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Improved radiation damage tolerance of titanium nitride ceramics by introduction of vacancy defects

Jia-Xiang Xue[a], Guo-Jun Zhang[a,*], Li-Ping Guo[b], Hai-Bin Zhang[c], Xin-Gang Wang[a], Ji Zou[a], Shu-Ming Peng[c], Xing-Gui Long[c]

[a] *State Key Laboratory of High Performance Ceramics and Superfine Microstructures, Shanghai Institute of Ceramics, Shanghai 200050, China*
[b] *Accelerator Laboratory, School of Physics and Technology, Wuhan University, Wuhan 430072, China*
[c] *Institute of Nuclear Physics and Chemistry, China Academy of Engineering Physics, Mianyang 621900, China*

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Abstract

TiN and $TiN_{0.7}$ were irradiated using a 100 keV Ar-ion beam at 600 °C to target doses of 3×10^{17} ions cm^{-2}. SRIM estimation, GIXRD and fluorescence analysis have been performed to evaluate the effect of pre-existing vacancy defect on the radiation tolerance. The lattice parameter of TiN increased after irradiation due to interstitial atoms and vacancies in as-irradiated TiN. In contrary, the lattice parameter decreased for as-irradiated $TiN_{0.7}$, which indicates that the nitrogen atom vacancies in $TiN_{0.7}$ acted as sinks for displacement atoms generated by irradiation to limit interstitial atoms existing. The intensity of peaks in fluorescence spectrum of as-irradiated TiN was higher than that of as-irradiated $TiN_{0.7}$. That attributed to the presence of color centers formed by Frenkel defects in as-irradiated TiN. All of the results indicate that introducing vacancy defect in materials would offer capability to realize self-heal of irradiation damage.

Keywords: Radiation tolerance; Titanium nitride; Vacancy defect; Self-heal

1. Introduction

To reduce the toxicity of nuclear waste and enhance the safety of nuclear power plants, the concept of Generation-IV systems was proposed during the last few years.[1,2] Both the gas-cooled fast nuclear reactor (GFR) and the accelerator driven sub-critical system (ADS) project to transmute transuranium elements using inert matrix fuels (IMF) and to optimize the burn up of nuclear fuel. The IMFs work at very high temperature and fast neutron irradiation.[1–4] Titanium nitride (TiN) has been proposed as a promising candidate material for fast neutron systems due to its high melting temperature, low neutron absorption cross-section, high thermal conductivity at high temperature, extreme hardness, good corrosion resistance, and its phase stability.[5–7] In addition, its FCC lattice structure is isostructural with many actinide mononitrides (NaCl structure) to facilitates TiN to form a solid solution with actinide nitrides, such as PuN. Therefore, TiN is a promising ceramic matrix to prepare IMF to host minor actinitrides (MA: Np, Am, Cm) materials for transmutation.[8–12]

As is known, the nuclear materials would be used in extreme irradiation environment, where every atom in the structure of the material will be displaced hundreds of times, i.e. hundreds of dpa (displacement per atom). As results, interstitial atoms and vacancies will be generated as primary damage. Furthermore, these point defects can aggregate to form obstacles, which result in swelling, hardening and embrittlement of irradiated materials.[13] So, how to enhance radiation resistance is extremely important for all nuclear materials. Misra et al. prepared Cu–Nb nanolayered composites to enhance radiation damage tolerance via the interfaces acting as sinks for radiation-induced defects.[14] Bai et al. used three atomistic simulation methods to investigate defect-grain boundary interaction mechanisms in copper and proposed that grain boundaries have a surprising “loading-unloading” effect, which results in self-healing of the radiation-induced damage.[15] Based on the morphological stability of the Cu/W multilayered structure, Gao et al. also suggested

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[*] Corresponding author. Tel.: +86 21 52411080; fax: +86 21 52413122.
E-mail address: gjzhang@mail.sic.ac.cn (G.-J. Zhang).

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that interfacial structure and grain boundary can serve as sinks for radiation-induced defects.[16] Many researches focused on the effect of grain boundary on tolerance of irradiation damage.

For titanium nitride, the metal atoms occupy FCC lattice sites and the N atoms fill the octahedral interstices. The binary Ti-N equilibrium phase diagram (Fig. 1) shows a single phase within a wide composition ranging from $TiN_{0.6}$ to $TiN_{1.0}$ is thermodynamically stable.[17] In other words, the stable TiN_x ($0.6 < x < 1.0$) material with inherent nitrogen (N) vacancy defects can be prepared. The nitrogen vacancies in TiN_x may serve as sinks for the interstitial atoms produced by irradiation to recombine and annihilate the interstitial atoms to self-heal damage. The purpose of the present work is to seek another way, inherent vacancies, instead of interfaces acting as sinks for radiation-induced defects to enhance the tolerance of radiation damage. In this study, TiN and $TiN_{0.7}$ materials were fabricated, irradiated and studied the effect of vacancy defect on the radiation tolerance of TiN_{1-x}.

