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# The scaling behavior and mechanism of $Ti_2AlC$ MAX phase coatings in air and pure water vapor

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ABSTRACT

The scale behavior of $Ti_2AlC$ coating at 750 °C in air and pure water vapor was investigated. A four-layered scale, a thick $TiO_2$ and $Al_2O_3$ mix oxide outer layer, followed by a thin $\alpha$-(Al, Cr)$_2$O$_3$ sublayer, a thick $Fe_2O_3$ and $TiO_2$ mix oxide mid-layer and a thin $Al_2O_3$-rich oxide inner layer in sequence, developed on the $Ti_2AlC$ coatings in air. Whereas internal oxidation occurred, no distinct oxide scale formed on the $Ti_2AlC$ coating in the case of the oxidation in pure water vapor. The $Ti_2AlC$ coating improved the oxidation resistance of 316LSS in air, especially in wet air.

## 1. Introduction

MAX phases are a group of nanolaminated materials, where M is an early transition metal, A an A-group element, and X either C or N [1]. This group of materials possess unique properties, such as high electrical and thermal conductivity, good machinability, excellent thermal shock resistance and damage tolerance, high elastic modules, high temperature strength, superior oxidation and corrosion resistances [2,3]. As one member of MAX phases, $Ti_2AlC$ was attractive for high temperature structural applications. The high temperature oxidation behaviors of bulk $Ti_2AlC$ have received great attention in the past decade [4–10]. At high temperature in dry air and water vapor a discontinuous $TiO_2$ outer layer and a continuous protective $Al_2O_3$-rich sub-layer form on the bulk $Ti_2AlC$, suggesting that $Ti_2AlC$ exhibits excellent oxidation resistance. In contrast, $Ti_3Al$ with higher Al content could not form a protective $Al_2O_3$ scale during oxidation [4–10].

Therefore, $Ti_2AlC$ phase is expected to be one of the promising materials for high temperature corrosion protective coating applications. $Ti_2AlC$ coating has been successfully prepared by numerous physical vapor deposition (PVD) processes [11–17] and high velocity oxy-fuel spray [18]. Thereafter, the oxidation behaviors of $Ti_2AlC$ coating at high temperature in dry air were investigated [15–17]. The scale on the surface of $Ti_2AlC$ coating by PVD consisted of a $TiO_2$-rich layer, $Al_2O_3$-rich layer, and a $TiO_2 + Al_2O_3$ mixed layer in sequence at 800–900 °C in dry air. For TiAlC coating deposited by high velocity oxy-fuel spray technique there exist TiC and $Ti_3AlC$ phases in the TiAlC which produce a discontinuous alumina, hence, decreasing its oxidation resistance [18]. Thus, the phase purity and microstructure have great influence on oxidation behavior of $Ti_2AlC$ coating.

In addition, pure water vapor is a typical environmental condition in many energy related systems such as coal-fired power plant and nuclear power plant. Water vapor slightly accelerated the oxidation of $Ti_2AlC$ due to the enhanced mass transportation process through the increased oxygen vacancy [8,9], while the influence of the presence of water vapor on the oxidation of $Ti_2AlC$ coating is still unclear. Up to now, few works has focused on the oxidation behavior of $Ti_2AlC$ coating at high temperature in pure water vapor.

In the present work, the oxidation behavior of the $Ti_2AlC$ MAX phase coating, prepared on austenitic stainless steel by DC magnetron sputtering deposition and annealed, was investigated at 750 °C in dry air and pure water vapor, respectively. The scaling behavior was discussed based on the phase formation and microstructure evolution of the $Ti_2AlC$ coating.

