



# Transforming the amorphous Ti-Al-C coatings to high-purity Ti<sub>2</sub>AlC MAX phase coatings by prolonged annealing at 550 °C

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## ABSTRACT

Ti<sub>2</sub>AlC MAX phases have been considered as the promising protective coating materials in nuclear energy and other harsh environments due to their unique properties. However, high preparation temperatures of Ti<sub>2</sub>AlC coatings, generally  $\geq 700$  °C, are the main barriers to their further application on temperature-sensitive substrates. Taking the concept of surface dynamics during prolonged annealing at low-temperatures, herein we reported a quite facile strategy to fabricate high-purity Ti<sub>2</sub>AlC coatings by transforming amorphous Ti-Al-C coatings at 550 °C. The transformation mechanisms of Ti<sub>2</sub>AlC MAX phase were also discussed in terms of their microstructural evolutions.

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## 1. Introduction

Ti<sub>2</sub>AlC belongs to a new group of ternary nanolaminated ceramics with the general formula M<sub>n+1</sub>AX<sub>n</sub> (n = 1–3), where M is an early transition metal, A is predominantly a IIIA or IVA element, and X is C and/or N [1]. After the pioneering works on Ti<sub>2</sub>AlC [2], interests were stimulated by the fact that Ti<sub>2</sub>AlC is the most stable phase, and has the lowest density of 4.11 g/cm<sup>3</sup> in Ti-Al-C family. Barsoom et al., [3] reported that Ti<sub>2</sub>AlC was relatively stable even under neutron irradiation conditions of up to 0.1 dpa at 695 °C, showing the strong candidate for high-temperature nuclear energy applications. In addition, Ti<sub>2</sub>AlC exhibited excellent oxidation resistance under both air and steam atmospheres at 1000–1300 °C by forming a continuous inner layer of  $\alpha$ -Al<sub>2</sub>O<sub>3</sub> [4]. Because of these superior properties, Ti<sub>2</sub>AlC has the potential to be a protective coating in nuclear energy and other harsh environments [5].

Generally, Ti<sub>2</sub>AlC coatings could be obtained by two typical methods within the physical vapor deposition (PVD) techniques: the epitaxial growth on single-crystal sapphire/SiC substrates or transition metal carbides seed layers by magnetron sputtering (MS), and transforming the as-deposited coatings with amorphous, multilayer, and nanocomposite structure by short time annealing (0.5–3 h) [6]. However, Ti<sub>2</sub>AlC coatings require relatively high

synthesis temperatures of 700–1000 °C due to its large unit cell (a = 3.04 Å; c = 13.6 Å) [7]. This makes Ti<sub>2</sub>AlC impossible for applications on temperature sensitive substrates, such as Zr cladding alloys, etc. Therefore, it is highly desirable to seek a facile method that can significantly reduce the preparation temperature of Ti<sub>2</sub>AlC coatings.

In our previous work [8], high-quality Ti<sub>2</sub>AlC coatings were fabricated by prolonged annealing of  $\alpha$ -TiC<sub>0.65</sub>/Al multilayer coatings at 550 °C. More importantly, it was demonstrated that surface dynamics played a key role in the formation of MAX phase during the long-time annealing treatment. However,  $\alpha$ -TiC<sub>0.65</sub>/Al multilayer structure was complicated, and it was difficult to achieve the large-area deposition with uniformity. Therefore, a facile method was further developed in this study, where high-quality Ti<sub>2</sub>AlC coatings were manipulated by annealing the pre-designed Ti-Al-C amorphous coatings at 550 °C for 100 h. Moreover, the formation mechanism of Ti<sub>2</sub>AlC MAX phase was also discussed.

## 2. Material and methods

Amorphous Ti-Al-C coatings were prepared on the Zirloy alloy substrates at room temperature by DCMS system. A rectangular Ti<sub>1.5</sub>Al alloy target (400 mm × 100 mm × 7 mm; purity: 99.5%) was applied as the sputtering source. Gas mixtures of Ar and CH<sub>4</sub> (flow rate ratio: CH<sub>4</sub>/Ar = 1/40), at a total pressure of 1.0 Pa, were introduced as reactive gas sources. The DC sputter current to the

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Ti<sub>1.5</sub>Al target was controlled at 4.5 A, and a DC negative bias voltage of  $-150$  V was used to the substrates. Substantially, the as-deposited Ti-Al-C coatings were subjected to 100 h annealing at  $550$  °C in a tube furnace under flowing Ar atmosphere. Meanwhile, 1 h annealing at  $750$  °C was also implemented for comparison.

