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Microstructural evolution of epitaxial Ti_3AlC_2 film on sapphire under ion irradiation and nanoindentation-induced deformation

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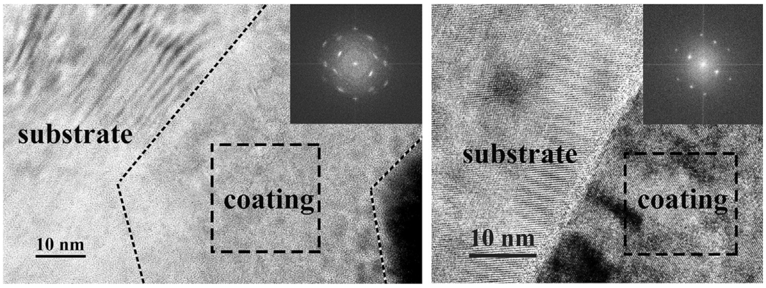
GRAPHICAL ABSTRACT



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ABSTRACT

Feasibility of Ti_3AlC_2 phase as the protective coatings of accident tolerant fuels (ATFs) was investigated by means of ions irradiation, nanoindentation and transmission electron microscopy. Au ions irradiation was carried out on thin Ti_3AlC_2 film to simulate the high displacement damage induced by the energetic particles in the nuclear reactors. Nanoindentation on the Ti_3AlC_2 film was followed subsequently as a source of external stress to simulate the high pressure applied on the cladding in nuclear reactor cores of pressurized water reactors (PWRs). TEM was used to characterize the microstructural evolution of Ti_3AlC_2 film after irradiation and nanoindentation. TEM analysis shows that Ti_3AlC_2 film remains pristine layered structure and no amorphization was detected after irradiation to ~14 dpa. The combined nanoindentation and TEM show that no rupture and exfoliation of the Au-irradiated Ti_3AlC_2 film occur even the extern stress and total elongation induced by nanoindentation reach to 16.6 GPa and ~5%, respectively. The above results show good irradiation resistance and good ductility as well as excellent adhesion of the Ti_3AlC_2 coating on the substrate after high dose irradiation and under high external stress. This indicates the good feasibility of Ti_3AlC_2 thin films as the coatings of ATF claddings.

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1. Introduction

The safe operation of nuclear reactors is a critical issue during the lifetime of nuclear power plants. Among the many factors affecting the safety of nuclear reactors, the safety of nuclear fuels cladding is of great importance. A new concept of accident tolerant fuels (ATFs) is therefore required to improve the safety of the nuclear reactors. As one of the proposals for the development of ATFs, advanced coatings on fuel claddings have received significant attention [1–3]. However, due to the lack of practical evaluation of fuel cladding coatings in nuclear reactors (e.g. PWRs), it is important to investigate the behavior and microstructure evolution of the protective coatings itself under irradiation conditions, especially when external stress is applied (to simulate the water pressure).

ATFs will serve under extreme conditions in nuclear reactors, such as intense radiation fluxes, high temperature and high stresses, aggressive corrosion by coolants, etc. [4]. Consequently, fuel cladding coatings are required to endure the harsh environment and exhibit a good performance at the same time. Among the many candidate materials for cladding coatings, $M_{n+1}AX_n$ phases have attracted increasing attention due to their excellent mechanical properties, thermal conductivities and excellent resistance to high-temperature oxidation and corrosion [5–9]. The $M_{n+1}AX_n$ phases belong to the family of layered ternary compounds, where M is an early transition metal, A is an A-group element and X is nitrogen or carbon, n = 1, 2, or 3. For example, in a typical MAX phase, Ti_3AlC_2, the Ti_3C_2 layers are interleaved with the Al layers. Recently, experimental evidences indicate that some of them exhibit good irradiation induced swelling resistance and high tolerance of radiation damage, such as Ti_3AlC_2 and Ti_3SiC_2 [10–13]. Theoretical investigation on the irradiation resistance of a series of $M_{n+1}AX_n$ phases by Xiao et al. [12] concluded that increasing the A/MX layer ratio in $M_{n+1}AX_n$ system (e.g. Al/TiC for Ti-Al-C $M_{n+1}AX_n$ system), decreasing the formation energy of M_A-A_M antisite pair in $M_{n+1}AX_n$ phases (e.g. Ti_{Al}-Al_{Ti} antisite pair for Ti-Al-C $M_{n+1}AX_n$ system) can improve the irradiation resistance. They also found a positive correlation between the irradiation tolerance of $M_{n+1}AX_n$ phases and the irradiation stability of the corresponding MX (e.g. TiC shows a better irradiation stability than CrC and the Ti-based M_2AlC ternaries shows a better irradiation tolerance than Cr-based M_2AlC ternaries, correspondingly). What is more, the weaker bonding of M-A and the weaker interaction of X-A in $M_{n+1}AX_n$ materials also promote annihilation of irradiation-induced defects and improve the irradiation resistance effectively [12]. This helps explain the excellent irradiation resistance of some members of the $M_{n+1}AX_n$ phase, such as Ti_3AlC_2, Ti_2AlC, Ti_4AlN_3, etc. [11,14–16]. For these reasons, Ti_3AlC_2 was chosen as the coating material in this study because of its prominent irradiation resistant property among the $M_{n+1}AX_n$ phases, excellent thermal conductivity, mechanical properties, etc. [10–14,17].

