JOINT INSTITUTE FOR NUCLEAR RESEARCH

Flerov Laboratory for Nuclear Reactions

FINAL REPORT ON THE

SUMMER STUDENT PROGRAM

SWIFT HEAVY IONS IRRADIATION OF TITANIUM ZIRCONIUM NITRIDE LAYER ON A ZIRCONIUM ALLOY AT DIFFERENT TEMPERATURES FOR APPLICATION IN NUCLEAR FUEL CLADDING

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Overview

There is a fast growing demand for energy and concerns about climate change, so it is necessary for nuclear energy to play a greater role, in combination with other energy sources, to satisfy the future energy needs of mankind[13]. Given that energy generation currently accounts for 66% of the worldwide greenhouse gas emissions, nuclear energy is considered as an important resource in the management of atmospheric greenhouse gases, since nuclear power has very low carbon emissions[15]. The fission of the uranium and plutonium nuclei generates a number of radioactive fission products that could escape into the environment and be widely dispersed if a severe accident occurs. These radionuclides are prevented from escaping into the environment by the zirconium alloy tubes within which the uranium oxide fuel pellets are sealed in[3]. For safety, economics and reliability of the nuclear energy generation the issues that affects the cladding material (i.e. Zirconium alloy) such as waterside corrosion which is associated with hydrogen pick leading up to the formation of brittle hydride that limits the life time of the fuel cell must be resolved.

Zirconium alloy is the main physical barrier between the coolant system and the fuel cell[4]. Its principal role is to keep the radioactive products produced during fission process (which is the power source in the nuclear reactor) contained in the fuel pin[4]. The solution is to find a way to cover the zirconium alloy with a protective coating against this oxidation and hydrogen pick up. When oxidation takes place in the waterside of zirconium alloy the hydrogen is released to the coolant and the cladding material absorb some percentage of it which leads to formation of zirconium hydrides which are brittle in nature[8]. The use of ceramic coatings such as zirconium nitride, titanium nitride, chromium nitride etc. on zirconium alloys had been identified as good candidates to prevent the hydrogen absorption to the alloy. Since these ceramics will be subjected to the extreme nuclear conditions such as high pressure, high temperature, corrosive environments and radiation environment, it is essential to investigate the behaviour of these ceramics due to radiation damage caused by fission process where the nucleus of the ^{235}U is split into two smaller nuclei along with few neutrons, energy in the form of heat and fission fragments (figure 1). These fission fragments are around the mass 95 (Krypton) and 137 (Barium) and tends to interact strongly with the surroundings so it is important to test the properties of these ceramic layers against these fragments.

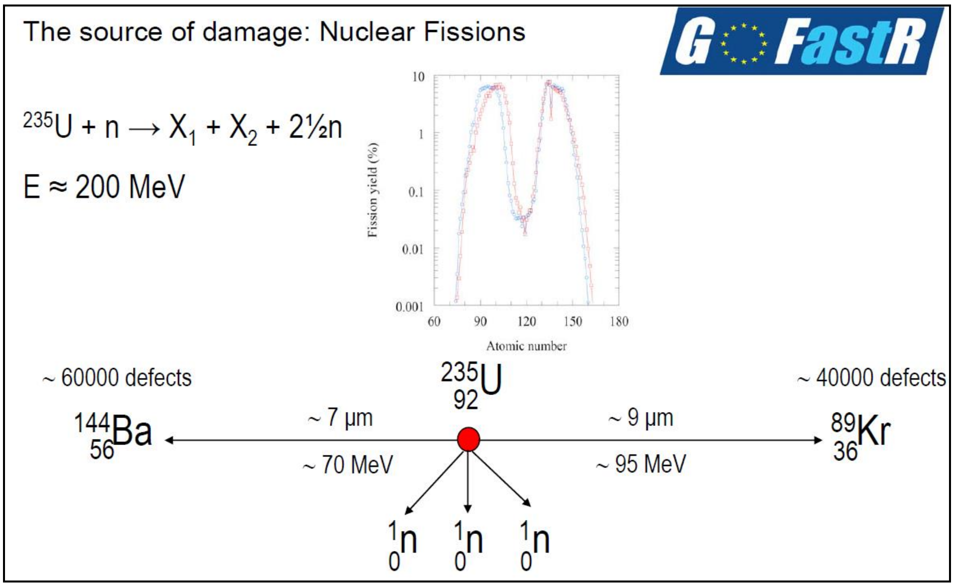

Figure 1: fission of ^{235}U producing ^{144}Ba and ^{89}Kr fission fragments.

