# Studies on the behaviour of titanium activation foils during long-term exposure at the JET tokamak

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## Abstract

Titanium activation foils for neutron studies were irradiated inside the JET tokamak vessel during the entire 15 months experimental campaign with deuterium fuelling. During the foil retrieval process, following the completion of the campaign, it was found that some of the titanium foils have been damaged and others totally or partly deteriorated. The analyses showed that the defects produced in some materials by cutting during the sample preparation promoted the degradation of the titanium crystal structure upon exposure to hot plasmas in JET. In some cases, the passive oxide layer on the surface of the Ti foils effectively protected the other foils from a transformation into a titanium hydride.

# Keywords

Titanium, titanium hydride, hydrogen embrittlement, titanium oxide film, activation method, JET

### 1. Introduction

Wall components of fusion power reactors, especially Plasma-Facing Components (PFCs), divertor and breeding blanket, will suffer irradiation by intense fluxes of 14.1 MeV neutrons from D-T fusion reactions in plasma. These fusion neutrons will induce nuclear transmutation reactions and atomic displacement cascades, leading to the generation of impurities, defects and material activation. Development of materials that can withstand high temperature and strong magnetic fields when exposed to intense radiation environment inside a fusion machine is one of the most challenging tasks faced by fusion research. Understanding the processes leading to the degradation and changes of material properties throughout the reactor operational life is a key issue to allow the engineering design of a fusion power plant [1]. Therefore, it is important to develop and improve capabilities for simulating radiation effects in materials, such as neutron-induced damage, activation and transmutation processes, via benchmarking and validation under realistic fusion conditions [2].

## 2. Experimental activities

## 2.1. Exposure conditions

Within the framework of technology projects at the Joint European Torus (JET) [3], a set of samples of ITER-relevant materials, used in the manufacturing of the main tokamak components, was irradiated [2, 4]. The measured neutron-induced activity is compared with the one predicted by neutronics and activation simulations performed with the Monte Carlo-based radiation transport code MCNP6.1 [5] and the FISPACT-II inventory code [6]. Before that, during the 2015-2016 D-D campaign at JET, a range of dosimetry foils were irradiated inside the tokamak vessel to characterize the nuclear environment at the relevant irradiation locations [7].

The selection of foils was based on the following criteria:

- high cross-section for neutron-induced reaction in isotopes occurring naturally in the activated materials,
- high abundance of a parent nuclide for which a neutron-induced reaction is observed,
- long half-life (>50 days) of a daughter radionuclide,
- high intensity of gamma-lines emitted by a radionuclide,
- high melting temperature of the a material (at least 610 ± 50°C),
- appropriate physical and chemical form of the material (ideally a pure metal sample).

Fulfilling the above mentioned criteria, the materials which were chosen for experiments were: Sc, Ti, Mn, Fe, Co, Ni, Y and Ta. All these materials have been already used during previous experimental campaigns at JET [8]. However, for the first time, the irradiations were performed outside the JET activation system, also referred to as the KN2 system - and they lasted for more than a single discharge. The foils were set in two, so-called Long-Term Irradiation Stations (LTIS) shown in Fig.1. These assemblies, manufactured from stainless steel, were covered with a tungsten shim and mounted inside the tokamak vessel in Octants 4 (hereinafter denoted as 4D) and 8 (8D) at the outboard midplane close to the poloidal limiters. Each of the thirty cavities within the two LTIS assemblies housed up to 4 foils (stacked one on top of the other). The total thickness of the various materials (foils) stacked within a cavity could not exceed 2 mm. The foils had a shape of discs: 18 mm in diameter and 0.1 to 1 mm in thickness. In total 176 foils, provided by CCFE (UK), ENEA (Italy), IFJ PAN (Poland) and NCSRD (Greece), were irradiated during 3682 plasma discharges (23.4 h of plasma operation) [7]. During this period, a neutron budget of 2.26 x  $10^{19}$  was recorded in measurement with the JET fission chambers diagnostic system (the KN1 system) [2].



Fig.1 An image of the Long Term Irradiation Station with activation foils and the layout of the foils' positions inside LTIS.

Following the end of the experimental campaign, the holders were removed from JET. The foils were retrieved from the assemblies in the Beryllium Handling Facility (BeHF) at JET, to assure that the samples were free of beryllium dust and radiological contamination assuring the safe shipment at laboratories involved in the project. The sample analysis consisting of gamma spectrometry measurements. During the foil retrieval process, it was found that some of the Ti foils had been

damaged, while several others were totally or partly deteriorated. Most of the pure Ti disk-shaped foils with a thickness of 0.5 mm turned into a dark grey powder. Data in Table 1 provide information about respective foils inside the assemblies and about the damage to some Ti specimens. Foil layers 1 - 4 at each cavity are denoted by F1 - F4 with F1 being closest to the plasma and F4 closest to the vacuum vessel's wall. The positions 1 - 30 are as in Fig.1. The deteriorated Ti foils were in positions #4 at 4D and 8D, #11 at 4D and #29 at 4D and 8D. These were all the ten foils provided by NCSRD and one foil from CCFE. Fig. 2 shows some pictures of one of the LTIS assembly and the foils which deteriorated during the campaign. Among nine Ti foils provided by IFJ, two foils, located in the position #11 8D and #7 4D, were slightly damaged at the edge (see Fig.3).