Although irradiation resistant properties of bulk MAX phases are frequently reported [11–17], the behavior of MAX phase in the form of thin films under irradiation conditions are rarely reported. Moreover, studies on the responses of irradiated Ti_3AlC_2 coatings to external stress are fewer. Among the few works on the related issues, Maier et al. investigated the feasibility of MAX phase as a candidate coating material for ATFs from the standpoint of wear resistance and oxidation resistance [18]. And the results turned out to be very promising. However, the irradiation resistant property of the coating is not mentioned. Therefore, to investigate the adhesive behavior and mechanical behavior of the Ti_3AlC_2 coatings and gain an understanding of microstructure evolution of the coating-cladding system under irradiation and under conditions when external stress is applied are important to understand the behavior of coating-cladding system in the environment of pressurized water reactors.

In this study, the Ti_3AlC_2 film was grown to a thickness of ~40 nm using magnetron sputter epitaxy from elemental Ti, Al and C sources on sapphire substrate. The detail synthesis process can be found in Ref. [19]. The Ti_3AlC_2-sapphire system was irradiated with Au ions to a high dose level to simulate the irradiation induced displacement damage in nuclear reactors. After the irradiation, nanoindentations were carried out to simulate the situation when external stress was applied. Focused ion beam (FIB) lift-out technique was used to prepare TEM samples at the location of nanoindentation. Transmission electron microscopy (TEM) was employed to investigate the microstructure evolution of the coating-substrate system after irradiation and nanoindentation.

Sapphire is chosen as the substrate in this study, while in the practical situation, Zr alloy substrates are more relevant. This is due to the reason that the sapphire substrate guarantees the formation of epitaxial single crystalline Ti_3AlC_2 phase while MAX films synthesized on Zr alloys is polycrystalline. The microstructure of MAX coating on Zr alloys evolves from the randomly oriented small grains to large grains along the growth direction [20]. Therefore, it is difficult to analyze the irradiation induced microstructure evolution and external stress induced phase transition due to the various microstructure features at different locations of the coating. However, up to now, to synthesize epitaxial single Ti_3AlC_2 film on Zr alloys remains a great challenge world widely. What is more, this study aims to investigate the irradiation resistant property and external stress induced deformation behavior of the MAX coating, the substrate effects are not included. Thus, the epitaxial single Ti_3AlC_2 phase coating on sapphire substrate is chosen to be studied.

2. Experimental

The irradiation experiment was carried out with a tandem 1.7 MV ion accelerator at Peking University. The Ti_3AlC_2-sapphire system was irradiated with 4-MeV Au ion at room temperature to a fluence of 5×10^{19} ions/m^2. The displacement damage caused by Au ions was calculated by the SRIM code with “Kinchin-Pease quick calculation” mode. The threshold energies were set to 20 eV for Al and 70 eV for O, respectively, for sapphire [21] and 25–28 eV for each element for Ti_3AlC_2 [11]. The calculated distribution of displacement damage as a function of penetration depth is shown

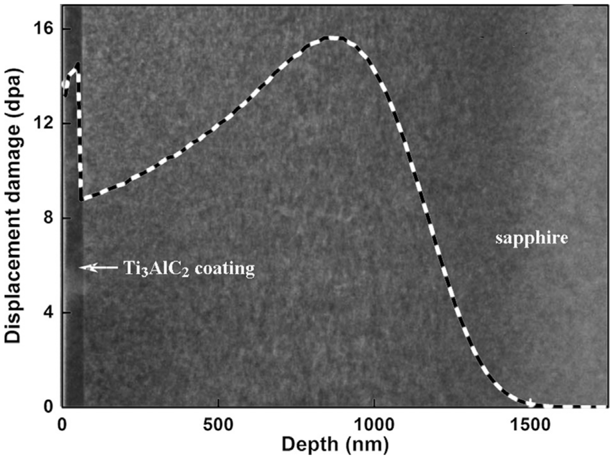

Fig. 1. The displacement damage as a function of depth for Ti_3AlC_2 coating and sapphire substrate system irradiated with 4-MeV Au ions to a dose of 5×10^{19} ions/m^2. The displacement damage curve represented by the dashed line is overlaid on top of a low-magnification bright-field TEM image. The Ti_3AlC_2 coating is visible as regions of darker contrast with width of 40 nm near surface indicated by the white arrow.