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Diffusion and retention of helium in titanium carbide

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ABSTRACT

The knowledge of helium migration in TiC is an important issue due to its possible use as fuel coating in fission reactors and as first wall material coating in fusion reactors. Helium release measurements and diffusion coefficient calculations of helium in polycrystalline TiC have been carried out in the temperature range (1000–1600 °C) for the time period of 2 h. Polished bars of TiC were implanted with 3 MeV $^3He^+$ ions in normal incidence at a dose of 5×10^{20} at./m^2 at room temperature. Helium depth profile was measured at each step using the $^3He(d, p_0)^4He$ nuclear reaction by varying the incident deuteron energy from 900 to 1800 keV. Effective diffusion coefficients vary from 4.20×10^{-18} to 2.59×10^{-17} m^2 s^{-1} and activation energy values obtained are in the range 0.8–2.5 eV. Due to scarce availability of stoichiometric TiC, challenges in this study came from native vacancies present in the samples. The helium distribution and its release were affected by the presence of grain boundaries. He is considered to undergo two distinct populations into the sample and different values of diffusion coefficient have been determined for each population.

1. Introduction

Titanium carbide is a transition metal carbide also known as interstitial carbide due to the presence of carbon atoms on the interstitial positions (or octahedral voids) of the parent metal (titanium) lattice, thus giving TiC a pure fcc or NaCl structure.

Due to the complexity of chemical bonds, transition metal carbides have a unique set of properties. They exhibit the properties of refractory ceramics such as high hardness along with metallic properties such as good thermal and electrical conductivities [1].

Titanium carbide coatings are considered as potential protective layer in plasma-facing parts of nuclear fusion devices. This consideration was not only due to its high hardness and high thermal stability but also due to the presence of light element carbon in TiC. The collisions of the plasma with low mass carbon atoms help in less dissipation of heat and thus maintains high temperature inside the plasma [2].

TiC is also commonly considered as a good candidate material for ceramic fuel forms for gas cooled fast reactor. They consist of a fuel kernel made up of UC or UN which is coated with two shells (in form of a buffer and a coating). These two shells will be made up of titanium carbide. The role of TiC is to absorb the stresses produced in the micro fuel particles from differential thermal expansion, fission gas release, swelling and creep during reactor operation [3].

The use of titanium carbide under such high irradiation and high temperature conditions induces defects in the material. One of the major defect comes from helium accumulation due to emission of α-particles from (n, α) nuclear reaction and other sources. The accumulation of helium into the bulk material can lead to microscopic and macroscopic swelling that may result in cracking of the material. Therefore, it is important to obtain a fundamental understanding of helium behaviour in TiC.

Various experimental tools are available to study the mobility of He (^{3}He or ^{4}He) in wide range of materials (ranging from inorganic compounds to metals; from alloys to oxides, silicates and phosphates). These tools include thermal desorption spectrometry (TDS), nuclear reaction analysis (NRA), elastic recoil detection analysis (ERDA). We have chosen nuclear reaction analysis (NRA) to examine the helium (^{3}He) mobility in TiC after annealing at temperatures ranging from 1000–1600 °C and have extracted diffusion coefficient and activation energy values. This method to study helium (^{3}He) mobility has already been used by many authors in different materials for e.g., Costantini on britholite [4], Trocellier in different model crystalline ceramics [5], Gosset on britholite [6], Miro in SiC [7], Cherniak in rutile and titanite [8]. The helium diffusion coefficient values can be used to quantify the helium fraction that would be released and may provide additional understanding of diffusion behaviour.

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The study following the same procedure as [4–8] consisted of four steps:

- implantation of helium-3 in TiC samples and annealing of samples at various temperatures (1000–1600 °C) to induce diffusion;
- measurement of the helium profile in as-implanted and annealed samples by the resonant ^{3}He(d, p$_0$)^{4}He nuclear reaction;
- analysis of data obtained from NRA by SIMNRA code and AGEING code to derive helium migration parameters;
- comparison of the two methods of data analysis for better understanding of results.

In the following sections, we will describe the experimental procedure and the data processing methods. Then we will discuss the results and present our main conclusions obtained.

2. Experimental procedure

2.1. Sample preparation

The titanium carbide used in this study was synthesized at LTMEX Laboratory, CEA Saclay [9] by hot isostatic pressing (1600 °C, 1600 bars). The compositional information on major elements (Ti and C) was obtained by Rutherford backscattering spectrometry (RBS) and deuteron-induced nuclear reaction analysis (NRA). RBS was used to find the quantitative information on the heavy element (titanium) into the sample. NRA was used to find the quantitative information on light elements like carbon. The stoichiometric ratio of Ti/C obtained was (0.94 ± 0.02) that means that a large concentration of vacancies is present in the sample. Information on trace elements was obtained from scanning electron microscope (SEM); the presence of Fe (<wt. 400 ppm), W (<wt. 6500 ppm) in the form of small precipitates of 1 μm diameter was seen by SEM. The value of density observed was 99% (TiC density = 4.91 g/cm^3). The average grain size is around 8–10 μm with a very low density (<1%) of intragranular porosity.

