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# Vacancy defects study in Fe based alloys induced by Irradiation under various conditions

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**Abstract.** In this study, a pure FeNiCr (D302) model alloy has been investigated in parallel with an industrial 316L alloy. Both alloys have been irradiated in different conditions with 5 MeV Ni<sup>2+</sup> at high temperature (HT) 450°C, and to damage doses: 0.5 or 1 dpa (displacement per atom), or with 1.5 MeV <sup>4</sup>He<sup>2+</sup> at room temperature (RT) and to damage dose between 1x10<sup>-4</sup> and 1x10<sup>-2</sup> dpa. The positron annihilation spectroscopy (PAS) implemented on a slow positron beam has been used to characterize vacancy defects. The results are compared to other analysis methods such as: TEM (Transmission Electron Microscopy) and APT (Atomic Probe Tomography) reported in [1]. Main results show that only single vacancies have been observed in the case of 316L alloy regardless the irradiation conditions, while vacancy clusters seem to be formed in the case of D302 alloy under HT irradiation conditions and from 1x10<sup>-3</sup> dpa at RT. The difference observed between 316L and D302 alloys could be linked to a role played by the alloying elements such as silicon.

## 1. Introduction

Austenitic stainless steels are widely used in nuclear industry as internal structures. The exposure of these elements to high irradiation doses (the accumulated dose after 40 years of operation can reach 80 dpa), at temperature close to 350°C, modifies the macroscopic behavior of the steel and thus limits the operational lifetime of the reactor. In the framework of PERFORM60<sup>1</sup> project, twenty European organizations and universities involved in the nuclear field are engaged in the development of experimentally validated multi-scale modeling tools with the main concern to predict the operational lifetime of the reactor pressure vessel (RPV). CEMHTI laboratory is involved in this program to provide experimental data on the evolution of the microstructure of studied materials as a function of irradiation conditions (temperature, fluence, etc.). Then, results obtained will be used by the other program teams to validate their simulation models.

In this work, the Slow positron beam Doppler broadening spectroscopy (SPBDBS) has been used to study the vacancy defects induced by irradiation of a pure FeNiCr (D302) model alloy and an industrial 316L alloy. Results obtained will be interpreted with the help of those obtained on a pure Fe by He and *al.* [2]. Materials were irradiated in different conditions: either with heavy Ni<sup>2+</sup> ions to

<sup>1</sup>PERFORM 60: Prediction of the Effects of Radiation For RPV and in-vessel Materials using MSM-60 years foreseen plant life time.



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simulate reactor neutron irradiations, or with light  $^4\text{He}^{2+}$  ions to obtain based data complementary to those with  $\text{Ni}^{2+}$ . The results obtained by PAS will be compared to APT and TEM observations performed in [1].

## 2. Experimental

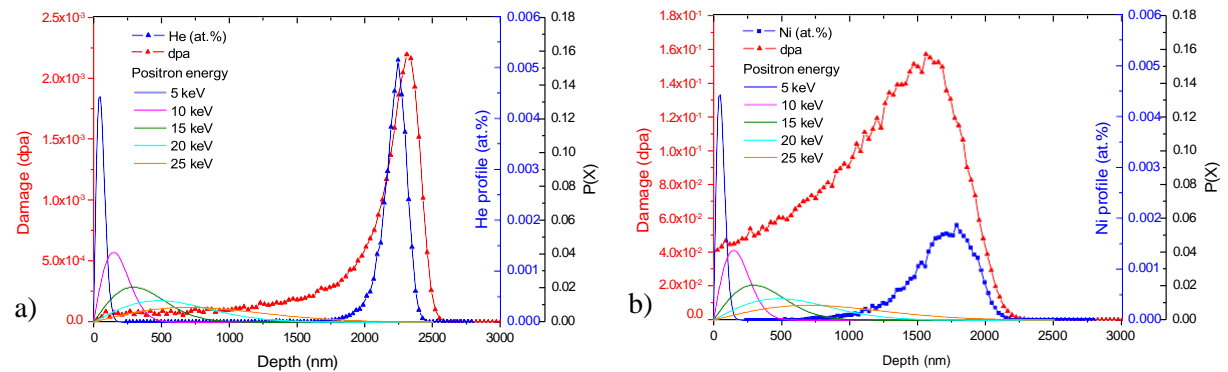
The metal alloys (fcc) were provided by OCAS company. Their composition is given in Table 1. Before irradiation, samples ( $5 \times 5 \text{ mm}^2$ ) have undergone several stages of preparation (mechanical polishing, electro-polishing, and annealing) in the aim to get "virgin" samples with fewer defects as possible checked by SPBDBS measurements. Samples have been irradiated in different conditions: either with 5 MeV  $\text{Ni}^{2+}$  at high temperatures (HT)  $450^\circ\text{C}$  and to 0.5 or 1 dpa, or with 1.5 MeV  $^4\text{He}^{2+}$  at RT and with damage dose between  $1 \times 10^{-4}$  and  $1 \times 10^{-2}$  dpa (fluence between  $1 \times 10^{14}$  and  $1 \times 10^{16}$  ions. $\text{cm}^{-2}$ ). The pure Fe has been also irradiated with 1.5 MeV  $^4\text{He}^{2+}$  at RT and to damage dose between  $1 \times 10^{-5}$  and 0.1 dpa (fluence between  $1 \times 10^{13}$  and  $1 \times 10^{17}$  ions. $\text{cm}^{-2}$ ) and studied. Irradiations at HT have been performed on the JANNUS platform using ARAMIS Tandem (Orsay France), and the ones at RT using the Van de Graaff accelerator (CEMHTI Orléans, France).

