Å) was used to identify the phases in the oxide scale at 50 kV and 200 mA with a diffraction angle (2θ) from 10° to 100° at a step size of 0.02° and 1 s in each step. SEM (Nova Nano SEM 450) was used to observe the surface morphology and cross-sectional structure of the oxide layer. For the observation of the oxide cross-section, it was necessary to mount the sample with resin, use sandpapers from grit #400 to #1200 to grind, and then diamond paste to polish the sample to a smooth mirror surface. Since the oxide is an insulator, it is necessary to perform carbon deposition on the polished surface before SEM observations. Elemental distribution in different regions on the cross-section of the oxide scale was characterized by using an electron probe microanalyzer (EPMA, Shimadzu1720) with a resolution of 1 μm and secondary-electron image resolution of 6 nm using a beam current of 10 nA. TEM (FEI TECNAI G2 S-TWIN F20) was used to examine the structures of the oxide scale as well as the scale/substrate interface. To locate the scale/substrate interface more precisely TEM samples were prepared via the cutting of a focused ion beam (FIB, FEI, Helios nanolab 600). The dimension of FIB-TEM samples is: 5 μm in length, 4 μm in width, ~35 nm in thickness for the scale, and ~65 nm in thickness for the scale/substrate interface.

**Results**

**Microstructures of as-cast Ti2AlNb alloy.** Ti2AlNb-based alloy contains different volumes of the ordered phases β2 (Strukturbereicht: B2, space group: Pm3m, Person symbol: cP2), α2-Ti3Al (Strukturbereicht: DO19, space group: P63/mmc, Pearson symbol: hP8), and the ordered orthorhombic O-Ti2AlNb phase (Strukturbereicht: A2B2C, space group: CmCm, Person symbol: oC16). There exist crystallographic orientations of these phases 1–3: (110)β2//(0001)α2, (011)β2//(0001)α2, (0001)α2//(0010)β2, (110)β2//(110)α2, (110)β2//(111)α2 - X-ray diffraction pattern, stereochemical image, back-scattered electron (BSE) SEM micrograph, and TEM bright field image along with the relevant selected area electron diffraction (SAED) patterns of as-cast Ti2AlNb alloy are shown in Fig. 1(a–g). XRD results reveal the presence of O-Ti2AlNb phase, B2 phase, and α2 phase in Fig. 1(a). The stereoscopic image indicates coarse grains in the Ti2AlNb-based alloy (Fig. 1(b)). The SEM image in Fig. 1(c) shows dark α2 phase, gray O-Ti2AlNb phase and B2 phase, which can be better seen in a magnified TEM image in Fig. 1(d). In Fig. 1(c), a small amount of α2 phase is mainly located at grain boundaries in the Ti2AlNb-based
alloy. Then there are only B2 phase (matrix) and O-Ti$_2$AlNb phase (lath) presented in Fig. 1(d–g), with crystallographic orientations between them: $[111]_{\text{B}2} // [110]_{\text{O-Ti}_2\text{AlNb}}$, (110)$_{\text{B}2} // (001)_{\text{O-Ti}_2\text{AlNb}}$.

Isothermal oxidation kinetics. Figure 2(a) shows a curve of isothermal oxidation kinetics of Ti$_2$AlNb-cast alloy at 800 °C. The obtained weight gain of this alloy after 100 h at 800 °C was about 9.3 mg/cm$^2$. The relationship between oxidation and mass gain could be obtained by fitting the experimental data using the following equation,

$$\Delta M^n = k_n t,$$

where $\Delta M$ represents the weight gain per unit area (mg/cm$^2$), $n$ is an oxidation exponent ($n = 1$, liner relationship; $n = 2$, parabolic relationship), $k_n$ is a rate constant (mg$^n$/cm$^2$·h), and $t$ is oxidation time (h). The obtained oxidation exponent was $n \approx 0.83$, being close to 1, thus suggesting that the oxidation kinetics of Ti$_2$AlNb-cast alloy at 800 °C obeyed basically a linear relationship and the oxide layer is not protective at this temperature.

