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Breakaway oxidation of Ti_3AlC_2 during long-term exposure in air at 1100 °C

Xichao Li[a,b], Lili Zheng[a], Yuhai Qian[a], Jingjun Xu[a], Meishuan Li[a,*]

[a] Shenyang National Laboratory for Materials Science, Institute of Metal Research, Chinese Academy of Sciences, Shenyang 110016, China
[b] University of Chinese Academy of Sciences, Beijing 100039, China

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ABSTRACT

Catastrophic breakaway oxidation of Ti_3AlC_2 occurs during long-term oxidation at 1100 °C in air up to 4000 h. Correspondingly, the oxidation kinetics transforms from cubic law to linear law. The transition time is about 3171 h, and the corresponding critical Al content is about 5.99% lower than the initial content. Afterwards, Ti and C start to be oxidized instead of selective oxidation of Al, and Al_2O_3 scale loses its protectiveness. Meanwhile, voids generated at the Al_2O_3/Ti_3AlC_2 interface reduce the oxide scale adhesion. After 3250 h oxidation, Ti_3AlC_2 still maintains its crystal structure, indicating the capability of bearing great Al lack.

1. Introduction

The layered ternary ceramics, named MAX phases, where M is an early transition metal, A is an A group element, and X is C and/or N [1–3], have attracted increasing attention due to their unique combination of the properties of both ceramics and metals [4], such as high modulus and strength, good thermal shock resistance, high electrical and thermal conductivity, good machinability, high damage tolerance [5–11]. Among the reported MAX phases, Ti_3AlC_2 [12], Ti_2AlC [13] and Cr_2AlC [14] exhibit the most excellent high temperature oxidation resistance, which endow them potential applications as high-temperature materials. Therefore, the oxidation behaviors of these MAX phases, especially Ti_3AlC_2, have been investigated widely.

Wang and Zhou [12] reported that Ti_3AlC_2 exhibited good oxidation resistance at 1000–1300 °C for 20 h in air due to the formation of a continuous and adherent Al_2O_3 scale, indicating that the preferential oxidation of Al in Ti_3AlC_2 happened. The oxidation kinetics followed parabolic law, and the inward diffusion of oxygen through the oxide scale was dominant step. Song et al. [15] presented that at the early oxidation stage of Ti_3AlC_2 at 1100 °C in air for short time (≤900 s), predominantly α-Al_2O_3 nuclei generated and grew to form a thin Al_2O_3 layer firstly. Variously, during the oxidation of Ti_3SiC_2, one of most typical MAX phases, both Ti and Si were oxidized to form duplex oxide scale of TiO_2 outer layer and $TiO_2 + SiO_2$ mix inner layer [16]. That is to say, although Ti_3SiC_2 has the identical crystal structure and components except Si replacing Al, its selective oxidation could not happen. Lin et al. [17] investigated Al distribution in Ti_3AlC_2 adjacent to the Al_2O_3/Ti_3AlC_2 interface by utilizing STEM, found that the oxidation induced Al depletion only existed in the narrow range of about 50 nm, which indicates that the outward diffusion of Al in Ti_3AlC_2 was quite rapid. Li et al. [18] proposed that the selective oxidation of Ti_3AlC_2 based materials was attributed to high oxygen affinity and diffusion coefficient of Al in Ti_3AlC_2.

Based on Wagner's theory about selective oxidation of alloys (such as Fe–Cr–Al alloys [19]), it is well known that there is a critical content C_{Al}' of Al, only when the content of Al in the alloys is higher than the critical value, can the initial selective oxidation of alloys and sustainable growing of protective Al_2O_3 happen. With increasing oxidation time, Al in the alloys is consumed constantly by the growth of Al_2O_3 scale. When the oxidation time is long enough, the alloys suffer from breakaway oxidation in two main failure modes [20]: mechanically induced chemical failure (MICF), involving in scale cracking and spallation; intrinsic chemical failure (InCF), resulting from depletion of aluminum content within the substrate bellow C_{Al}' [21–23].

For Ti_3AlC_2, it is necessary to conduct long-term oxidation of Ti_3AlC_2, in order to determine the critical content of Al needed for

* Corresponding author at: High-performance Ceramic Division, Shenyang National Laboratory for Materials Science, Institute of Metal Research, Chinese Academy of Sciences, 72 Wenhua Road, Shenyang 110016, China. Fax: +86 24 23891320.
E-mail address: mshli@imr.ac.cn (M. Li).