Phase structural analysis was characterized by X-ray diffraction (XRD, Bruker D8 Advance) using Cu K $\alpha$  radiation. Cross-sectional transmission electron microscopy (XTEM), high-resolution TEM (HRTEM) and scanning transmission electron microscopy (STEM) analyses were carried out on a Talos F200X system. Specimens for TEM characterization were prepared using a focused ion beam (FIB) equipment (Auriga, Zeiss).

### 3. Results and discussion

Fig. 1 shows the TEM and EDS mapping results of as-deposited Ti-Al-C coatings. According to the HRTEM and EDS mapping results, no elemental enrichment and crystalline grains were present in the coatings. In the insets of Fig. 1a, the halo ring of the SAED patterns confirmed the amorphous nature of the pre-designed Ti-Al-C coatings, which was due to the low kinetic energy of the growth process. Meanwhile, some weak polycrystalline rings appeared in the SAED patterns, probably indicating the presence of some clusters or short-range ordering, but no any lattice fringes were visible in the HRTEM results (Fig. 1b). Therefore, the amorphous Ti-Al-C coatings with uniform elemental distribution were successfully prepared. This result was consistent with the previous reports, in which the coatings prepared by DC magnetron sputtering at low temperature were amorphous [9]. In addition, the thickness of the as-deposited coatings and the atomic ratio of Ti, Al and C were determined to be  $3.5$   $\mu\text{m}$  and 52:28:20, respectively.

Fig. 2 illustrates the XRD patterns of pre-designed amorphous Ti-Al-C coatings and those annealed at  $550$  °C for 100 h and  $750$  °C for 1 h. For the as-deposited coatings, a broad diffraction peak was observed at  $\sim 39^\circ$  and no other crystalline peaks could be found apart from several diffraction peaks of the substrate. This indicated that the as-deposited coatings were amorphous, which was in accordance with the TEM results. After 1 h annealing at  $750$  °C, the amorphous phase completely transformed to the Ti<sub>2</sub>AlC

MAX phase, as expected from the results reported by Garkas and Li [10,11], who found that Ti<sub>2</sub>AlC coatings could be obtained by annealing Ti-Al-C coatings at temperatures beyond  $750$  °C. The preferred diffraction planes of the MAX phase presented a full width at half-maximum (FWHM) of  $0.4^\circ$ , indicating good crystallinity of the coatings. On comparing with the characterization results obtained for coatings annealed at  $750$  °C, it is interesting to note that an approach was discovered here to reduce the synthesis temperature to  $550$  °C while obtaining high-quality Ti<sub>2</sub>AlC coatings that involves prolonging the annealing time to 100 h. No traces for the formation of intermetallic phases were observed. However, the crystallization transition from the non-MAX competing phases to the Ti<sub>2</sub>AlC MAX phase reportedly appeared in the range of  $600$ – $700$  °C [1,6], while the present  $550$  °C was the lowest synthesis temperature as reported so far [12–18] (see in Fig. 2b). Therefore, it was concluded that prolonging the annealing time could significantly reduce the synthesis temperature of the Ti<sub>2</sub>AlC MAX phase.

The cross-sectional HRTEM and corresponding FFT images are obtained to identify the formed Ti<sub>2</sub>AlC MAX phase after 100 h annealing at  $550$  °C. Fig. 3a displays a typical HRTEM image of Ti<sub>2</sub>AlC in the annealed coatings, recorded with the electron beam direction parallel to the [11-20] zone axis. Fig. 3b is the enlarged image of the marked area with “A” in Fig. 3a. The periodic stacking sequence along the (0 0 0 *l*) direction of the Ti<sub>2</sub>AlC phase is clearly visible, where the Ti-Ti-Al sequence (carbon atoms are not visible) with periodical contrasts is repeated and shows the nano-laminated hexagonal nature of the Ti<sub>2</sub>AlC phase. The distance of repetition was determined to be  $\sim 1.36$  nm, consistent with the *c* values calculated in other reports [18]. Fig. 3c shows the fast-Fourier transformed (FFT) image of area “A”, which can be indexed as [11-20].