Surface morphology and structure of scale. Secondary electron micrograph, XRD pattern, back-scattered electron SEM micrograph, and EPMA mapping are shown in Fig. 2(b–e). Randomly-oriented and fairly-dense laminar-shaped oxides of about 2–3 μm long are observed to cover the alloy surface, as seen in Fig. 2(b).
X-ray diffraction patterns of oxide scale on Ti$_2$AlNb alloy are shown in Fig. 2(c). It is seen that a large amount of AlNbO$_4$ and TiO$_2$ is present in the scale after oxidation at 800 °C. According to our previous studies, the laminar-shaped oxide is AlNbO$_4$. The cross-section of the overall scale can be seen from an SEM back-scattered electron (BSE) image shown in Fig. 2(d). The scale appears dense with a thickness of ~60 μm, and it consists of three layers based on the EPMA mapping in Fig. 2(e). The structure can be deduced to be (Al,Nb)-rich mixed oxide layer (I)/mixed oxide layer (II)/oxygen-rich layer (III) from the outside to inside. However, the presence of some Al$_2$O$_3$ is also found in layer I through TEM investigations.

EPMA point microanalyses were used to reveal the chemical composition in various locations of the cross-sectional scales in Fig. 2(d). According to XRD results in Fig. 2(c) and the chemical composition of points 1–10 in Table 1, AlNbO$_4$ and TiO$_2$ can be confirmed to be the main oxides in the scale. However, Al and Nb are richer at points 1–2 (in the outermost scale of ~5 μm thick) than at points 3–6, i.e., the (Al,Nb)-rich mixed outer layer (I) and mixed mid-layer (II). This should be a result of the rapid growth of TiO$_2$. The consumption of oxygen leads to a reduction in the oxygen partial pressure, but there is still sufficient oxygen (compared to the interior of...
TEM study of oxide layer. TEM samples were taken from the outer scale (right) and at the scale/substrate interface (left) via FIB, as shown in Fig. 3(a). Figure 3(b) shows a TEM bright-field image, with the SAED pattern of point 1 given in Fig. 3(c), indicating the presence of AlNbO₄ phase. Figure 3(d) is an HRTEM image of point 2 in Fig. 3(b), where Fourier transformations of 2A, 2B, and 2C were performed to obtain diffraction patterns shown in Fig. 3(e) to (g), corresponding to α-Al₂O₃, δ-Al₂O₃ and α-Al₂O₃. This suggests the co-existence of different types of Al₂O₃ oxides. It should be noted that, to the best of the authors’ knowledge, such a co-existent phenomenon of different forms of Al₂O₃ oxides observed via HRTEM has not been reported in the literature, where α-Al₂O₃ is a thermodynamically stable form (corundum form) while δ-Al₂O₃ is one of metastable transformation forms/polymorphs of alumina. Figure 3(h) is a SAED pattern of point 3 in Fig. 3(b), which corroborates the presence of TiO₂.

Figure 4 shows the microstructures of interface between Ti₂AlNb substrate and oxide scale, from a TEM sample taken at the interface of oxide layer/substrate (i.e., the left TEM sample shown in Fig. 3(a)). Figure 4(a,b) present a TEM bright-field image and a high angle annular dark-field (HAADF) image, respectively, where the left side represents the substrate and the right side represents the oxide scale. It should be noted that the white spots in the oxide layer in Fig. 4(a) are pores. The rutile-TiO₂ is found at point 1 in Fig. 4(c,d), with an amorphous surrounding. Nb content at point 1 is very high, and it has been identified as AlNb₂ (Fig. 4(e)), which is also one of the common oxidation products of the Ti₂AlNb-based alloy. Point 3 shows a TiO₂ polycrystalline ring (Fig. 4(f)), which is further oxidized to become rutile-TiO₂. In Fig. 4(g,h) for point 4, Nb₂O₅ is revealed to be present at the boundary of two phases. This is due to the fact that the diffusion of oxygen at the phase boundary is faster as a result of the presence of phase (or grain) boundary energy, along with the reduced reaction activity of Ti and Al. Point 5 shows a lamellar O-Ti₂AlNb phase where brookite TiO₂ and O-Ti₂AlNb phases are present, which are shown in Fig. 4(i). In Fig. 4(j), TiO₂, γ-Al₂O₃, and Nb₂O₅ are observed to co-exist in the O-Ti₂AlNb laths, with the orientation relationships of \( \gamma \)-Al₂O₃ and TiO₂: \( (211)_{\gamma \text{-Al}_2\text{O}_3} // (220)_{\text{rutile- TiO}_2}, (003)_{\gamma \text{-Al}_2\text{O}_3} // (112)_{\text{rutile- TiO}_2}, [120]_{\gamma \text{-Al}_2\text{O}_3} // [\bar{1}10]_{\text{rutile- TiO}_2} \).
Gibbs free energy, however, the energy is not high enough at an oxidation temperature of 800 °C, resulting in the presence of metastable alumina. To the best of the authors' knowledge, there is no report about the structure of Al₂O₃ in the oxidation of a Ti₂AlNb-based alloy. In the present work, the unique formation of alumina is observed via HRTEM in the alloy after oxidation at 800 °C for 100 h. That is, the presence of three adjoining oxide grains and oxides in O-Ti₂AlNb laths, as shown in Figs 3(d) and 4(j), suggests the occurrence of phase change among three types of Al₂O₃, i.e., α-Al₂O₃, δ-Al₂O₃, and γ-Al₂O₃. The γ-Al₂O₃, α-Al₂O₃, and δ-Al₂O₃ are common metastable phases in TiAl alloys at 900 °C. According to Yang et al., γ-Al₂O₃ formed with twins in the oxidation of NiAl, and γ-Al₂O₃ twins were observed to play an important role in the scale growth. Cowley et al. reported that {111} γ-Al₂O₃ twin boundaries provide a fast diffusion path for Al cations. This would improve the oxidation resistance of an alloy. However, in the present study of the Ti₂AlNb-based alloy at 800 °C, there exists δ-Al₂O₃ (monoclinic, a = 11.74 Å, b = 5.72 Å, c = 11.24 Å, β = 103.34°), while no γ-Al₂O₃ twins are observed. As reported by Levin and Brandon, there is a route for the formation of Al₂O₃: Amorphous (anodic film) → γ → δ → α-Al₂O₃. This would be the phase change route of Al₂O₃ in the present Ti₂AlNb-based alloy. Further studies in this aspect are needed at different oxidation temperatures.