Since the nuclear core is highly radioactive there is no way that the material exposed to such environment can be analysed. Swift Heavy Ions Irradiation with the same energy as fission fragments was used to simulate the damage that could be caused by fission fragments in the nuclear core of the power plant. In this study IC-100 with E ≈ 1.2 MeV/amu accelerator was used to accelerate Xe ions to the target material.

Problem statement

Zirconium alloy have been a cladding material for uranium oxide fuel for more than four decades in Boiling Water Reactors. This makes it one of the best cladding option over other materials such as stainless steel, beryllium and aluminium due to the combination of its small neutron capture cross section, reasonable corrosion resistance and structural integrity under normal operating conditions. Since there are concerns about the life time of the fuel, developments to extend the life time of the fuel had to be considered. These developments include the way to prevent the hydrogen produced during oxidation of the alloy from penetrating through the cladding material. Metal nitrides had been considered to be the best candidates for the preventing the hydrogen infiltration, but these nitrides will be exposed to the fission fragments. The studies done on these metal nitrides showed that they have high hardness, high thermal and chemical stability and this could improve the life time of the fuel in a reactor core.

Background

Protective coating

A protective coating is usually an artificially synthesized layer covering the surface of the bulk material, having a thickness of more than one micron. This concept aims to enhance the surface properties and/or improve the aesthetic appearance of a material and it was recognized officially in the 1950s. Coatings can be classified in terms of their compositions and function. From a compositional point of view coatings can be made of metals, organic compounds, cement mortars or enamels and from a functional point of view coatings can be made for decorative, protective, decorative-protective or technical purposes[2]. Generally, coatings reduce the corrosion rate of the protected materials by acting as the physical barrier to minimize the direct interaction between the corrosive species and the susceptible metallic materials. To guarantee coating performance, good coating adhesion, high mechanical resistance, low internal stress, high chemical stability and low permeability for corrosive components are important properties[12].

Nitride coating

Since improvement of the oxidation and hydrogen absorption resistance of the alloys only by adding alloying elements is not sufficient to meet the requirements for their practical applications, applying protective coatings is an effective and economical method to guarantee their resistance requirements of the actual components[14]. Nitride coatings are known to improve the oxidation resistance of refractory metals and alloys, which exhibit most of the requirements for high temperature applications.

Transition metal nitrides such as TiN, ZrN and HfN compounds have attracted attention for various applications due to their high hardness, high thermal and chemical stability and low electricity resistivity[10]. These hard coatings of metals nitrides are now commonly used in tribological applications and the first generation of these coated tools featured TiN as a hard coating and were applied interrupted cutting tools such as milling of steels and the superior performance of these TiN coated tools prompted their use in other machining applications such as turning, threading and boring as well as industries such as wear resistant or protective layer on the dies[7]. Other metal nitrides such as CrN, AlN etc. have also been considered.

Ternary nitride coatings

During the past 20 years the interest in transition metal nitride has grown and various nitrides have been considered for their attractiveness and useful properties. Among the fourth group transition metal nitrides, TiN have the most successful application in industry. However, ZrN has also attracted attention for its superior corrosion and better mechanical properties than the corresponding properties of the TiN[6].

In the last decade, ternary nitride A-B-N coatings where A and B are two different transition metals, have been shown to provide excellent mechanical and chemical properties and have been extensively investigated for applications as protective coatings. These coatings were reported to form a nanocomposite material or a solid solution depending on the chemical properties of the deposited elements/compounds and on process parameters. In both case, the mechanical and tribological properties of these materials were optimized to be far superior to those constituent binary nitrides[1]. In this study TiNZrN had been considered.

