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# Microstructure evolution of $V_2AlC$ coating on Zr substrate under He irradiation and their mechanical behavior

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ABSTRACT

$V_2AlC$ coatings prepared by magnetron sputtering on a Zr substrates were irradiated with He ions to simulate the behavior of accident tolerant fuels (ATFs) in a reactor. TEM analysis and scratch test showed that the He bubbles preferentially nucleated along the substrate-coating interface and resulted in a loss of mechanical resistance of the $V_2AlC$ coating (i.e., reduced the adhesion of coating). This study provides a first insight into the irradiation-induced mechanical behavior of $V_2AlC$ coating on the Zr substrate and demonstrates the importance of improving the irradiation resistance of the cladding-coating system by optimizing the interfacial structure between the cladding and the coating materials for the development of ATFs.

The accident at the Fukushima Daiichi Nuclear Power Plant has led to a reappraisal of the traditional Zr-based alloy cladding system for current light water reactors (LWR). A new generation of fuel systems (i.e., accident tolerant fuels, ATF) are thus required to improve the accident tolerance under both the conditions of design-basis accident (DBA) and beyond design-basis accident (BDBA). Considering that over 400 nuclear reactors using the state-of-the-art $Zr\text{-}UO_2$ fuel system are in operation around the world and the lack of practical operating experience of alternative fuel claddings and fuel pellets, the modification of current Zr-based alloy claddings through surface modification by coating is a more reliable and cost-efficient way to improve the safety of ATF systems [1–3]. As part of promising strategies for ATFs, the coatings should withstand severe irradiation-induced displacement damage, possess good mechanical compatibility with the Zr-based alloys, and prevent hydrogen generation from oxidation reaction between the Zr-based alloys and high-temperature steam under DBA or BDBA events. Owning to the excellent irradiation resistant property [4,5] and the combined merits of high thermal conductivity, good ductility, excellent high-temperature oxidation resistance, and good corrosion resistance, MAX phases are proposed as candidate coating materials for ATFs [6–8].

However, before the cladding coating technology comes into practical use in nuclear reactors, many issues need to be addressed. Among them, the interfacial structure of the cladding-coating system is a crucial factor because it may act as sinks for irradiation-induced defects and may subsequently affect the mechanical resistance of the coating. Previous studies have suggested that interfaces between different lattice structures act as strong sinks for irradiation-induced defects, such as He element produced by $(n, \alpha)$ transmutation reactions, and vacancies and interstitials produced by the displacement of lattice atoms [9,10]. Once the irradiation-induced defects accumulate along the interfaces and form large clusters (e.g., bubbles and cavities), it will cause severe property degradation such as irradiation-induced embrittlement [11]. As in the case of cladding-coating systems, migration and aggregation behavior of irradiation-induced defects in the areas near the interfaces will probably have a great impact on the mechanical properties of the coating, especially the adhesion of the coating materials. However, the migration and aggregation behavior of the irradiation-induced defects near the cladding-coating interfaces and the mechanical evolution of the cladding-coating system under irradiation have not been reported till date. Therefore, the main aim of this study is to investigate the migration and aggregation behavior of He atoms (a massive and detrimental transmutation element) near the cladding-coating interface and its subsequent effects on the adhesion of the coating materials.

MAX phases such as $Ti_3AlC_2$, $Ti_3SiC_2$ have been extensively studied, and it has been proven that they have a good irradiation resistance

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[12–14]. However, synthesis of MAX film always requires high temperature [15]. $V_2AlC$ was chosen as the coating material in this study not only because of its excellent irradiation resistant property [16], but also the low temperature required to be synthesized [17]. Prior to deposition, the Zr substrates with dimensions of 5 mm × 10 mm × 1 mm were mechanically polished and ultrasonically cleaned for 10 min in acetone and ethanol, respectively, followed by preheating in the deposition chamber at 600 °C for 30 min. $V_2AlC$ coatings were prepared using a magnetron co-sputtering system equipped with a $V_{50}C_{50}$ target (99.9 at% in purity) and a $V_{50}Al_{50}$ target (99.99 at% in purity). The $V_{50}C_{50}$ target was controlled by DC power, the $V_{50}Al_{50}$ target was controlled by the DC power and simultaneously superposed radio frequency (power supply, Comdel CV-1000, 81 MHz) on the DC voltage. The deposition was carried out in argon gas atmosphere with a pressure of 0.7 Pa at 600 °C.

Ion irradiation is a very effective and popular way to simulate neutron-induced damage [18]. He atoms can be created by (n, α) reactions with energetic neutrons. We therefore performed He irradiation experiment to simulate migration and aggregation behavior of He atoms generated by (n, α) transmutations in reactors. Irradiation was carried out in a terminal chamber of the 320 kV multidiscipline research platform for highly charged ions at the Institute of Modern Physics (IMP), Lanzhou, China. The samples were irradiated with 500 keV He ions at a constant flux to doses of $2 \times 10^{16}$ ions/cm$^{-2}$ and $5 \times 10^{16}$ ions/cm$^{-2}$ at room temperature (corresponding to a maximum He concentration of 1.24% and 3.1% at a depth of ~1.3 μm from the surface, respectively, as calculated by the SRIM code in full cascade mode [19]), respectively. After irradiation, the samples were annealed at 450 °C for 5 h in a high vacuum chamber (~$10^{-4}$ Pa). Cross-section TEM samples were prepared by ion milling with 3.5 keV Ar ions at a low angle (<5°). TEM analysis was performed in a FEI-TF20 transmission electron microscope operating at 200 keV. Finally, scratch tests were performed on the pristine samples and the He irradiated samples by Revetest Scratch tester equipped with a 200 μm radius Rockwell-C diamond stylus to investigate the adhesive behavior of the $V_2AlC$ coating under different irradiation conditions. During the scratch test, a loading rate of 10 N/mm and a load range of 1–40 N were applied.