The question was; what is the reason for the different behaviour of the Ti foils provided by CCFE, IFJ, and NCSRD. Looking at Table 1 and Fig.1 one can see that there was no major difference at least related to their location within LTIS. However, only one of the CCFE foils was in the positions where it was directly facing the plasma. This foil "survived" the irradiation. All of the other CCFE Ti foils were always between the IFJ samples and the Fe sample, which was the closest to the wall. Without fail, the foil's location inside LTIS would not explain why all the NCSRD and one of the CCFE Ti foils had deteriorated. Also on differences in the samples' thickness (IFJ Ti foils were 2 times thicker than the CCFE and NCSRD foils) cannot explain the fate of individual specimens.

The main aim of this work was to identify the reason for the different behaviour of pure titanium samples and any possible differences between the samples used in the activation experiments performed at JET. The answer to the posed questions may help to define under which conditions titanium can be used in similar experiments in the future.

ID	FOIL 1 (F1) PLASMA FACING	FOIL 2 (F2)	FOIL 3 (F3)	FOIL 4 (F4) WALL FACING	
Position	Material/ Thickness (mm)/ Organisation				
1	Ta/ 0.5/ NCSRD	Ta/ 0.5/ NCSRD	Ta/ 0.5/ NCSRD	Fe/ 0.5/ CCFE	
2	Co/ 0.5/ NCSRD	Co/ 0.5/ NCSRD	Co/ 0.5/ CCFE	Fe/ 0.5/ CCFE	
3	Ni/ 0.5/ NCSRD	Ni/ 0.5/ NCSRD	Ni/ 0.5/ NCSRD	Fe/ 0.5/ CCFE	
4	Ti/ 0.5/ NCSRD deteriorated	Ti/ 0.5/ NCSRD deteriorated	Shim/ 0.5	Fe/ 0.5/ CCFE	
5	Co/ 0.5/ IFJ	Co/ 0.5/ IFJ	Co/ 0.5/ CCFE	Fe/ 0.5/ CCFE	
6	Ni/ 1/ IFJ		Ni/ 0.5/ CCFE	Fe/ 0.5/ CCFE	
7 4D	Ti/ 1/ IFJ slightly damaged		<b>Ti</b> / 0.5/ CCFE	Fe/ 0.5/ CCFE	
7 8D	Ti/ 1/ IFJ		Shim/ 2 x 0.1	Fe/ 0.5/ CCFE	
8	Shim/ 0.5	Shir	n/ 1	Fe/ 0.5/ CCFE	
9	Sc/ 0.5/ IFJ	Sc/ 0.5/ IFJ	Shim/ 0.5	Fe/ 0.5/ CCFE	
10	Ta/ 0.5/ CCFE	Ta/ 0.5/ CCFE	Ta/ 0.5/ CCFE	Fe/ 0.5/ CCFE	
11 4D	<b>Ti</b> / 1	/ IFJ	Ti/ 0.5/ CCFE heavily damaged	Fe/ 0.5/ CCFE	
11 8D	Ti/ 1/ IFJ slightly damaged		Shim/ 2 x 0.1	Fe/ 0.5/ CCFE	
12 4D	Shim/ 2 x 0.1 +1		Y x 3/ 3 x 0.1/ CCFE	Fe/ 0.5/ CCFE	
12 8 D	Shim x 3 + Y x 2/ CCFE	Shir	n/ 1	Fe/ 0.5/ CCFE	
13	Sc/ 0.5/ IFJ	Sc/ 0.5/ IFJ	Sc/ 0.5/ IFJ	Fe/ 0.5/ CCFE	
14	Co/ 0.1/ ENEA	Shim/ 1.4		Fe/ 0.5/ CCFE	
15 4D	<b>Ti/</b> 1/ IFJ		<b>Ti/</b> 0.5/ CCFE	Fe/ 0.5/ CCFE	
15 8D	Ni/ 1/ IFJ		Ni/ 0.5/ CCFE	Fe/ 0.5/ CCFE	
16 4D	Ni/ 1/ IFJ		Ni/ 0.5/ CCFE	Fe/ 0.5/ CCFE	
16 8D	<b>Ti/</b> 1	/ IFJ	Shim/ 0.4	Fe/ 0.5/ CCFE	
17	Ni/ 1	Ni/ 1/ IFJ		Fe/ 0.5/ CCFE	
18 4D	<b>Ti/</b> 1	/ IFJ	Shim/ 0.4	Fe/ 0.5/ CCFE	
18 8D	<b>Ti/</b> 0.5/ CCFE	<b>Ti/</b> 0.5/ CCFE	<b>Ti/</b> 0.5/ CCFE	Fe/ 0.5/ CCFE	
19	Co/ 0.1/ ENEA	Shim	/ 1.4	Fe/ 0.5/ CCFE	
20	Ni/ 1	/ IFJ	Ni/ 0.5/ CCFE	Fe/ 0.5/ CCFE	
21	<b>Ti/</b> 1	/ IFJ	Shim/ 0.4	Fe/ 0.5/ CCFE	
22	Co/ 0.5/ CCFE	Co/ 0.5/ CCFE	Co/ 0.5/ CCFE	Fe/ 0.5/ CCFE	
23	Fe/ 0.5/ CCFE	Shir	n/ 1	Fe/ 0.5/ CCFE	
24	Ta/ 0.5/ CCFE	Shir	n/ 1	Fe/ 0.5/ CCFE	
25	Ni/ 1	/ IFJ	Ni/ 0.5/CCFE	Fe/ 0.5/ CCFE	
26	Ta/ 0.5/ NCSRD	Ta/ 0.5/ NCSRD	Ta/ 0.5/ CCFE	Fe/ 0.5/ CCFE	
27	Co/ 0.5/ IFJ	Co/ 0.5/ IFJ	Co/ 0.5/ IFJ	Fe/ 0.5/ CCFE	
28	Ni/ 0.5/ NCSRD	Ni/ 0.5/ NCSRD	Shim/ 0.5	Fe/ 0.5/ CCFE	
29	Ti/ 0.5/ NCSRD deteriorated	Ti/ 0.5/ NCSRD deteriorated	Ti/ 0.5/ NCSRD deteriorated	Fe/ 0.5/ CCFE	
30	Co/ 0.5/ NCSRD	Co/ 0.5/ NCSRD	Co/ 0.5/ NCSRD	Fe/ 0.5/ CCFE	