Formation of AlNbO₄. As described above, there are TiO₂, Al₂O₃, and AlNbO₄ in the outer oxide layer, as presented in Fig. 3. Zheng et al. assumed that the fast-growing Nb₂O₅ could react with Al₂O₃ that developed at the early stage of oxidation to form AlNbO₄. In the present work, Dmol3 module in Materials Studio 6.0 is used to calculate the Gibbs free energy change of reaction: Nb₂O₅ + Al₂O₃ → 2AlNbO₄, however, the temperature in the software is up to 1000 K only, which is lower than the temperature of the present oxidation experiment, 1073.15 K. Thus, the following equation is used to fit the relationship between the Gibbs free energy and temperature,
Figure 4. Microstructures of interface between as-cast Ti$_2$AlNb-based alloy substrate and oxide scale. (a) TEM bright field image of interface, where white regions reflect pores, (b) high angle annular dark field (HAADF) image of (a); (c) HRTEM of point 1, and (d) FFT image of (c); (g) HRTEM of point 4, and (h) FFT image of (g); (e), (f), (i) and (j) the corresponding SAED patterns of points 2, 3, 5, 6, where point 1 represents rutile-TiO$_2$, point 2 represents AlNb$_2$, point 3 represents TiO, point 4 represents Nb$_2$O$_5$, point 5 represents brookite TiO$_2$ and O-Ti$_2$AlNb phase, point 6 represents rutile TiO$_2$, Nb$_2$O$_5$ and γ-Al$_2$O$_3$.

Figure 5. Gibbs free energy curves of Al$_2$O$_3$, Nb$_2$O$_5$ and AlNbO$_4$ before and after fitting.
\[
G = H_0 + aT \ln T + bT^2 + c/T + IT,
\]

where \(H_0\), \(a\), \(b\), \(c\), and \(I\) are fitting parameters. The results show an excellent matching close to 100%, as shown in Fig. 5 and Table 2. The relationships between the Gibbs free energy and temperature for \(\text{Al}_2\text{O}_3\), \(\text{Nb}_2\text{O}_5\), and \(\text{AlNbO}_4\) can thus be expressed as follows,

\[
G_{\text{Al}_2\text{O}_3} = 1.18577 - 0.00368 \ln T - 1.4271 \times 10^{-6} T^2 + \frac{3.88868}{T} + 0.01932T,
\]

\[
G_{\text{Nb}_2\text{O}_5} = 2.0799 - 0.01388 \ln T - 2.54067 \times 10^{-6} T^2 + \frac{10.8132}{T} + 0.05475T,
\]

\[
G_{\text{AlNbO}_4} = 6.74954 - 0.01287 \ln T - 8.12388 \times 10^{-6} T^2 + \frac{16.08122}{T} + 0.06692T.
\]