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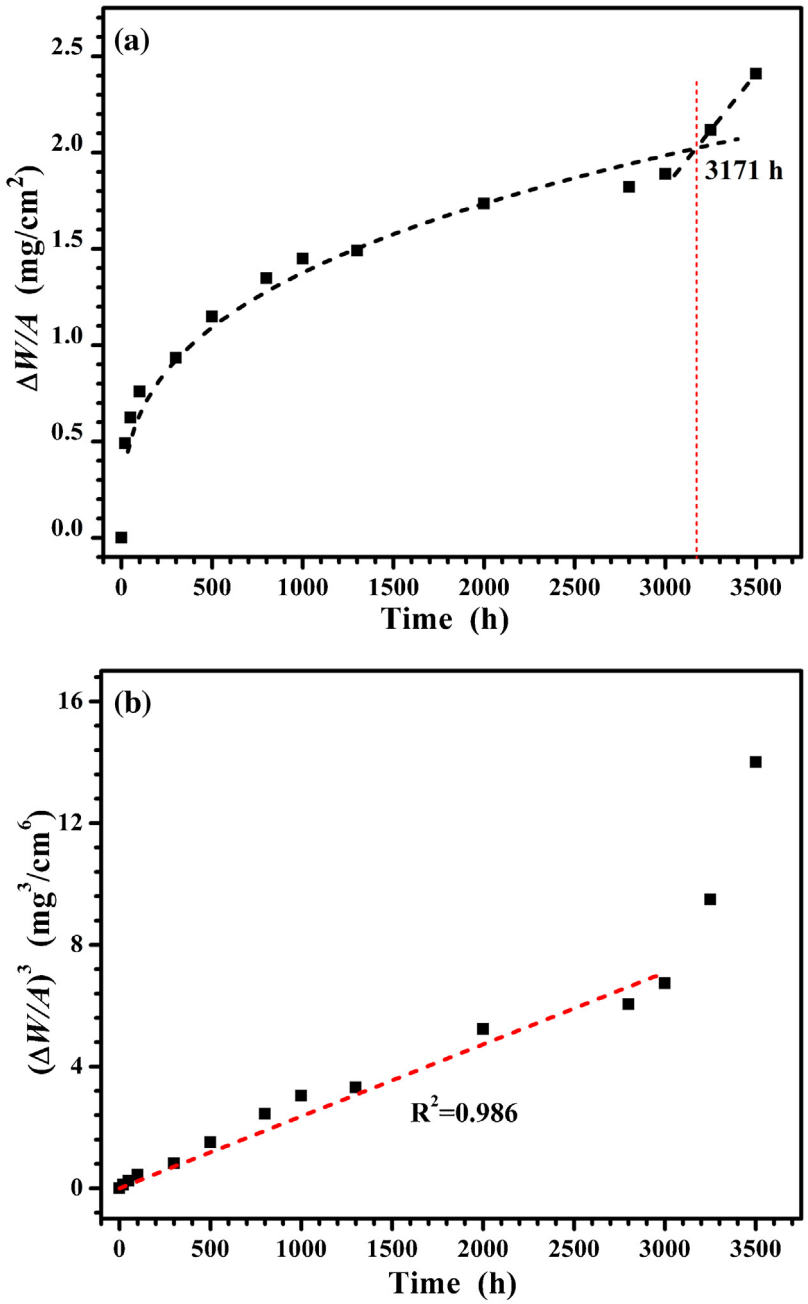

Fig. 1. Oxidation kinetics of Ti_3AlC_2 at 1100 °C in air up to 3500 h, (a) $\Delta W/A$ vs. t, (b) $(\Delta W/A)^3$ vs. t.

sustaining the protectiveness of Al_2O_3 scale. On the other hand, severe consumption of Al may results in phase transformation of Ti_3AlC_2 to more stable Ti–C binary carbides [24,25]. In fact, Cr_2AlC also exhibited good oxidation resistance up to 1300 °C in air for 20 h due to the formation of protective Al_2O_3 scale [14]. However, differing from Ti_3AlC_2, Cr_2AlC transformed to Cr–C carbides (Such as Cr_7C_3, Cr_3C_2) easily due to the depletion of Al within Cr_2AlC in the areas adjacent to the Al_2O_3/substrate interface [14]. When the oxidation time was prolonged, Cr_2O_3 nodules formed on the oxide layer [26], even voids generated in the Cr_7C_3 layer destroyed the subscale area and deteriorated the scale adherence under the oxidation condition at 1300 °C in air up to 336 h [27].

It is believed that Ti_3AlC_2 would also lose its good oxidation resistance at some time due to the scale cracking and spallation without healing or depletion of Al in the substrate. Unfortunately, it is difficult to determine the lifetime of Ti_3AlC_2 and failure mode by previous work. Firstly, nothing about the critical Al content for selective oxidation of Ti_3AlC_2 or its breakaway oxidation has been reported up to now. Secondly, although there is no Al depletion zone found beneath the protective Al_2O_3 scales for short-time oxidation [28], the distribution of Al in the Ti_3AlC_2 substrate after long-term oxidation has not been determined. Thirdly, cracking, spallation and crack-healing ability of Al_2O_3 scale on Ti_3AlC_2 after long-term oxidation (>1000 h) are unclear. Therefore, it is imperative to study the long-term oxidation behaviors of Ti_3AlC_2 as well as to determine critical content of Al for sustaining protection of Al_2O_3 scale or phase stability of Ti_3AlC_2.

In the present work, a long-term oxidation of Ti_3AlC_2 up to 4000 h at 1100 °C in static air has been conducted to study the evolution of oxidation kinetics and oxidation products of Ti_3AlC_2. Meanwhile, the critical Al content within Ti_3AlC_2 below which breakaway oxidation occurred is determined. Oxide adhesions