Oxidation Resistance of Materials Based on Ti₃AlC₂ Nanolaminate at 600 °C in Air

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Abstract

The oxidation behavior of Ti₃AlC₂-based materials had been investigated at 600 °C in static air for 1000 h. It was shown that the intense increase of weight gain per unit surface area for sintered material with porosity of 22 % attributed to oxidation of the outer surface of the specimen and surfaces of pores in the bulk material. The oxidation kinetics of the hot-pressed Ti₃AlC₂-based material with 1 % porosity remarkably increased for the first 15 h and then slowly decreased. The weight gain per unit surface area for this material was 1.0 mg/cm² after exposition for 1000 h. The intense initial oxidation of Ti₃AlC₂-based materials can be eliminated by pre-oxidation treatment at 1200 °C in air for 2 h. As a result, the weight gain per unit surface area for the pre-oxidized material did not exceed 0.11 mg/cm² after 1000 h of exposition at 600 °C in air. It was demonstrated that the oxidation resistance of Ti₃AlC₂-based materials can be significantly improved by niobium addition.

Keywords: Nanolaminates, MAX phase, Ti₃AlC₂, Microstructure, Oxidation behavior

Introduction

Recently, new classes of materials based on layered carbide Ti₃AlC₂ have attracted great attention of material scientists due to their exceptional properties. This carbide belongs to the so-called MAX phases which have a chemical formula Mₓ₋₁AXₓ₋₁—where M is an early transition metal, A is an A-group element, and X is carbon and/or nitrogen. The crystal structure of MAX phases can be described as octahedral ternary metal carbide and/or nitride sandwiched by close-packed layers of A-element. These materials have good thermal and electrical conductivity, low density, high strength and Young’s modulus, excellent thermal shock resistance, high chemical resistance, relatively low thermal expansion coefficient, and good machinability [1–3]. Owing to such combination of properties, they have been suggested for various applications, especially as high-temperature structural materials. This requires comprehensive investigations of oxidation resistance of Ti₃AlC₂-based materials. Barsoum et al. [4] had demonstrated that for Ti₃n₋₁Alₓn compounds oxidized in the 800–1000 °C temperature range, the scale composed mainly of rutile-based solid solution (Ti₁₋₅Alₓ)O₂₋₅y, where y < 0.05 and some Al₂O₃. The oxidation process occurred by the inward diffusion of oxygen and the outward diffusion of Al, Ti, C, and N. It was revealed that the formation of a thin layer of Al₂O₃ preceded the nucleation and growth of TiO₂ at the early stages of oxidation [5]. The scale formed at higher temperatures consisted of a continuous Al₂O₃ inner layer and outer layer, changed from rutile TiO₂ at temperatures below 1200 °C to a mixture of Al₂TiO₅ and TiO₂ at 1300 °C [6]. Taotao [7] had reported that the scale of an un-dense Ti₃AlC₂ material containing 3 wt. % TiC oxidized at 1000 °C in air consisted of three layers, including an outer un-dense TiO₂ layer adhering to a little Al₂O₃, a thick intermediate TiO₂ + Al₂O₃ mixed layer, and a thin inner Al₂O₃ layer with some pores.

In spite of thorough research of oxidation behavior of Ti₃AlC₂-based materials at high temperature, only a few results obtained at intermediate temperatures have been reported [8, 9]. Taking into account the anomalously intense oxidation of Ti₃AlC₂-based material at 500 °C and especially at 600 °C [8], the investigation of oxidation behavior of these materials at intermediate temperatures has a great importance.

In this work, the Ti₃AlC₂-based materials have been oxidized at 600 °C in air for 1000 h. The influence of porosity, pre-oxidation treatment, and niobium addition
on the oxidation resistance of these materials has been investigated.

**Review**

**Experimental**

The materials used in this work were initially sintered in vacuum from mixture of TiC, TiH₂, and Al powders and then hot pressed at 1350 °C under pressure of 30 MPa for 1 h. The phase composition of a sintered material consisted of 95 wt. % Ti₃AlC₂ and 5 wt. % TiC. Figure 1a shows the back-scattered electron image of a polished surface of this material. The equiaxed grains of Ti₃AlC₂, fine particles of TiC, and big pores were observed. The porosity of the material was 22 %. After hot pressing, refinement of the structure and reduction of the porosity to 1 % occurred (Fig. 1b). The amount of Ti₃AlC₂ was decreased to 92 wt. % and TiC increased to 6 wt. % (Fig. 2a). Additionally, 2 wt. % Al₂O₃ was revealed in this material. The material alloyed with 3.5 wt. % Nb fabricated by the same process as previous material consisted of 56 wt. % (Ti, Nb)₃AlC₂, 41 wt. % TiC, and 3 wt. % Al₂O₃ (Fig. 2b). The structure of this material includes equiaxed grains of Ti₃AlC₂ and TiC and uniformly distributed fine particles of Al₂O₃ and small pores (Fig. 1c).