Table 2. Fitting results of free energy curve of \(\text{Al}_2\text{O}_3\), \(\text{Nb}_2\text{O}_5\), and \(\text{AlNbO}_4\) in Fig. 5.

| Phase     | \(H_0\)   | \(a\)       | \(b\)          | \(c\)          | \(I\)          | Adj R-Square |
|-----------|-----------|-------------|----------------|----------------|----------------|--------------|
| \(\text{Al}_2\text{O}_3\) | 1.18577   | -0.00368    | -1.4271E-6     | 3.88868        | 0.01932        | 1            |
| \(\text{Nb}_2\text{O}_5\) | 2.0799    | -0.01388    | -2.54067E-6    | 10.8132        | 0.05475        | 1            |
| \(\text{AlNbO}_4\) | 6.74954   | -0.01287    | -8.12388E-6    | 16.08122       | 0.06692        | 0.99999      |

Figure 6. Schematic diagram showing a summary of high-temperature oxidation process of \(\text{Ti}_2\text{AlNb}\)-based alloy. Stage 1, by inward diffusion of oxygen B2 phase is transformed into TiO, and \(\text{O}-\text{Ti}_2\text{AlNb}\) is abound with oxygen. Stage 2, TiO is transformed into rutile-TiO2 and AlNb2 is formed in the areas of B2 phase. Oxidation occurs in \(\text{O}-\text{Ti}_2\text{AlNb}\) phase. Stage 3, \(\text{O}-\text{Ti}_2\text{AlNb}\) phase breaks down into \(\text{Al}_2\text{O}_3\), \(\text{Nb}_2\text{O}_5\), and TiO2. Al2O3 reacts with \(\text{Nb}_2\text{O}_5\) to form \((\text{AlNbO}_4 + \text{TiO}_2)\) mixed oxide layer. At last, nitrogen dissolves in the alloy.
Substituting $T = 1073.15 \text{ K}$ into the above equations yields the Gibbs free energy values for the formation of $\alpha_\text{Al}_2\text{O}_3$, $\text{Nb}_2\text{O}_5$, and $\text{AlNb}_2\text{O}_4$, respectively, in the present oxidation condition of a higher temperature. As a result, the Gibbs free energy change of the reaction $\text{Nb}_2\text{O}_5 + \text{Al}_2\text{O}_3 \rightarrow 2\text{AlNb}_2\text{O}_4$ becomes $-1.00873 \text{ kJ/mol}$. This means that the reaction is thermodynamically possible. Also, $\text{Al}_2\text{O}_3$ reacted completely with $\text{Nb}_2\text{O}_5$ to form $\text{AlNb}_2\text{O}_4$ in $\text{Nb}_2\text{O}_5-\text{Al}_2\text{O}_3$ ceramics. While $\text{Nb}_2\text{O}_5$ is consumed as a reactant, the formed $\text{AlNb}_2\text{O}_4$ makes the scale unprotective as well\cite{35}. Furthermore, $\text{Nb}_2\text{O}_5$ is not observed in the XRD results (Fig. 2(c)), which can be mainly attributed to its reaction with $\text{Al}_2\text{O}_3$ as discussed above, in conjunction with the lower diffusion coefficient of Nb, the rapid growth of $\text{TiO}_2$, and the hindering effect of alumina.

### Oxidation process at the interface.

Based on the above observations and analyses, the high-temperature oxidation process of the Ti$_2$AlNb-based alloy can be summarized below and schematically shown in Fig. 6. Stage 1: Oxygen absorbs on the surface of the Ti$_2$AlNb-based alloy, which later penetrates into it. The B2 phase is oxidized to produce TiO$_2$, and oxygen dissolves in the O-Ti$_2$AlNb phase. Stage 2: TiO$_2$ is transformed into rutile-TiO$_2$ and AlNb$_2$, and is formed in the areas of the B2 phase. Oxidation occurs, i.e., brookite-TiO$_2$ is generated inside the O-Ti$_2$AlNb phase and Nb$_2$O$_5$ outside the O phase. Stage 3: O-Ti$_2$AlNb phase breaks down to TiO$_2$, Nb$_2$O$_5$, and Al$_2$O$_3$. In the scale there is a reaction: $\text{Al}_2\text{O}_3 + \text{Nb}_2\text{O}_5 \rightarrow 2\text{AlNb}_2\text{O}_4$, and N atoms are dissolved in the alloy because of the consumption of O atoms. The corresponding crystallographic structures of the related oxides of the Ti$_2$AlNb-based alloy are summarized in Table 3.