## 2. Experimental

Type 316 L austenitic stainless steels (316LSS) were used as the substrates alloy for the present work, with the nominal composition of 316LSS given as follows: Fe, bal; Cr, 16.0–18.0; Ni, 10.0–14.0; Mo, 2.0–3.0; $C \leq 0.03$; $Mn \leq 2.00$; $Si \leq 1.00$; $P \leq 0.045$; $S \leq 0.03$. The steel plates were cut into specimens with the size of 15 mm × 10 mm × 2 mm,

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followed by grinding with 1000-grit SiC paper, and degreasing with acetone. The Ti–Al–C coating was deposited on the substrate by reactive DC magnetron sputtering with compound $Ti_{50}Al_{50}$ (at.%) target ($400 \times 100 \times 10$ mm$^3$) in Ar/$CH_4$ atmosphere with $CH_4$ as the reactive gas. The sputtering parameters were as follows: background vacuum $4.6 \times 10^{-3}$ Pa; argon pressure 0.5 Pa; power 1.6 kW; room temperature; and sputtering time 10 h. Annealing treatment of the as-deposited coating was conducted at 800 °C in vacuum for 1 h to form the $Ti_2AlC$ MAX phase. The details of the coating preparation can be found in our previous work [19].

The oxidation of the uncoated and coated 316LSS was isothermally conducted at 750 °C, which is a typical working temperature of next generation coal-fired power plant and nuclear power plant, in air and pure water vapor for 200 h, respectively. The air oxidation was carried out in static air. The pure water vapor oxidation was conducted in a high temperature tube furnace with a quartz tube as the reaction chamber. Ultrapure water with 5–7 mg/L dissolved oxygen content was pumped into the 400 °C preheated device to produce pure water vapor, which then flows into the reaction chamber. The pure water vapor flow rate was controlled to be 100–120 ml/s. The pressure of the pure water vapor was 0.1 MPa.

X-ray diffraction (XRD) using a Bruker D8 diffractometer with Cu $K_a$ radiation source was employed to characterize the phase formation. The surface and cross-sections of the samples were also examined by a FEI Inspect FSEM equipped with an Oxford energy dispersive X-ray (EDX) microanalysis.

## 3. Results and discussion

The $Ti_2AlC$ MAX phase coating is mainly composed of $Ti_2AlC$ phase with small amount of $Ti_3AlC$ antiperovskite phase (Fig. 1a). Fig. 1b and c shows the surface morphology and cross-sectional morphologies of the $Ti_2AlC$ coating. Due to the mismatch of thermal expansion coefficient between the $Ti_2AlC$ phase and 316LSS, some through-cracks formed in the $Ti_2AlC$ coatings. An Al-rich diffusion layer was also observed at the coating/substrate interface.

XRD analysis (Fig. 2a) reveals that 316LSS after oxidation at 750 °C in air for 200 h consisted of only Fe-rich $(Cr,Fe)_2O_3$. Fig. 2b and c shows the surface and cross-sectional morphologies of 316LSS after oxidation at 750 °C in air for 200 h. The steel oxidation in air formed a uniform scale mainly composed of Fe-rich oxides. Cross-sectional morphology showed that the thin Fe-rich scale was porous with poor adhesion to the substrate.

XRD analysis (Fig. 3a) indicates that the scale formed on the $Ti_2AlC$ coating after oxidation at 750 °C in air for 200 h is mainly composed of $\alpha$-$(Al,Cr)_2O_3$, $\theta$-$Al_2O_3$ and rutile $TiO_2$. The surface morphology of the $Ti_2AlC$ coating after oxidation at 750 °C in air for 200 h (Fig. 3b) showed clearly that the through-cracks present in the as-prepared coatings have been filled with Ti-rich oxides. However, no spallation was observed. The cross-sectional morphologies of $Ti_2AlC$ coating after oxidation at 750 °C in air for 200 h showed that the scale exhibited a four-layered microstructure, a thick $TiO_2$ and $Al_2O_3$ mix oxide outer layer, followed by a thin $\alpha$-$(Al,Cr)_2O_3$ sublayer, a thick $Fe_2O_3$ and $TiO_2$ mix oxide mid-layer and a thin $Al_2O_3$-rich oxide inner layer in sequence (Fig. 3c and d). No micropores or cracks were found at the $Al_2O_3$-rich oxide layer/substrate interface. Fig. 3e shows the corresponding EDX line scanned along the black line in Fig. 3d. EDX analysis indicated that the shape of the Cr curve agrees with that of Al curve. It is strongly confirmed that the sublayer is $\alpha$-$(Al,Cr)_2O_3$. An Al-rich layer was detected at the coating/substrate interface, while an Al-depleted zone formed next to the coating/substrate interface. Beneath the Al-depleted zone, large amounts of Al-rich phase precipitation could be observed.