The isothermal oxidation tests were carried out at the temperature of 600 °C in static air using tree rectangular bars with dimensions of 20 × 5 × 3 mm for each material. The specimens were cut by the electrical discharge method, abraded to 1000 grit with SiC paper, and polished by diamond past. The oxidation tests were divided into five stages which had the duration: first stage, 15 h; second stage, 245 h; and the last three stages, 250 h. Each stage consisted of heating to 600 °C in air, exposition during determined time, and cooling to room temperature. The weight of the specimens was measured before the test and after each stage by analytical balance. The accuracy of the weight measuring was ±10⁻⁴ g. The oxidation resistance of materials tested was characterized by weight gain per unit surface area ΔW/S. The phase composition of the materials was analyzed by X-ray diffractometry (Dron-3M, Russia). Diffraction data were processed by the Rietveld method using the Powder-Cell program. Scanning electron microscopy (EVO 40 XVP (Carl Zeiss, Germany)) coupled with energy dispersive spectroscopy (EDS) (INCA ENERGY 350 (Oxford Instruments, UK)) was used to study the structure and quantitative elemental content of the bulk material and the oxidized scale.

**Results and Discussion**

The dependences of weight gain per unit surface area on oxidation time at 600 °C for Ti₃AlC₂-based materials tested are presented in Fig. 3. It can be seen that the ΔW/S for material with porosity of 22 % monotonically increases and reaches the value of 24 mg/cm² after exposition of 437 h. Because of the very high value of the ΔW/S, the test for this material had

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![Fig. 1](image_url)  
**Fig. 1** Back-scattered electron images of the polished surfaces: a Ti₃AlC₂-based material with 22 % porosity, b Ti₃AlC₂-based material with 1 % porosity, and c Nb alloyed Ti₃AlC₂-based material with 1 % porosity
been stopped. The rapid oxidation of the Ti$_3$AlC$_2$-based material with porosity of 22% can be explained by intense penetration of oxygen into the material through the pores. As a result, not only outer surface of the specimen but also the surfaces of pores in the bulk material were oxidized (Fig. 4a, b).

The oxidation kinetics for the Ti$_3$AlC$_2$-based material with 1% porosity at 600 °C remarkably increases on the first stage of the test (Fig. 3). After 15 h, the weight gain per unit surface area increases more slowly, and after 1000 h, exposition is 1.0 mg/cm$^2$. Table 1 presents an average quantity of chemical elements in bulk material and scale, obtained by the EDS method. It can be seen that carbon misses instead of oxygen were present in the scale. This means that the surfaces of Ti$_3$AlC$_2$ and TiC particles completely oxidized to TiO$_2$, Al$_2$O$_3$, and gaseous CO or CO$_2$ phases which volatilized from the scale. The
volatilization of gaseous phases leads to pore formation in the oxide layer (Fig. 4c). The overall equations for the oxidation reactions are:

\[
4\text{Ti}_3\text{AlC}_2 + 23\text{O}_2 = 12\text{TiO}_2 + 2\text{Al}_{2}\text{O}_3 + 8\text{CO}_2(g), \text{TiC} + 2\text{O}_2 = \text{TiO}_2 + \text{CO}_2(g).
\]

Wang and Zhou [8] had demonstrated that the scale formed at 600 °C on the surface of a Ti$_3$AlC$_2$ material with 5 val. % TiC consisted of amorphous Al$_2$O$_3$, anatase, and rutile TiO$_2$. The formation of anatase from Ti$_3$AlC$_2$ led to the increase of stress due to the difference of their volume expansion. Therefore, the rapid increase of $\Delta W/S$ value for the Ti$_3$AlC$_2$-based material with 1 % porosity on the first stage of the test can be associated with intense scale formation as well as with low protective property of the thin scale due to microcracks and also with penetration of oxygen through micropores into the bulk material (Fig. 4c). After long-term exposition, when micropores were covered with oxides and the scale thickness was increased (Fig. 4d), the inward diffusion of oxygen and outward diffusion of Ti and Al became slow. As a result, the oxidation kinetics was decreased. Based on these results, it can be assumed that the preliminary oxidation to form the protective layer of oxides would increase the oxidation resistance of Ti$_3$AlC$_2$-based materials. The pre-oxidation at 1000–1300 °C for 2 h provides the formation of a dense scale.

![Fig. 4 Back-scattered electron images of the scales formed at 600 °C for 1000 h: a Ti$_3$AlC$_2$-based material with 22 % porosity, b oxidized pores of Ti$_3$AlC$_2$-based material with 22 % porosity, d Ti$_3$AlC$_2$-based material with 1 % porosity, e Nb alloyed Ti$_3$AlC$_2$-based material with 1 % porosity, and c scale surface of Ti$_3$AlC$_2$-based material with 1 % porosity after 15 h oxidation](image)