Radiation of materials

Irradiation of materials by high energy, heavy ion is referred to as swift heavy ions or SHI, results in highly excited lattice atoms with negligible contribution from elastic displacements and structural modifications of such a lattice brings out interesting changes in the materials. Depending on the interaction between the ions and the matter the changes that may form are point defects, electronic defects, track formation and void formation etc.

Interaction of ions with atoms of a matter

When ion beam is directed towards the matter, the ions interact with the matter exciting and ionizing the atoms of the matter ions tends to continuously change their direction and energy. Finally come to rest within the matter as implanted ions or leave the matter as transmitted or reflected ions. When these ions interact with the matter, atoms of the matter can be displaced creating point defects that may lead to extended defects and also these ions can also excite the atoms of the matter creating electronic defects. In the case of swift heavy ions irradiation which is the collective energy transfer the structure of the solid target matter can be changed by formation of tracks and extend to void formation. When the ions rest within that may change the local chemical composition of the matter. Interaction between ions and atoms happens in two ways Elastic interaction and Inelastic interaction. Elastic ion atom interaction, the configurations of the electrons of the ion and the target atom remain uncharged whereas, inelastic ion atom interaction is characterized by the changes of the configurations of the electrons of the ion and the target atom resulting mainly in an energy loss of the ion.

Experimental setup

TiNZrN layers on zirconium alloy were irradiated with Swift Heavy Ions with the same energy as fission fragments with the varying parameters that are shown in the table below

Table 1: Irradiation parameters of TiNZrN (i) and AlNSiN (ii)

Sample no	Temperature/°C	Fluence/ion/cm^2
1(i)	20°C	1.15×10^{15}
2(i)	500°C	2×10^{13}
3(i)	500°C	1×10^{14}
4(ii)	20°C	1.07×10^{15}

Since the boiling water reactor operates at approximately 360°C the samples were irradiated at room temperature and 500°C for the worst scenario case. figure 2 shows the image of the IC-100 accelerator with energy (E>1 MeV/amu) heavy ions beam which was used to accelerate the Xe $^{+25}$ ions.

Figure 2: Image of the IC-100 accelerator

Figure 3 is the screen shot of the IC-100 accelerator control system at the bottom of the screen shot there is a schematic showing its components. The beam direction is from left to right. The beam of ions is scanned using 2 scanning magnets namely vertical scanning magnets (VSM) and horizontal scanning magnets (HSM) as shown on the left side the schematics. These scanning systems are responsible for the homogeous ion beam distribution. On top of the schematic of the IC-100 there are 2 histograms which shows the beam distribution in horizotal direction and vertical direction.