Table 1. Activation foils positions in the LTIS assemblies in JET Octants 4 and 8 (referred to as 4D and 8D respectively). The lack of additional note "4D" or "8D", indicates a similar arrangement in both assemblies.



Fig.2. (right) LTIS assembly (back side) after removal from the JET tokamak; (left) appearance of the deteriorated Ti foils.



Fig.3. Images of the Ti foil (ID #11 8D) provided by IFJ PAN (held with tweezers). The foil was only slightly damaged at the edge. The foil unique ID (not visible here) and the name of the country which provided the foil was etched prior to irradiation.

### 2.2. Experimental analyses

To identify possible reasons for so different behaviour of the Ti foils, a comprehensive material analysis was performed by means of X-ray diffraction (XRD), proton induced X-ray emission (PIXE), time-of-flight elastic recoil detection analysis (ToF-ERDA), optical and scanning electron microscopy (SEM).

# 2.2.1 XRD

The structure and composition of the deteriorated Ti foils were analysed by XRD performed at NCSRD (Greece) using a Bruker D8 diffractometer equipped with a Copper K-alpha (Cu K $\alpha$ ) X-ray source, a parallel beam stemming from a Göbbel mirror and a scintillator detector. The high-angle XRD spectra of IFJ Ti foils were collected at IFJ PAN (Poland) with a X'PertPro PANalytical diffractometer with Cu K $\alpha$  X-ray source The diffracted signal was collected by a solid-state stripe X'Celerator detector operating in a scanning mode with an angular width of 2.122°. The XRD patterns were measured in a standard  $\theta$ -2 $\theta$  geometry for 2 $\theta$  angles ranging from 10° to 90°. The measuring step size was 0.00167°

and the total measurement time was 1 h 4 min (100 s of counting time per step). The spectra are discussed in section 3 below.

# 2.2.2 PIXE

The analysis of the IFJ Ti foils chemical composition was carried out using PIXE. In this method, a 2.2 MeV proton microbeam delivered from the linear, electrostatic Van de Graaff accelerator (HVEC K-3000) was used. The beam's diameter was equal to 24  $\mu$ m. The induced X-rays were registered by a semiconductor Si(Li) detector (Canberra) characterized by the energy resolution (FWHM) of 160 eV at 5.9 keV (Mn K $\alpha$  line). For each sample, the characteristic X-ray spectra have been acquired for 820 s. The quantitative determination of the element concentrations was possible as a result of the use of the Guelph PIXE software package [9].

# 2.2.3 ToF-ERDA

Quantitative depth profiles of light elements in the first few hundreds of nm beneath the surface of the IFJ damaged foil were measured at the Tandem Accelerator Laboratory (Uppsala University, Sweden) by ToF-ERDA. The sample was analysed using a 36 MeV  $^{127}I^{8+}$  ion beam knocking out the atoms from the target in single collision events that were analysed by ToF detectors and gas ionization chambers (GIC) [10]. The mass of each ion was calculated by combining the velocity and the energy of the ions knocked out from the surface (recoiled ions). Then the depth at which the interaction takes place was calculated from the energy lost by ions passing through the sample material.

