Helium implanted RAFM steels studied by positron beam Doppler Broadening and Thermal Desorption Spectroscopy

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Abstract. Reduced Activation Ferritic/Martensitic steels are being extensively studied because of their foreseen application in fusion and Generation IV fission reactors. To mimic neutron irradiation conditions, Eurofer97 samples were implanted with helium ions at energies of 500 keV and 2 MeV and doses of 5×1015–1016 He/cm², creating atomic displacements in the range 0.07–0.08 dpa. The implantation induced defects were characterized by positron beam Doppler Broadening (DB) and Thermal Desorption Spectroscopy (TDS). The DB data could be fitted with one or two layers of material, depending on the He implantation energy. The S and W values obtained for the implanted regions suggest the presence of not only vacancy clusters but also positron traps of the type present in a sub-surface region found on the reference sample. The traps found in the implanted layers are expected to be HeₙVₘ clusters. For the 2 MeV, 10¹⁶ He/cm² implanted sample, three temperature regions can be observed in the TDS data. Peaks below 450 K can be ascribed to He released from vacancies in the neighbourhood of the surface, the phase transition is found at 1180 K and the peak at 1350 K is likely caused by the migration of bubbles.

1. Introduction

Eurofer97 is a Reduced Activation Ferritic/Martensitic (RAFM) steel used as reference structural material for future fusion reactors. Eurofer97 steel known to possess a high resistance against swelling from gaseous transmutation products (hydrogen, helium) has attractive mechanical properties and shows reduced activation behavior in a fusion neutron spectrum [1]. The effects of neutron irradiation and the accumulation of defects in this material are extensively studied (e.g. [2]) as Eurofer97 will be used for constructing test blanket modules in the ITER fusion reactor [1, 3]. As a consequence of the neutron irradiation, displacement damage will be created together with the production of hydrogen and helium [1, 3]. This leads to changes in the microstructure and ultimately to alterations in the material’s mechanical properties. The work described here is part of a larger project in which Thermal Desorption spectroscopy (TDS) and electron microscopy studies will be performed on Eurofer97 neutron irradiated in the High Flux Reactor at NRG. To mimic these neutron irradiations, samples are
implanted with 500 keV and 2 MeV He⁺ ions. The defect structures after implantation and annealing treatments are characterized with the positron beam Doppler Broadening technique (DB). The thermal behavior of the implanted He is studied in parallel by TDS.

2. Experiment

The samples used in this study were cut from the European Union Eurofer97 batch, produced by Böhler, Austria, with a nominal composition of Fe-9Cr-1W-0.2V-0.1Ta-0.1C (wt.%). Samples of 12x12x0.5 mm³ were machined so that after the He implantation nine small rectangular cuboids of 2x2x0.5 mm³ (for TDS) could be detached from the larger central piece with dimension of 10x10x5 mm³ (for DB). In order to obtain a tempered martensitic microstructure the samples were annealed after machining in two steps of 30 min at 1253 K and 90 min at 1033 K, both followed by cooling in argon ambient.

Low dose (5x10¹⁵ and 5x10¹⁶ He/cm²) room temperature helium implantations were performed at CEMHTI-CNRS. For the 500 keV and 2 MeV implantations the beam current was 270-280 nA and 120-212 nA, respectively, with implantation times ranging from 1 up to 15 hours. TRIM calculations for the dose of 1x10¹⁵ He/cm² show that the defect production (dpa) has a maximum value of 0.08 at a depth of 1 µm for 500 keV and 0.07 dpa at 3 µm for 2 MeV. The maxima in the He distributions are slightly deeper, with a Full Width at Half Maximum of 0.2 µm. For the dose of 1x10¹⁶ He/cm² similar defects and He distributions are obtained with 10 times higher dpa levels. The positron beam DB measurements were performed up to energies of 25 keV, corresponding to a maximum probing depth of approximately 1 µm. He desorption spectra were obtained in a 10⁻⁸ Torr vacuum, using a linear heating rate of 0.33 K/s from RT up to 1500 K.

3. Results and discussion

Figure 1 shows the DB S and W parameters as a function of the positron implantation energy (bottom axis) and positron mean implantation depth (top axis) for the reference and the four implanted samples. The lines through the data are the fits obtained with the VEPFIT program [4]. In case of the 2 MeV implantation, one layer defining the S and W parameters and the positron diffusion length was sufficient to obtain a good fit. For the 500 keV implantation two layers (with thicknesses of 200 and 800 nm) plus a layer representing the bulk of the material were needed. This is consistent with the TRIM results which show that for the 2 MeV implantation the defect production is flat over the positron probing range while for the 500 keV implantation the defect profile peaks at the end of the positron range. The decrease of S (increase of W) for positron implantation energies up to 2 keV is ascribed to non-thermal positrons annihilating at the surface. In the VEPFIT model the S and W parameters for thermal positrons back-diffused to the surface are found to be rather independent of the implantation conditions. For the reference sample a positron diffusion length (Lₑ⁺) of approximately 50 nm is obtained. Due to the He implantation Lₑ⁺ has decreased to less than 10 nm, indicative for high positron trapping efficiency.