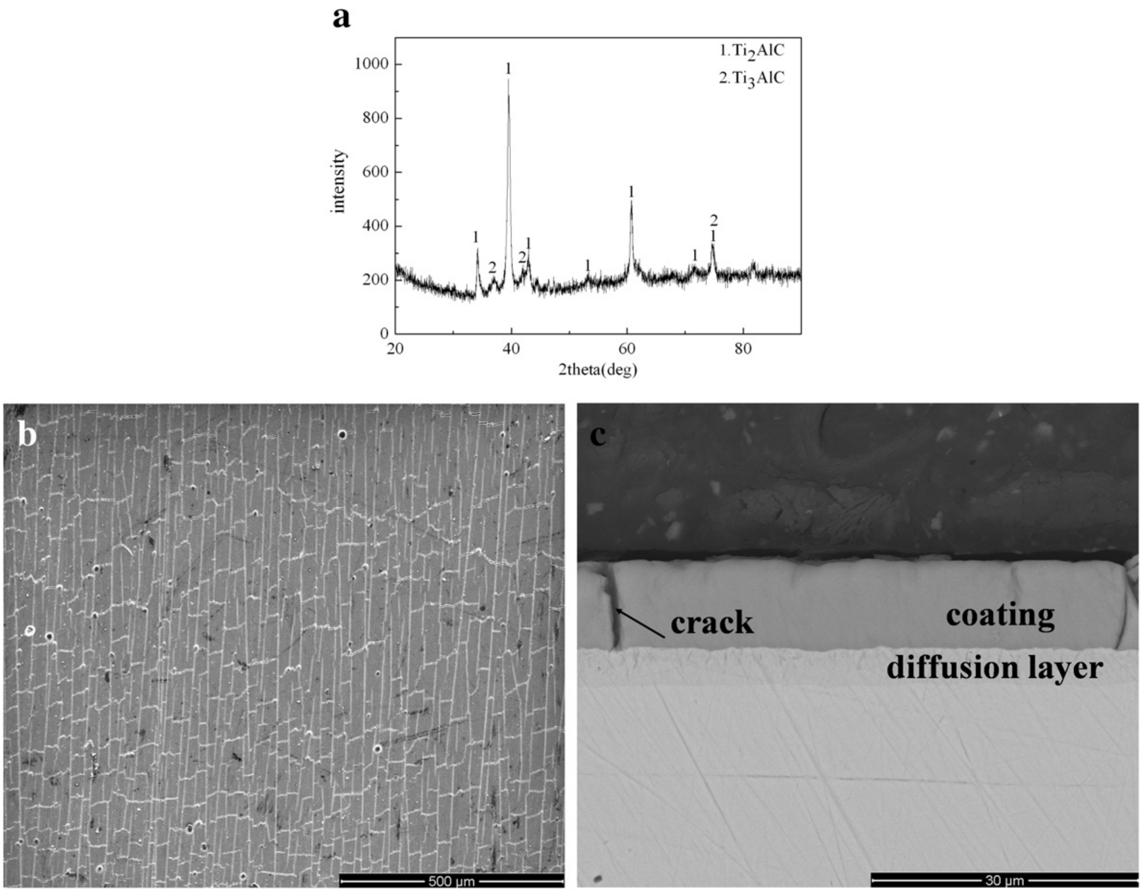

**Fig. 1.** XRD pattern (a), surface morphology (b) and cross-sectional morphologies (c) of the $Ti_2AlC$ coating.