# 2.2.4 Microscopy

The optical microscopic images of both sides of the IFJ Ti samples were obtained using a universal microscope Brunel SP400-BD in Tallinn University in Estonia. Moreover, the surface was analyzed by using scanning electron microscope Zeiss HR-FEG ULTRA 55.

# 2.4. Experimental conditions

Titanium, with its high melting point (1668°C) and high corrosion resistance in many aggressive environments [11] has been used in the activation experiments in the previous campaigns at the JET tokamak [8]. However, during those times the irradiation conditions were not the same as in the mounted LTIS assemblies during our experiments. In the former case, the foils confined in a polythene capsule were transported by a pneumatic system to one of the eight irradiation positions, e.g. the 3 Upper irradiation end (3U IE), located in the vacuum vessel wall in Octant 3. The foils in KN2 are not in the vessel vacuum, as they are inside a closed tube which is inserted inside a vertical port through a flange. Because of the high temperature near tokamak's first wall, the IE is additionally cooled by water [12]. During our experiments, the samples in the LTIS assemblies were not shielded by the polythene capsules and the assembly as a whole had no additional cooling system. Moreover, the activation foils were kept inside the vacuum vessel for the whole duration of the D-D campaign, thus exposed to hydrogen isotopes (H & D). Therefore, the hydrogen environment and high temperature could cause the transformation of titanium into a titanium dihydride (TiH<sub>2</sub>). According to work by Baymakov and Lebedev [13], at the temperature of ca. 330°C (603.15 K) titanium rapidly absorbs hydrogen due to the increase of hydrogen solubility within the titanium lattice. This, on the other hand, leads to the formation of hydride particles through the entire thickness of the metal, which results in complete embrittlement of a Ti sample[14].

# 3. Results and discussion

The XR diffractograms for three NCSRD foils and a reference diffractogram of a non-irradiated Ti foil are shown in Fig. 4. The measurements of the deteriorated Ti foils #4 8D, #29 4D and #29 8D confirmed the formation of  $TiH_2$ .

However, not all Ti has been transformed into  $TiH_2$ . Due to the non-homogeneous powder thickness of the flakes, the quantification of the amount of Ti transformed into  $TiH_2$ , was not performed since it might have led to erroneous results.



Fig. 4. XRD patterns of the deteriorated NCSRD Ti foils irradiated in LTIS at positions #4 8D, #29 4D and #29 8D. As a reference, a signal from the non-irradiated sample is shown. Al Bragg peaks are due to the aluminium stub on top of which the damaged Ti flakes were stuck.

Tracing back details of the baking sequence of the JET vessel during the 2015-2016 D-D campaign (Fig.5), a hypothesis can be formulated that the formation of TiH<sub>2</sub> could occur even before the irradiation period began. Baking of a vacuum vessel is a standard procedure accompanying not only the pump-down after vessel venting but the elevated wall temperature is maintained during the entire experimental campaign. The vessel is heated to a certain temperature to desorb impurities, to achieve a better vacuum during the experiment. In general, the process consists of a few stages. The first one is to pump down the vessel to rough vacuum and bake it at about 200 °C with the water-cooled elements drained to remove impurities. Once the pressure starts to drop, and so does the temperature, the vessel is again heated up to 80 °C and water is pumped into the water cooling system. The vessel is then baked to 320 °C for a couple of cycles, whereas, during plasma operations, the vessel is usually kept at around 200 °C. Due to the diverse problems on JET during the 2015-16 campaign, there were multiple bake-out throughout the operation. There is also the possibility that the desorption of hydrogen from the JET walls during the bake-out phase could lead to a reaction with Ti and thus to the formation of TiH<sub>2</sub>.



Fig.5. The baking scenario of the JET vacuum vessel during the 2015-2016 D-D campaign.

However, not all Ti foils turned into a grey powder (TiH<sub>2</sub>). For all the surviving Ti samples, the XRD measurements revealed only a set of intense reflections from pure titanium with no diffraction peaks for TiH<sub>2</sub>. The XRD patterns, collected for the irradiated (located at LTIS positions #11 4D, #11 8D and #16 8D) and non-irradiated IFJ Ti samples are presented in Fig. 7. The background and the input from Cu K $\alpha$ 2 radiation were subtracted so that only the signal from the K $\alpha$ 1 line would remain. The intensities of the reflections vary slightly from sample to sample (see Fig.6). The location of the observed reflections and their intensity does not change significantly from sample to sample. It was hard to match these peak profiles with any specific element or compound at this stage of research. Since non-stoichiometric compounds, which composition varies continuously do not give rise to X-ray diffraction peaks, the presence of some phases (or one phase) of a non-stoichiometric titanium oxide could not have been completely eliminated.



Fig. 6. XRD patterns of IFJ Ti samples irradiated in LTIS at positions #11 4D, #11 8D and #16 8D. As a reference, a signal from the non-irradiated sample is shown.