As well known, diffusion-related processes, including crystallization and grain growth, are expected to be slow in materials with a complex structure, such as MAX phase and other superlattice-like phases. Besides, the presence of an incubation period before crystallization was reported during annealing of amorphous materials at low temperature, and the incubation time was very long [19]. However, no experimental data are currently available for determining the crystallization temperature of the

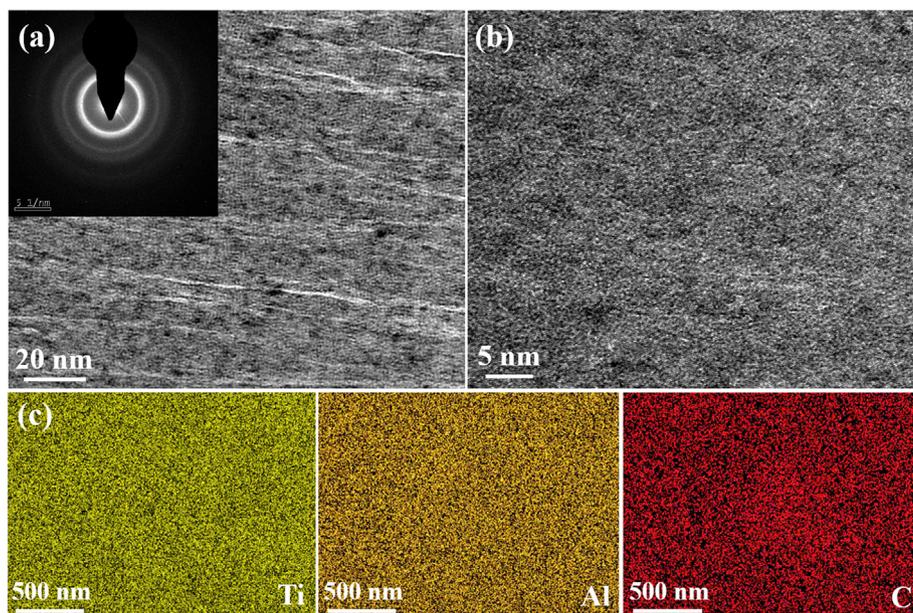


Fig. 1. TEM results of the as-deposited amorphous Ti-Al-C coatings, (a) bright-field image with the corresponding SAED pattern, (b) HRTEM image, (c) EDS mapping.

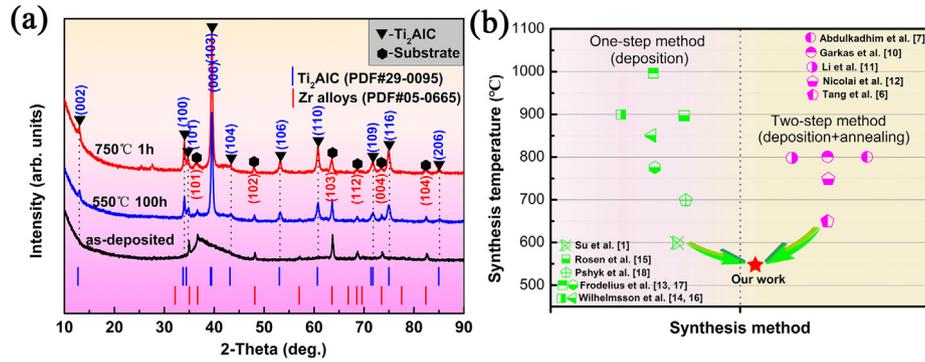


Fig. 2. (a) XRD spectra of the as-deposited and annealed Ti-Al-C coatings, (b) comparative results of the synthesis temperature of our work and the references.