2. Experimental procedure

All properties, including density, hardness, and thermal conductivity, of the TiN_x δ phase with nitrogen deficient (Fig. 1) vary greatly with amount of nitrogen deficient. Therefore, the ratio of Ti to N must be exactly controlled during material preparation. The starting materials used in this study were commercial stoichiometric Titanium Nitride (TiN) powder (20 nm, purity 99.99%, nitrogen content 21.8 wt%, Hefei Kaier Nanopowder Co., Ltd.) and Titanium (Ti) powder (30 μm, purity 99.99%, Shaanxi Fengxiang Titanium Powder Co., Ltd.). Usually, the stoichiometry can be verified by lattice parameter, and lattice parameter can be obtained by XRD. For example, Wang et al. fabricated various ZrC_{1-x} and verified the value of x using XRD.[18] In this study, N/Ti ratio was 0.7 which was verified by raw materials and the lattice parameter. In order to express accurately, titanium nitride of nominal N/Ti ratio of 0.7 was named $TiN_{0.7}$. To prepare $TiN_{0.7}$, TiN powder and Ti powder were weighted in the stoichiometrical fractions for reaction (1) and mixed by planetary ball milling in acetone for 8 h in a polyethylene jar, using Si_3N_4 medium.

$$7TiN + 3Ti = 10TiN_{0.7} \tag{1}$$

The slurry was then dried by rotary evaporation at 60 °C and sieved through a 200-mesh screen to form granules, which were placed in a graphite die (diameter 22 mm) and then heated (10 °C min^{-1}, vacuum level < 10 Pa). When temperature reached to 1000 °C, a pressure of 30 MPa was applied and the furnace was backfilled with argon gas. After that, the samples were heated at a heating rate of 10 °C min^{-1} to the final temperatures, (1700 °C for TiN and 1500 °C for $TiN_{0.7}$) and held at the final temperature for 60 min for densification. The furnace was then cooled down naturally. The bulk densities of the hot pressed samples were measured using the Archimedes method. Disk specimens with about 3 mm diameter were cut from the hot-pressed samples. The disks were ground to thicknesses of ~30 μm, followed by polishing with a 30 nm diamond lapping film to produce a mirror finish. Nitride ceramics, especially titanium nitrides, exposed to air are easily contaminated by adsorbed oxygen and water vapor. In this work, we tried to minimize oxygen contamination and other contamination. Before irradiation, all of the disk with mirror surfaces were stored in a vacuum desiccator till irradiating. And after irradiation, the samples still were stored in vacuum desiccators till testing.

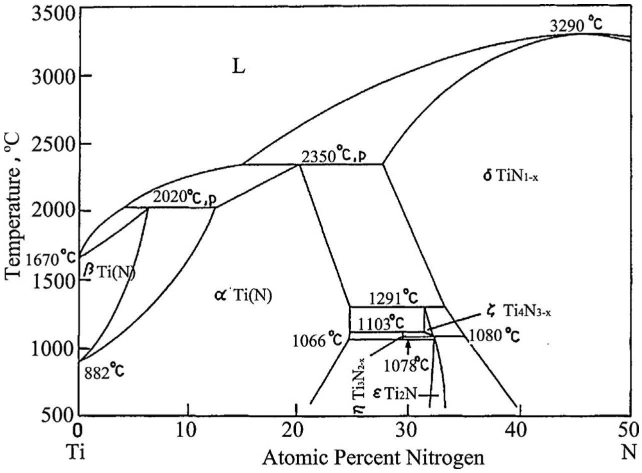

Fig. 1. The binary Ti-N equilibrium phase diagram.

Table 1
Irradiation conditions.

Materials	Irradiation source	Beam energy	Fluence	Temperature
TiN, $TiN_{0.7}$	Ar-ion beam	100 KeV	3E17/cm^2	600 °C

The interactions occurring in reactors are essentially elastic (or nuclear) collisions due to primary knock-on atoms from neutrons, and recoil atoms arising from alpha-decays and fission fragments. In order to simulate these interactions, low energy ion irradiations are usually performed. Thus, the polished faces of the dish samples were irradiated with a 100 keV Ar-ion beam at 600 °C to reach doses of 3×10^{17} ions cm^{-2}. In the gas-cooled fast nuclear reactor (GFR), the temperature of reactor core is 600~1200 °C.[1] However, in this study, the highest temperature of the irradiation equipment is only 600 °C, and this terminal temperature was selected in experiments. Temperature of the irradiated samples was monitored via three type-K thermocouples spot-welded to a steel plate and positioned adjacent to the samples. The irradiation parameters for the samples investigated in this study are listed in Table 1. The number of displacements per atoms (dpa) of the target samples after irradiation along of the depth within the irradiated material was calculated with SRIM 2008 in full cascade mode,[19] using Ar-ion energy of 100 keV and displacement energies of 25 and 28 eV for Ti and N, respectively.

The samples after irradiation were named i-TiN and i-$TiN_{0.7}$. The phase compositions and lattice parameters of the samples before and after irradiation were determined by XRD (D/Max 2550 V, Rigaku, Tokyo, Japan) using CuK$_{\alpha1}$ ($\lambda = 1.5405981$ Å) radiation. Since the irradiation only affects the very near surface, in order to analyze the structural modifications of the samples in irradiated, glancing incidence X-ray diffraction (GIXRD) was