Titanium is a very reactive metal and has a strong chemical affinity towards oxygen. Thus, it oxidizes immediately upon exposure to air, even at room temperature. A clean titanium surface exposed to air immediately forms an oxide layer 1.2 to 1.6 nm thick. This thin oxide film is relatively impervious and highly adherent. It continues to grow slowly with time. So, e.g. after 70 days it can reach a thickness of about 5 nm, after 545 days 8 to 9 nm and even 25 nm in 4 years [11, 14, 15, 16]. It all depends on the surface and manufacturing conditions. This behaviour leads to a natural passivity that provides excellent corrosion resistance.

What we know from the available literature [14], is that the presence of even thin oxide film on a surface of titanium sharply lowers the absorption rate of hydrogen. Only at temperatures exceeding 500°C, the oxidation resistance of titanium decreases rapidly and, the metal becomes highly susceptible to embrittlement not only by hydrogen but also by oxygen and nitrogen, all of which dissolve interstitially in titanium [14]. Considering the information gathered so far, we can assume that the difference in the thickness of the oxide layer between the samples, as well as some damages introduced to the surface could have contributed to the different behaviour of the foils in the harsh environment inside the tokamak's vessel.

When analysing the basic distinctions between the samples provided by different institutions participating in the project, the information on samples' purity, the compositions of impurities, as well as the manufacturing processes, were compared. Both the NCSRD and CCFE foils had a purity of approx. 99.6+%. They were purchased from Goodfellow and Advent Research Materials Ltd respectively, in the form of a sheet (flat material with a thickness of 0.5 mm). The NSCRD foils were then laser cut from the sheet by a local company in Greece. Cutting had left burs on the sides which were removed with an angle grinder when etching<sup>1</sup> at CCFE. The technique used by a local English engineering company to cut the CCFE discs out of the titanium sheet was by punching. Both Goodfellow and Advent Research Material's temper (Table 3). Unfortunately, no such information was available for the IFJ Ti samples. Therefore, in the first instance, the Proton Induced X-ray Emission (PIXE) analysis was performed to confirm the samples' purity. It was determined to be at the same level as the NCSRD and CCFE foils. The impurities identified on IFJ Ti samples by the X-ray spectrum were Fe, Ni and Ca. Moreover, based on a microscopic image (see Fig.11), it was proved that the IFJ samples were cut mechanically.

<sup>&</sup>lt;sup>1</sup>All foils were etched using a vibro-etcher before loading into the LTIS holder.

	NCSRD	CCFE	IFJ
Supplier:	Goodfellow	Advent Research	N/A
		Materials Ltd	
Thickness :	0.5 mm	0.5 mm	1 mm
Purity :	99.6+%	99.6+%	99.6+% <sup>2</sup>
Temper :	Annealed	Annealed	N/A
Typical Analysis	Al 300, Ca 20, Cr 50, Cu	C 200, N 120, H 50, Fe	Fe, Ni, Ca <sup>3</sup>
(ppm) :	5, Fe 1500, Mn 100, Ni	1500 <i>,</i> O 1500.	
	50, Si 300, Sn 200, C		
	300, H 60, N 150, O		
	2000.		
Remarks:	- laser cut out of a	<ul> <li>punch cut from a</li> </ul>	<ul> <li>purchased as discs</li> </ul>
	sheet had left burrs	sheet	probably from
	on the sides which		Goodfellow but no
	were removed with		documentation
	an angle grinder		remained
	when etching		<ul> <li>mechanically cut<sup>4</sup></li> </ul>

Table 3. Information about analysed Ti samples.

Since the PIXE method is not sensitive to light elements, additional ToF-ERDA measurements were performed to determine the surface composition of the damaged IFJ Ti activation sample #11 8D. ERDA is the only method for quantitative depth profiling of the surface layer up to 600-700 nm. Depth profiles of several detected elements are presented in Fig. 7 and 8, showing respectively hydrogen isotopes and heavier species in the titanium substrates. The primary depth scale is given as the total amount of atoms/cm<sup>2</sup>, which is a natural depth scale for ion beam analysis as it cannot measure depth, but rather how many atoms the ions have passed while travelling through the sample. This depth scale can be converted to nm if the density of atoms is either known or assumed. In the top scale, the conversion was done assuming the density of Ti (4.5 g/cm<sup>3</sup>) to help interpret the depth scale. The use of at/cm<sup>2</sup> as a depth scale also means that a relative concentration in (at. %) for a given depth becomes natural. It does, however, mean that the depth scale in nm becomes unreliable if there are any fluctuations in density or even in the concentration of the elements. The total content of hydrogen isotopes (Fig. 7) in the analysed surface layer does not exceed 2 %. As shown in Fig. 8, oxygen is the dominant impurity species on the surface. The concentration ratio Ti:O approaches 1. The content of other elements such as carbon, nitrogen and metals does not exceed 2 atomic %. Iron stands here for steel and Inconel components eroded by plasma from the JET wall and the foil holder itself. This surface composition with mixed light and heavier species is typical for surfaces exposed to plasma in the scrape-off layer. Only the high oxygen content strongly indicates the titanium oxidation upon the foil exposure to air. Other species, e.g. F, Na, occurring only in the very surface in minute quantities (0.1-0.8%) are not discussed here because their presence is related rather to sample handling in one of laboratories than to exposure in JET.