| Table 1 | EDS analysis results of the Ti$_3$AlC$_2$-based materials with 1 % porosity (at. %) |
|---------|---------------------------------|
| Materials       | TiBulk | TiScale | AlBulk | AlScale | CBulk | CScale | NbBulk | NbScale | OBulk | OScale |
| Ti$_3$AlC$_2$   | 51.3   | 23.7    | 14.8   | 8.1     | 34.6   | 0      | 0      | 0      | 68.2   |
| Ti$_3$AlC$_2$ with Nb | 44.1   | 25.3    | 14.9   | 3.3     | 42.8   | 0      | 1.4    | 0.6    | 70.1   |
which consists of \( \text{Al}_2\text{O}_3 \) and rutile \( \text{TiO}_2 \) without anatase \( \text{TiO}_2 \) [10]. In the present study, the pre-oxidation of the \( \text{Ti}_3\text{AlC}_2 \)-based material with 1 % porosity was performed at 1200 °C in air for 2 h. The weight gain per unit surface area after pre-oxidation is 1.7 mg/cm\(^2\). The long-term oxidation resistance was investigated at 600 °C in air for 1000 h. As can be seen in Fig. 3, the pre-oxidized material demonstrates the negligible increase of weight gain per unit surface area during all tests. The value of \( \Delta W/S \) for this material not exceeds a 0.11 mg/cm\(^2\) after a 1000-h exposition.

The influence of Nb on the oxidation resistance of a \( \text{Ti}_3\text{AlC}_2 \)-based material with 1 % porosity had been investigated. The cross-sectional view of the oxidized surface is shown in Fig. 4e. Despite a greater content of TiC, the weight gain per unit surface area for this material increases more slowly as compared with material without Nb (Fig. 3). The \( \Delta W/S \) is 0.34 mg/cm\(^2\) after exposition at 600 °C for 1000 h. This value is approximately three times smaller than that for \( \text{Ti}_3\text{AlC}_2 \)-based materials without Nb. Barsoum et al. [11] had shown that TiC has a deleterious effect on the oxidation kinetics of \( \text{Ti}_3\text{SiC}_2 \)-based materials which also belong to isotypic structure \( M_n+1AX_n \). The contradiction of this conclusion with the results obtained in present work can be explained by a positive effect of Nb on the oxidation resistance of \( \text{Ti}_3\text{AlC}_2 \)-based materials. The EDS analysis shows that the content of Ti, Al, and Nb in the scale of the \( \text{Ti}_3\text{AlC}_2 \)-based material with Nb is less than that in the bulk material (Table 1). On the other hand, the content of Al in the scale of this material is significantly less than that of the material without Nb. This means that Nb impedes the outward diffusion of Al. As the result, the formation of \( \text{Al}_2\text{O}_3 \) is restricted. The XRD analysis shows that the scale of the \( \text{Ti}_3\text{AlC}_2 \)-based material with Nb consists mainly of \( \text{TiO}_2 \) and minor quantity of \( \text{Al}_2\text{O}_3 \) (Fig. 5). According to [6], the formation of a dense \( \text{Al}_2\text{O}_3 \) layer is responsible for high oxidation resistance of \( \text{Ti}_3\text{AlC}_2 \)-based materials. Thus, a material with Nb ought to be less oxidation resistant than a material without Nb. Jiang et al. [12] had concluded that Nb in solid solution with TiO\(_2\) impedes mass transfer in TiO\(_2\) and improves the oxidation resistance of Ti–Al–Nb alloys greater than Al. Evidently, in case of \( \text{Ti}_3\text{AlC}_2 \)-based materials, the positive effect of Nb manifests in the same manner.

**Conclusions**

The investigation of oxidation resistance of \( \text{Ti}_3\text{AlC}_2 \)-based materials had been carried out at 600 °C in static air for 1000 h. The results showed that the weight gain per unit surface area for sintered \( \text{Ti}_3\text{AlC}_2 \)-based materials with porosity of 22 % monolithically increased and after 437 h reached the value of 24 mg/cm\(^2\). The drastic increase of oxidation kinetics of this material caused by intense oxidation not only the outer surface of specimen but also the surfaces of pores. The weight gain per unit surface area for hot-pressed \( \text{Ti}_3\text{AlC}_2 \)-based materials with 1 % porosity intensively increased for the first 15 h of oxidation, and then the oxidation kinetics slowly decreased. The pre-oxidation at 1200 °C for 2 h eliminated the initial oxidation of this material at 600 °C. It was revealed that the niobium addition significantly improves the oxidation resistance of the \( \text{Ti}_3\text{AlC}_2 \)-based material.

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**Authors’ Contributions**

AI performed the oxidation tests and microstructural and energy dispersive studies and drafted Fig. 1 and Table 1 and the “Experimental” and “Results and Discussion” sections. VP performed the microstructural studies and drafted Figs. 2 and 3 and the “Introduction,” “Results and Discussion,” and “References” sections. OO analyzed the literature data and test results and helped in the “Introduction,” “Results and Discussion,” and “Conclusions” sections. TP analyzed the literature data and test results; contributed in the development of the materials; and helped in the “Experimental,” “Results and Discussion,” and “Conclusions” sections. TB performed the phase compositions and microstructural studies and helped in the “Experimental” and “Results and Discussion” sections. All authors read and approved the final manuscript.
Competing Interests
The authors declare that they have no competing interest.

Endnotes
None.

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