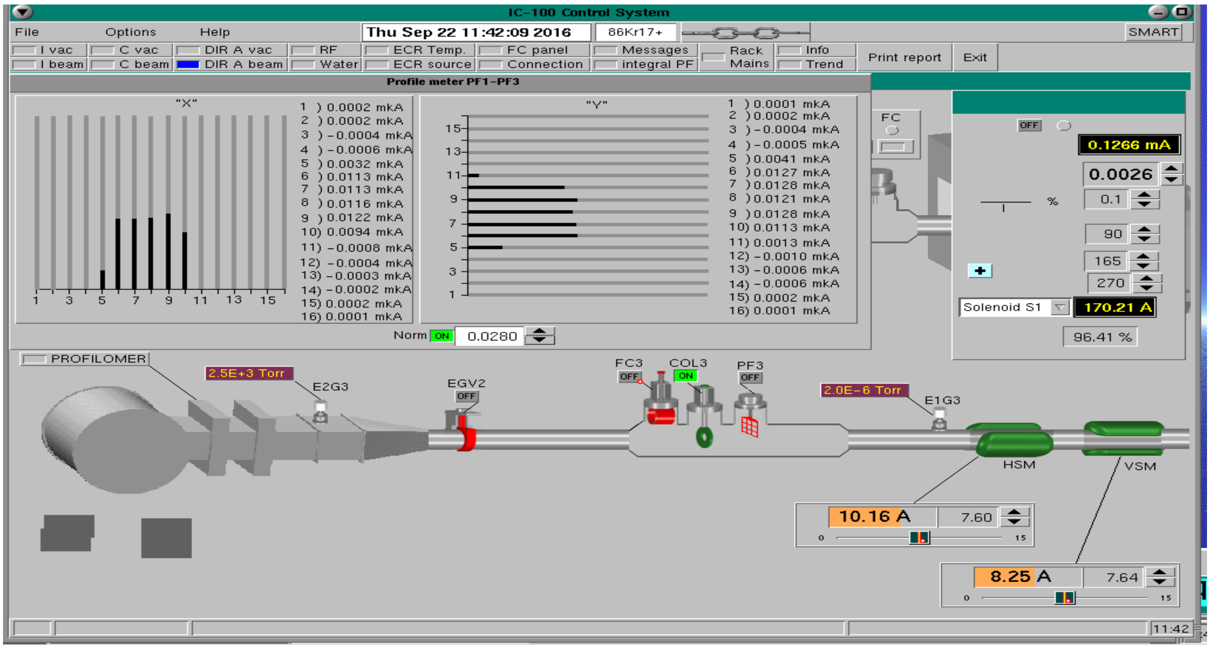

Figure 3: Screen shot of the schematic diagram of IC-100 and the controls to monitor the radiation.

Figure 4: Image of the target holders used in IC-100.

These sample holders operate at these temperatures:

(i) Operates between 80 K – 300 K

(ii) Operates between 300 K – 1000 K

The high temperature target holder uses water to cool down the samples after irradiation and to keep the temperature during irradiation constant.

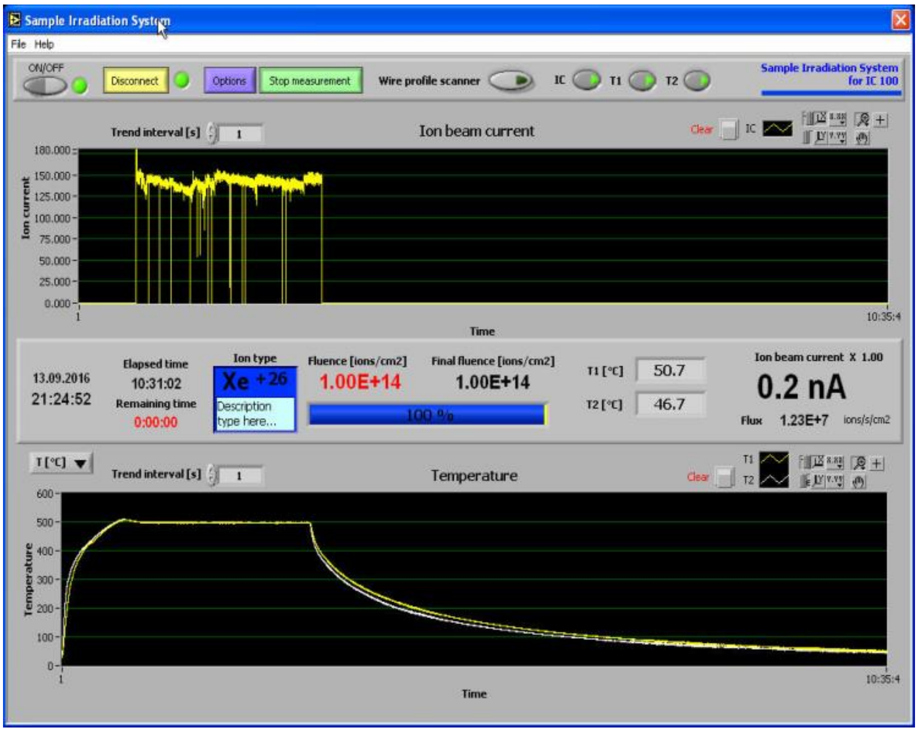

Figure 5: Screen shot of the ion beam parameters.

Before any work commences ion beam parameters are important and in this case the screen shows that the sample was irradiated at 500°C as shown by the temperature graph, and the ion beam current graph shows that between 0°C and 500°C no radiation took place and at 500°C the radiation occurred with fluence of 1.00E+14.

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