<sup>&</sup>lt;sup>2</sup> Information obtained from the PIXE analysis

<sup>&</sup>lt;sup>3</sup> Information obtained during X-ray spectrum analysis, exact proportions not known



Fig. 7. ToF-ERDA depth profile of IFJ Ti sample damaged during the irradiations at the JET tokamak. Only the hydrogen isotopes and Ti are shown.



Fig. 8. ToF-ERDA depth profile of IFJ Ti sample #11 8D damaged during the irradiations at the JET tokamak. Only the elements with a mass number of 12 (C), 14 (N), 16 (O), 48 (Ti) and Fe(56) are shown.

To obtain more information about the IFJ Ti foils, the samples were analyzed further by optical microscope. During those measurements, the non-irradiated IFJ Ti foil served as a control.

As none of the samples had been mirror-polished, grains were protruding and well visible on the rough surface. When the micrographs were taken and the samples analyzed, not many differences were observable neither on the samples nor their different sides. In Figure 9 is shown a selection of images with equal enlargements of two different samples with various characteristics that are apparent on all of the samples. In panel A of Fig. 9. is an image of grains in the sample irradiated in LTIS at position #7 4D. The picture has been captured near the damaged area. Panel B shows the control (non-irradiated) sample.

In general, the grain sizes do not differ from sample to sample, but on each of the samples, there are regions where the grain sizes either differ or the distinction between grains is difficult. This is apparent for example, in panel A of Fig. 9. in the vicinity of the etchings – the heating while etching has interfered with the structure of the material, apparently inducing recrystallization of the grained structure.



Fig. 9. In general, all of the samples look the same on both sides. A) sample #7 4D near the damaged section – damage is visible on the upper right corner; B) the surface of the control (non-irradiated) IFJ sample.

Figure 10 shows close-up of the damaged edge of sample ID #7 4D. The immediate origin of the damage is unknown. As we were not to use invasive methods that might damage the sample, we could not either confirm or contradict the possibility of the sample being damaged due to the formation of Titanium(II)Hydride.

The damaged area (in Fig. 10 panel A) is discoloured compared to the rest of the sample to the naked eye. The samples' microscopic analysis indicates that the dark substance on the sample's damaged area has broken off in small fragments, layer after layer, resulting in the damages to have a flake-like structure. Hydrogen is known to induce embrittlement in Ti and the spalling is known to occur due to the embrittlement; it is possible that the damages have occurred due to the formation of TiH<sub>2</sub>.



Fig. 10. The damaged area of sample #7 4D: A) erosion; B) close-up of the flake-like structure of the damage.

While analysing the damages, also the side of the sample #7 4D was investigated. The even and parallel straight lines in Fig. 11 suggest the IFJ samples also have been cut out of a sheet, most likely without heating the material but rather by mechanical cutting, perhaps punch-cutting.



Fig. 11. The edge of IFJ sample #7 4D indicates cutting.

SEM imaging was conducted for the selected samples, to obtain more information on the materials. Among them were: one irradiated IFJ sample #7 4D; two non-irradiated NCSRD samples and two CCFE samples irradiated in the LTIS positions #18 8D (F1 and F2). As the materials' production method and the samples' surface treatment had not been provided, at first a comparison of the representative areas of the surfaces was conducted (see Fig. 12). The results indicate that the materials have been with different surface structures from the very beginning and the irradiation has not altered them too much. It also suggests the difference in the initial grain structure from the samples manufacturing process such as e.g. rolling.



Fig. 12. Comparison of the SEM analysis of the representative surfaces of different samples, with equal magnifications: A) an irradiated IFJ sample, #7 4D; B) a non-irradiated NCSRD sample (referred to as GC#1); C) an irradiated CCFE sample, #18 8D (F1).

The non-irradiated NCSRD samples that had been "cut out and deburred" before the SEM analysis are the same type of material that all got deteriorated within JET. The analysis of the edge of one of these samples (referred to as GC#2) indicated that laser cutting caused the formation of a burr, both on the cut foil and also on the Ti sheet, where it was cut from. Interestingly the samples should not have had a burr during the SEM imaging, as the burrs were supposedly removed. Nevertheless, the burr on the foil is visible on the left-hand side in Fig. 13. Even with this magnification, the cut's uneven edge is visible and the possibility of the existence of the micro-cracks is present. These kinds of burrs are not necessarily well-visible to the naked eye.



Fig. 13. Burr on the laser cut NCSRD Ti foil GC#2.