The approximate size of each TiC sample was 2 cm × 0.5 cm × 0.5 cm approximately. These sample pieces were polished by 0.1 μm silicon carbide disc followed by a chemical polishing with colloidal silica to remove the surface defects. After polishing, the samples were cleaned ultrasonically with distilled water and ethanol.

2.2. Ion implantation and thermal annealing

The polished titanium carbide samples were mounted for ion implantation on a sample holder made up of stainless steel using carbon tape. The samples were homogeneously implanted with 3 MeV ^{3}He$^+$ ions at room temperature. The regular monitoring of temperature during implantation was done using thermocouples and temperature varied in the range of 28 ± 10 °C. The dose was about 5×10^{20} at/m^2 with an average dose rate of 4.75×10^{16} ions/m^2/s using the 3 MV Pelletron™ ÉPIMÉTHÉE at JANNUS Laboratory, CEA Saclay [10,11]. The values of the projected range (R_p = 6.78 μm) and lateral straggling (ΔR = 315 nm) were extracted from SRIM calculation [12]. For a ^{3}He implantation fluence of 5×10^{20} at/m^{-2}, the maximum ^{3}He concentration, located at R_p = 6.78 μm, is 1.8 at.%.

To avoid surface contamination during heating, the samples were sealed in small quartz tubes under low argon pressure. Then, these quartz tubes containing samples were heated at five different temperatures between 1000 °C and 1600 °C in PCI Laboratory at CSNSM Orsay. The time duration for annealing at each temperature was 2 h. Temperatures in furnaces were monitored with conventional thermocouples. These informations have been summarized in Table 1.

2.3. NRA analysis

To determine the helium depth distribution into the sample, nuclear reaction analysis (NRA) was done. It was carried out with the ^{3}He(d, p$_0$)^{4}He nuclear reaction, which has a wide resonance centered on E_d = 430 keV [13]. These measurements were performed on as-implanted and thermally annealed samples by using the 2.5 MV Van de Graaff accelerator Yvette at JANNUS Laboratory [10,11].

The deuteron milli-beam of 0.5–1 mm spot size with beam energy of 1300 keV was used in order to penetrate to a depth of 6.78 μm in the sample. The protons produced by various (d, p) and (d, α) reactions along with the backscattered deuterons were detected with a surface barrier detector located at an angle of 150° with respect to the incident beam. A 29 μm thin mylar ($C_{10}H_8O_4$) foil was placed in front of the 1500 μm thick surface barrier detector to stop all the backscattered deuterons. The solid angle subtended by the detector was 2.44 msr.

The detected spectrum (see Fig. 1a) contains several peaks from various deuteron-induced nuclear reactions e.g., ^{12}C(d, p$_0$)^{13}C, ^{3}He(d, p$_0$)^{4}He. The energy of each peak was checked by using the PYROLE code [14]. The proton signal from the ^{3}He(d, p$_0$)^{4}He

Table 1
Experimental configuration adopted for ^{3}He ion implantation and isothermal annealing.

	Ion implantation	Isothermal annealing
^{3}He energy (MeV)	3	
Average ion flux (m^{-2} s^{-1})	(4.75 ± 0.45) × 10^{16} atoms	
Average dose (m^{-2})	(5.00 ± 0.50) × 10^{20} atoms	
Projected range (μm)	6.78	
ΔRp (nm)	315	
Maximum ^{3}He concentration (%) at the Bragg peak	1.8 at.%	
Temperature (°C)		1000, 1100, 1400, 1500, 1600
Time duration (h)		2

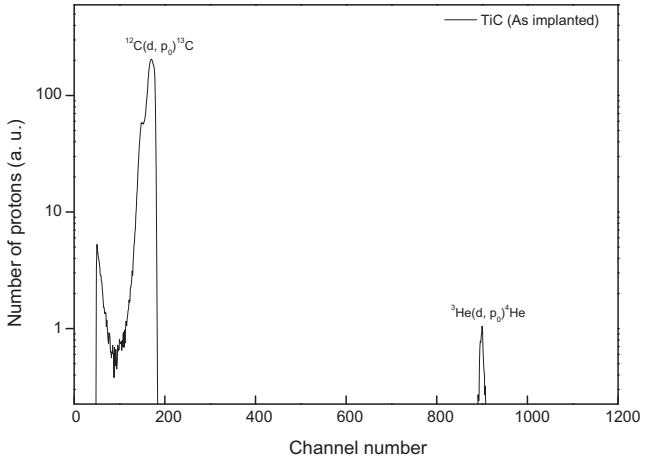

Fig. 1a. The raw proton energy spectrum obtained with 1.3 MeV deuteron energy for as-implanted TiC sample.