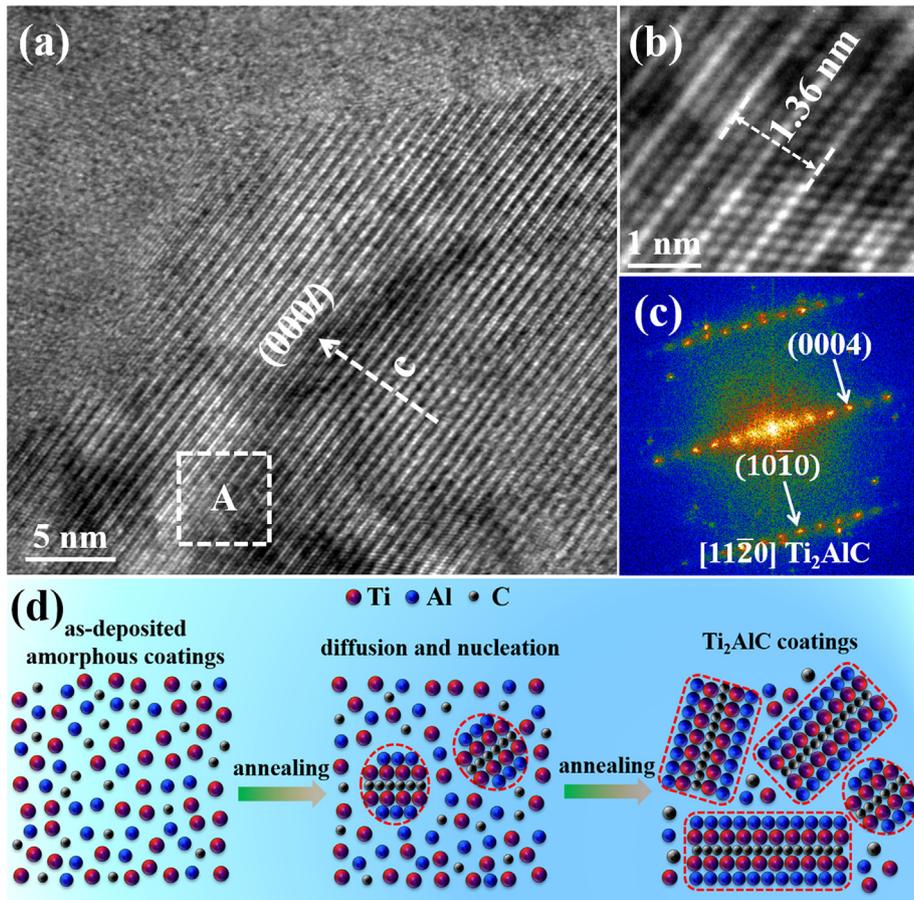


Fig. 3. TEM images of the Ti-Al-C coatings after 100 h annealing at 550 °C, (a) HRTEM image, (b) enlarged image of the square area marked in (a), and (c) corresponding FFT images, (d) formation mechanism of  $\text{Ti}_2\text{AlC}$  coatings in this work.

$\text{Ti}_2\text{AlC}$  MAX phase when the annealing time is long enough. Amorphous Ti-Al-C coatings with a homogenous composition were deposited by DCMS in this work. Taking these results as a reference, the amorphous Ti-Al-C coatings were annealed at 550 °C for 100 h. After 100 h annealing at 550 °C, the amorphous phases disappeared almost completely and  $\text{Ti}_2\text{AlC}$  MAX phase coatings with high-purity and high-crystallinity were obtained. This result is close to that obtained for coatings annealed at 750 °C for 1 h. Based on the XRD and TEM observations, it was concluded that the formation mechanisms of the  $\text{Ti}_2\text{AlC}$  MAX phase in coatings involved diffusion-controlled crystallization and growth processes, as presented in Fig. 3d.

#### 4. Conclusion

In summary, Ti-Al-C amorphous coatings were firstly prepared by the sputtering system, and then subjected to 100 h annealing at 550 °C and 1 h annealing at 750 °C, respectively. It was found that the  $\text{Ti}_2\text{AlC}$  coatings annealed at 550 °C for 100 h were comparable to those annealed at 750 °C. These results indicate that synthesis temperature of  $\text{Ti}_2\text{AlC}$  MAX phase coatings can be largely reduced by prolonging the annealing time of the as-deposited amorphous coatings, which provides a facile approach to prepare high-quality  $\text{Ti}_2\text{AlC}$  coatings at low temperature for wide applications.

## Declaration of Competing Interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper

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## Author contributions

P.L. Ke and A.Y. Wang conceived and supervised the project; Z.Y. Wang designed and carried out deposition and annealing experiments under the supervision of P.L. Ke and A.Y. Wang; W.T. Li and C.C. Wang carried out XRD and SEM measurements; H.C. Wu measured and analyzed the TEM results; Z.Y. Wang wrote the manuscript; All authors discussed the results and commented on the manuscript.

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