The CCFE samples' random characteristic surfaces look almost identical. Interestingly on the sample #18 8D F1 there was unexpected damage on the sample's surface, quite far from the sample's edge. Fig. 14. shows the damaged area on the sample and also magnifications of the damaged area. The damaged area is not well visible to the naked eye, but the SEM images indicate an area where strong cracking and erosion of material have taken place. Slight damages were also observed in IFJ plasma facing foils (F1 - when considering their sequence of distribution within the particular LTIS cavities, thus such damage is expected). What has induced such damages, remains not fully understood.



Fig. 14. Sample #18 8D F1 with a damage on the sample's surface: A) location of the damaged area, a combination of two photographs; B) magnification of the damaged area; C) a close up of the left-hand side of the panel B.

For comparison also Fig.15 has been compiled, of the different SEM images of the edges of the samples that have not yet been presented. The edge of foil #18 8D F1, on panel A, seems somewhat damaged, with a cellular structure. The least deteriorated of the three, is foil #18 8D F2, on panel B, with a nice clean edge. The strongly deteriorated sample #11 4D, on panel C, has an edge where flaking is apparent and seems that there has already been some erosion taking place, as well.



Fig.15. Some edges of the samples and their micro-structures: A) The edge of sample #18 8D F1, with it's cellular surface structures; B) clean edge of sample #18 8D F2; C) micro-structures and cracking on the sample #11 4D.

Based on all of the results, it is difficult to pinpoint why the damages started developing on the analysed Ti foils. Most of the time, the reasons are not related to the material's structural changes at all, as the surfaces of the foils do not indicate many changes due to the irradiation. This, once again, proves the effectiveness of the oxide layer on Ti. The reasons for the deterioration must thus be related to the micro-damages that occur on the cut edges of the samples, and the possibility that the oxidation must be insufficient within the micro-damaged areas.

Although our analysis has not provided us with a direct conclusion of why some of the samples were deteriorated and others not, the following line of reasoning offers some probable causes.

At first let's assume that all IFJ samples were mechanically cut similarly to CCFE's samples. Out of those 14 samples (9 IFJ foils and 5 CCFE foils) 1 was partly deteriorated (CCFE foil), 3 were slightly damaged (2 IFJ foils and 1 CCFE foil). All of the 10 samples that were laser cut (i.e. NCSRD samples) were deteriorated during the campaign.

All of the samples that were used during the campaign were mechanically processed prior to their mounting to the vessel – by vibro-etching and in some cases also by grinding. The later case refers to NCSRD foils, since the process of laser cutting out of the Ti sheet left some burrs at the edges of the foils, which had to be removed.

Ti is known to form an oxide layer on the surface rapidly. If the samples' destruction would be directly related to the damaging of the oxide layer on top of the Ti, all of the Ti samples would have been destroyed. Thus, most likely mechanical processing is not the primary reason that induced the Ti and H to react and form TiH<sub>2</sub>. Nevertheless, the breaching of the oxide layer, e.g. at the edge of the sample, during the mechanical processing, could explain the damages of the two IFJ foils.

Quite a different story could be true for samples with burrs on the samples edges – near a burr the oxide layer might not necessarily be with a constant thickness or with a complete coverage. This might enable to speed the diffusion of H to Ti and lead to their reaction. The diffusion could also happen faster and with more ease on samples that have received thermo-mechanical damages during cutting. The rapid heating and cooling might have induced the formation of micro-cracks on the edges of the laser cut samples. The cracks could be convenient passage-ways for the diffusing H, once again leading to a reaction. This might be the reason why NCSRD's samples were deteriorated.

### Conclusions

The work studies on Ti presented in this paper are more than simply the hydride effects of Ti in hydrogen environments at relatively high temperatures, but that the samples have been irradiated in fusion neutron environments. Undeniably, Ti and its alloys offer properties that can be worthy for consideration in fusion science and technology. Therefore, they are potentially useful as part of a radiation resilient activation diagnostic for fusion components (e.g. tritium breeding modules). Another example can be high-resolution coils applied into MHD analysis performed at the JET tokamak where the titanium wires on Alumina ceramic are used.

Although, Ti and its alloys are in use or are planned to be used as fusion components there are still some unknowns regarding their behaviour in fusion experimental conditions. The use of titanium in fusion technology where it is probable to be in contact with hydrogen and its isotopes can be problematic. However, there are many factors that play a role in the eventual damage and change of properties of a material exposed to particular irradiation. In the case of hydrogen embrittlement phenomena in titanium and its alloys, one can list such factors as the temperature dependence of hydrogen solubility in alpha and beta phases, alloy composition, the relative amounts of alpha and beta phases present, the hydrogen partial pressure around titanium, the prior mechanical and thermal history of the material, the stress-state, the operating temperature and the amount of hydrogen within the titanium as well as in the surrounding region [17].