Figure 1. S and W parameter vs. positron implantation energy and depth. Data fitted with VEPFIT.
Figure 2 shows the $S,W$ map (for clarity only fitted curves are shown) for all samples with the positron implantation energy as a running parameter starting from 1.5 keV. In this figure the filled symbols (●) represent the characteristic $S,W$ values for the reference bulk and surface annihilations. The open symbols (○) are the fitted $S,W$ values in the first layer which in case of 2 MeV implantation is the only layer defined. The triangles represent the $S,W$ values for the second deeper layer (500 keV only). In this image is also marked the $SW$ value of a chromium (Cr) sample annealed at 1200 K for 1 hour.

The $S$ and $W$ curves for the reference sample shown in figure 1 could be independently fitted using a single layer model. In the $S,W$ plot however, a small deviation from the expected straight line connecting the $S,W$ point of the surface and bulk is observed. This can be understood by assuming the presence of a near surface layer with $S,W$ values different from that of the reference bulk values. With this assumption, the $S,W$ analysis program SWAN [5] predicts a layer of 60 nm thickness with characteristic $S,W$ values denoted as “sub surface” in figure 2. Note that these values are close to those measured for chromium annealed at 1200 K. This indicates that in the near surface region of the reference sample a small fraction of the implanted positrons annihilates at Cr-rich trapping sites. These may have been formed during tempering treatment to obtain the desired ferritic/martensitic structure. A closer look at the location of all $S,W$ points obtained for the He implanted regions shows that they all lie on a single line which extrapolates to the $S,W$ point found for the sub-surface region in the reference sample. This means that after the He implantation the positrons annihilate at either vacancy type defects or at defects associated with Cr. The highest $S$ value, which is obtained for the implantation of 500 keV, $10^{16}$ He/cm$^2$, is about 15% higher than the bulk value. In metals this increase is typical for small vacancy clusters [6].

With increasing He dose the $S,W$ points shift towards this higher $S$ value indicating an enhanced fraction of positrons trapping at the vacancy clusters with the respect to the fraction trapped at vacancies associated with Cr.

In figure 3 a TDS measurement of a sample implanted at 2 MeV, $10^{16}$ He/cm$^2$ and the fitted $S$ values (measured at room temperature) after in situ annealing for 5 min are shown. From the TDS data it is calculated that the total amount of He desorbed is approximately 10% of the implanted dose.

At temperatures below 450 K two peaks can be observed. In literature, He desorption in this temperature range is attributed to the release of He trapped at a near surface vacancy [8]. At ~ 900 K the rate of desorption of He slightly increases reaching its peak value at ~ 1180 K. The large width of the peak indicates desorption of multiple trapping sites such as simple HeV or larger helium-vacancy clusters, He$_n$V$_m$ [8]. Retrapping of desorbed helium before reaching the surface can also occur at these temperatures and delays the release of He [8]. The peak at 1180 K is associated with the phase transition, expected to occur at 1160 K, and is likely delayed due to retrapping events. [9]. Finally, a peak is found at ~ 1350 K. It is known that during the annealing carbon-vacancy clusters can form and may combine with He$_n$V$_m$ to form complex clusters [10]. The thermal stability of these complexes is much greater...
higher than that of simple HeV and therefore these complexes are expected to desorb at higher temperatures, via dissociation or bubble diffusion mechanism [10].

The decrease of the $S$ parameter starting at 400 K can be attributed to the annealing of vacancies, as the first micrometer of Eurofer, when implanted with 2 MeV He ions is expected to have low He content (TRIM). The second step in the $S$ curve lies between the 1000 and 1100 K and can be associated with the beginning of the phase transition and the removal of defects by this process. At 1300 K the $S$-parameter increases slightly after which it finally drops to the near bulk value at 1500 K. This can be understood by the diffusion of He bubbles towards the surface thereby entering the depth region probed by the positrons.

4. Conclusions
He implantations have been performed in Eurofer97 steel with energies of 500 keV and 2 MeV and doses of $5 \times 10^{15}$ and $5 \times 10^{16}$ He/cm$^2$. The shape of the $S,W$ for the reference sample curve suggests the presence of a 60 nm thick sub-surface layer containing Cr related positron trapping sites. Two types of defects are found in the He implanted samples: vacancy type defects (expected to be He$_n$V$_m$ clusters) and defects associated with chromium.

In the TDS spectra the phase transition of the steel is observed and the desorption at temperatures above 1300 K can be attributed to migrating He bubbles that are formed during the annealing. In the DB measurements this is seen as an increase in $S$ due to the arrival of the He bubbles in the range probed by the positrons.

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