Before irradiation, the microstructure of the pristine sample was characterized by TEM in both plane view and cross-sectional view. Thickness of the coating was measured to be ~1.3 μm from the cross-sectional view of TEM (Fig. 1a). A columnar microstructure along the growth direction of the $V_2AlC$ film was evident from the cross-section TEM image at a low magnification, as shown in Fig. 1a. Furthermore, investigating the film structure at a higher magnification revealed that the $V_2AlC$ film was not fully crystallized and the grain size of the crystalline $V_2AlC$ particles along the film growth direction was not uniformly distributed. TEM image in Fig. 1b shows that the prominent feature near the substrate-coating interface is the fine-grained crystalline $V_2AlC$ particles mixed with amorphous $V_2AlC$, which affords plenty of boundaries between the crystalline $V_2AlC$ islands and the amorphous $V_2AlC$. The corresponding electron diffraction pattern (inset of Fig. 1b) reveals a relatively low degree of crystallinity. The sizes of the crystalline $V_2AlC$ particles gradually increased along the film growth direction and attained the highest value at the topmost layer of the coating. The areas near the topmost layer of the $V_2AlC$ film were predominantly composed of large grains with sizes in the range of 50–100 nm. The main feature of

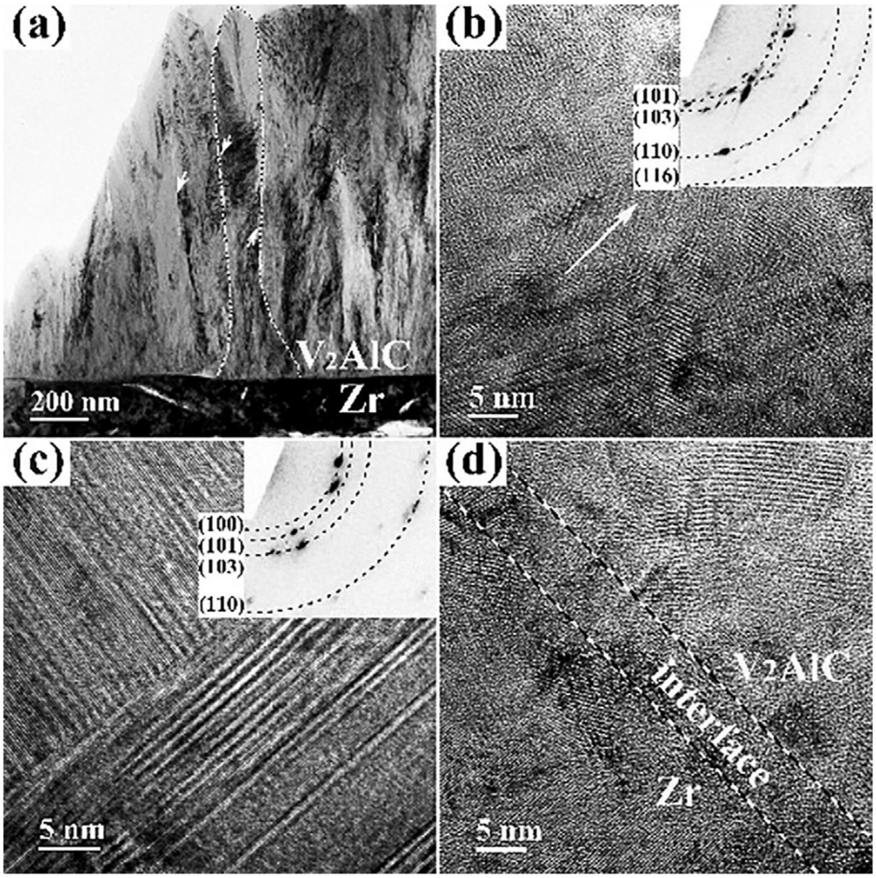

**Fig. 1.** TEM images of $V_2AlC$ coating. (a) Low magnification of cross-sectional view of Zr substrate and $V_2AlC$ coating. The dashed line shows the boundaries of a columnar structure and the arrows indicate the locations of three typical boundaries. (b) The HRTEM image of the $V_2AlC$ coating near the Zr substrate. The arrow shows the growth direction of the $V_2AlC$ coating. The corresponding electron diffraction pattern is inserted at the right up corner. (c) The HRTEM image of the microstructure of the $V_2AlC$ coating at the topmost area of the coating. The corresponding electron diffraction pattern is inserted at the right up corner. (d) HRTEM image recorded in the substrate-coating-interface region. The interface is located between the dashed lines.