The activation experiments, performed at the JET tokamak during the 2015-2016 D-D campaign, to evaluate the neutron field at the locations of the long-term irradiation stations (LTIS), showed how important a proper selection of materials to be irradiated is, and moreover the criteria for selecting the activation foils for particular experimental conditions needs proper adjustment. Although titanium has proven to be useful in the measurements with the use of 3U IE of the KN2 activation system, it turned out to be problematic in the long-term irradiations inside the tokamak vessel. During the foil retrieval process, following the completion of the D-D experimental campaign lasting 15 months, it was found that some of the foils have been damaged and others totally or partly deteriorated.

Our opinion is that the defects generated during the cutting process promoted the degradation of the titanium crystal structure after been exposed to the hydrogen environment at the high temperature plasma operation at JET. On the other hand, the passive oxide layer on the surface of the Ti foils effectively protected the other foils from a transformation into a titanium hydride. It seems that also, the initial grain structure from the manufacturing process (rolling) and the material thickness could have played a role in the distinct behaviour of titanium foils provided by different institutions.

Since it is not easy to define explicitly when or under which conditions in the fusion reactor the titanium would transform to the titanium hydride it is recommended to use titanium only in the encapsulated form (like in the standard neutron activation system e.g. at JET or the one designed for ITER [18, 19]) or in the locations where it can be vacuumed and effectively separated from the contact with the hydrogen plasma.

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### References

[1] "Fusion Electricity - A roadmap to the realisation of fusion energy", EFDA 2012

https://www.euro-fusion.org/fileadmin/user\_upload/EUROfusion/Documents/Roadmap.pdf ISBN 978-3-00-040720-8

[2] Packer, L. W. et al., Activation of ITER materials in JET: nuclear characterisation experiments for the long-term irradiation station, Nucl. Fusion 58 (2018) 096013.

[3] Batistoni, P. et al., Technological exploitation of Deuterium-Tritium operations at JET in support of ITER design, operation and safety, Fusion Eng.Des., 109–111 (2016) 278–285

[4] Packer, L.W. et al., Status of ITER material activation experiments at JET, Fus.Eng.Des. 124 (2017)

[5] X-5 Monte Carlo Team, MCNP – a general purpose Monte Carlo N-Particle transport code, version 5, volume II: User's guide, Los Alamos document number: LA-CP-03-0245. (2008 revision).

[6] Sublet, J.-C. et al., W. Arter, FISPACT-II: An Advanced Simulation System for Activation, Transmutation and Material Modelling, Nuclear Data Sheets 139 (Supplement C)(2017) 77 – 137, special Issue on Nuclear Reaction Data.

doi:https://doi.org/10.1016/j.nds.2017.01.002.

[7] Packer, L.W. et al.: Neutron spectrum determination at the ITER material irradiation stations at JET, submitted to Fusion Eng. Des.

[8] Prokopowicz, R. et al., Measurements of neutrons at JET by means of the activation methods, Nucl. Instrum. Methods Phys. Res. A 637 (2011) 119-127.

[9] Campbell, J.L. et al., The Guelph PIXE software package IV, Nucl. Instrum. Methods Phys. Res. B 268 (2010) 3356-3363.

[10] Ström, P. et al., A combined segmented anode gas ionization chamber and time-of-flight detector for heavy ion elastic recoil detection analysis, Rev. Sci. Instrum. 87 (2016) 103303.

[11] Prando, D. et al., Corrosion of titanium: Part 1: aggressive environments and main forms of degradation, J Appl Biomater Funct Mater, 15(4) (2017) e291-e302.

[12] Loughlin, M. J. et al., Neutron transport calculations in support of neutron diagnostics at JET, Rev. Scient. Instrum., Vol. 7 no. 1 (1999) 1126.

[13] Baymakov, Yu.V., Lebedev, O.A., Titanium and Hydrogen, Leningrad Polytechnic Institute, Trudy, No. 223 (1963) 25-34.

[14] Donachie, M.J. Jr., Titanium: A Technical Guide, Second Edition, ASM International (2000) 123-130.

[15] Cardarelli, F. Materials Handbook: A Concise Desktop Reference 2nd ed., London, England, UK: Springer-Verlang. (2008)ISBN 978-1-84628-668-1

[16] Emsley, J., Titanium, in Nature's Building Blocks: An A-Z Guide to the Elements, Oxford, England, UK: Oxford University Press (2001) ISBN 978-0-19-850340-8.

[17] Wille, G.W., Davis, J.W., Hydrogen in titanium alloys, Report prepared for the U. S. Department of Energy, April 1981

[18] Krasilnikov V., Cheon M., Bertalot L., Neutron Activation System for ITER Tokamak, November 2018

doi:https://doi.org/10.5772/intechopen.75966

[19] Lee Y., Dang J-J., Jo J., Chung K-J., Hwang Y.S., Cheon M.S., Lee H.G., Bertalot L., Preliminary study on capsule material for ITER neutron activation system, Fus. Eng. Des., Vol. 89, Issues 9–10, (2014) 1894-1898,