### Conclusions

1. After being exposed at 800 °C in static air for 100 h, the Ti$_2$AlNb-based alloy followed an almost linear kinetic law of oxidation and exhibited a multi-layered structure consisting of an (Al,Nb)-rich mixed oxide layer (I), mixed oxide layer (II), and oxygen-rich layer (III) from the outside to inside.
2. In the mixed outer scale, there existed $\alpha$-Al$_2$O$_3$ and $\delta$-Al$_2$O$_3$, $\text{Al}_2\text{O}_3$ reacted with $\text{Nb}_2\text{O}_5$ to form $\text{AlNb}_2\text{O}_4$, however, $\text{Nb}_2\text{O}_5$ and $\text{AlNb}_2\text{O}_4$ were not able to hinder the diffusion of oxygen.
3. The B2 phase was oxidized to form TiO$_2$, where Nb and Al were transformed into $\text{AlNb}_2$ at the interface during oxidation. $\text{AlNb}_2$ could hinder the diffusion of oxygen and improve the oxidation resistance of the Ti$_2$AlNb-based alloy, but its discontinuous nature allowed only a limited effect.
4. After long-term oxidation at 800 °C, O-Ti$_2$AlNb was oxidized to form TiO$_2$, Al$_2$O$_3$ and Nb$_2$O$_5$. $\text{Al}_2\text{O}_3$ and $\text{Al}_2\text{O}_3$ could hinder the growth of TiO$_2$ in the O-Ti$_2$AlNb laths and form a compact scale. Increasing the amount of the O-Ti$_2$AlNb phase in the alloy contributes to the improvement in its high-temperature oxidation resistance.

### Data Availability

The datasets generated and/or analyzed during the current study are available from the corresponding author on reasonable request.

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**Table 3.** Crystallographic structures of the related oxides.

| Phase         | PDF number | Space group | Crystal system |
|---------------|------------|-------------|----------------|
| $\text{AlNb}_2$ | #15-0598   | P42/mnm (136) | Tetragonal     |
| $\delta$-Al$_2$O$_3$ | #19-0864   | Primitive Monoclinic |
| $\text{Nb}_2$O$_5$ | #19-0864   | Primitive Monoclinic |
| $\gamma$-Al$_2$O$_3$ | #22-1196   | A2/m (12) Monoclinic |
| Brookit-TiO$_2$ | #29-1360   | Pcab (61) Orthorhombic |
| $\text{Al}_2$O$_3$ | #46-1212   | R-3c (167) Hexagonal |
| Rutile-TiO$_2$ | #21-1276   | P42/mnm (136) Tetragonal |
| $\text{Nb}_2$O$_5$ | #11-0517   | C2/m (12) Monoclinic |
| $\text{Al}_2$O$_3$ | #41-0347   | C2/m (12) Monoclinic |
| $\alpha$-Al$_2$O$_3$ | #10-0425   | Fd-3m (227) Cubic |
| $\beta$-Al$_2$O$_3$ | #11-0517   | C2/m (12) Monoclinic |

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Acknowledgements
The authors are grateful for the financial support provided by the National Natural Science Foundation of China (NSFC) (Grant Nos U1302275, 51471155 and 51305304) and the Natural Sciences and Engineering Research Council of Canada (NSERC) in the form of international research collaboration, Fundamental Research Funds for the Central Universities, and Major Science and Technology Project “High-end CNC Machine Tools and Basic Manufacturing Equipment” (2013ZX04011061). One of the authors (D.L. Chen) is also grateful for the financial support by the Premier's Research Excellence Award (PREA), NSERC-Discovery Accelerator Supplement (DAS) Award, Canada Foundation for Innovation (CFI), and Ryerson Research Chair (RRC) program. The authors also thank Prof. G.J. Cao of Harbin University of Science and Technology, for his assistance in the TEM/HRTEM observations.

Author Contributions
J.M. Xiang conducted the oxidation experiments. S.J. Qu and J. Shen designed and supervised the project, and produced the samples. J.M. Xiang, S.J. Qu, G.B. Mi, A.H. Feng, X. Huang, Z. Chen, J. Shen, and D.L. Chen analyzed the data. J. Shen and D.L. Chen assessed the outcome. J.M. Xiang, S.J. Qu, G.B. Mi, A.H. Feng and D.L. Chen wrote the paper. All the authors discussed the results and commented on the manuscript.

Additional Information

Competing Interests: The authors declare no competing interests.

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