**Table 1.** Chemical composition of 316L stainless steel and D302 model alloy (wt.%).

Composition	Cr	Ni	Mo	Mn	Si	C	S	P	Cu	Fe
<b>316L</b>	17.6	12	2.39	1.78	0.59	0.028	0.01	0.01	0.066	bal.
<b>D302</b>	18.27	12.4	-	-	-	0.008	0.003	-	-	bal.

Figure 1 (a) and (b) shows the calculated depth profiles of implanted ions concentration and the corresponding damage calculated for 316L alloy implanted with 1.5 MeV He ions and 5 MeV Ni ions, respectively. These calculations are performed by using SRIM software [3] with a displacement threshold energy of 40 eV (Fe), 44 eV (Cr), and 28 eV (Ni), a density =  $7.99 \text{ g.cm}^{-3}$  (316L), and for the fluence =  $1 \times 10^{14}$  ions. $\text{cm}^{-2}$ . In the same figure, the slow positron implantation profile is also illustrated for different energies [4]. We point out that the implantation with heavy Ni ions generates dpa greater than that observed with light He ions. The theoretical projected range ( $R_p$ ) for  $^4\text{He}^{2+}$  implanted ions is 2310 nm, while  $R_p$  for  $\text{Ni}^{2+}$  implanted ions is lower and equal to 1660 nm. Positrons probe mainly the low damage ( $1 \times 10^{-4}$  dpa) and low He concentration ( $< 4 \times 10^{-6}$  at.%) region for the He implantations, whereas the damage dose becomes strongly higher ( $7.8 \times 10^{-2}$  dpa) for Ni implantations (as calculated at depth of 810 nm). The calculations of the number of displaced Ni atoms by the pka (primary knock-on atoms) for 316L by using SRIM software (ignoring the other atoms of the lattice, Fe and Cr) showed that 56% of pka created by 1.5 MeV He ions is only be able to create Frenkel-pairs (number of displaced atoms  $\leq 1$ ), against 39% of pka in the case of 5 MeV Ni implantation, and 99% of pka created by 1.5 MeV He ions participates in the creating of displacement cascades containing less than 30 Ni atoms compared to displacement cascades of 518 Ni atoms when the target is irradiated with 5 MeV Ni ions. These calculations suggest that, positrons will probe a greater concentration of complex defects when irradiation is performed with Ni ions. Knowing that, the area of nuclear cascades may not be detected by SPBDBS technique, since, even the most energetic positrons rarely reach this zone especially when irradiation is done with He ions (Figure 1).

The Slow positron beam Doppler broadening spectroscopy (SPBDBS) [5] at the CEMHTI laboratory has been used to probe vacancy defects in the first  $\mu\text{m}$  of metals. This technique is based on the measurement of the low (S) and the high (W) momentum fractions of the 511 keV positron–electron annihilation line. S corresponds to annihilations in the momentum range  $(0 - |2.49|) \times 10^{-3} m_0 c$ , and W in the windows  $(|9.64| - |24.88|) \times 10^{-3} m_0 c$ , respectively. The measurements were performed at RT. The S and W parameters were recorded as a function of the positron energy E which changes by 0.5 steps in the range 0.5 to 25 keV. The SPBDBS uses a high purity germanium (Ge) detector with a good resolution ( $< 1.3 \text{ keV}$  at 511 keV) and a high efficiency ( $> 25\%$  at 1.33 MeV).

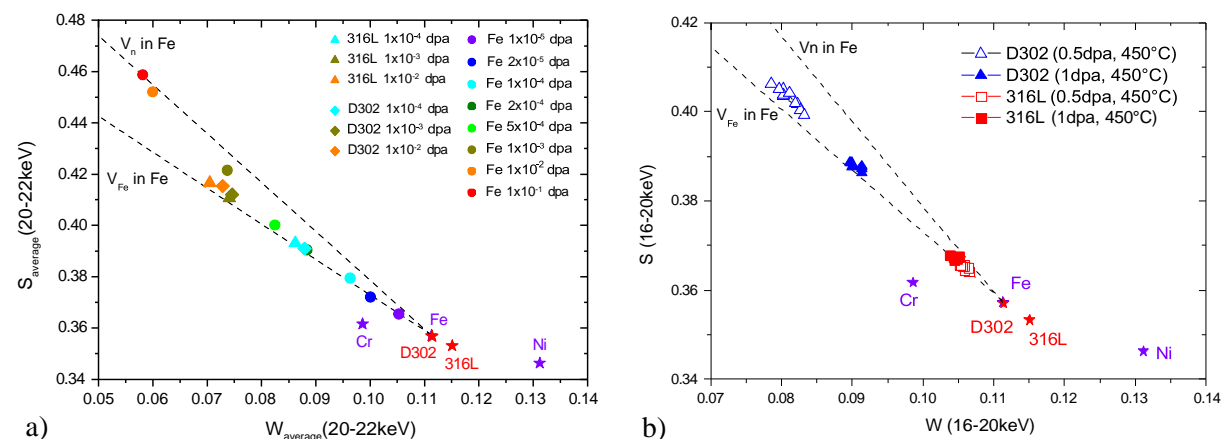


**Figure 1.** SRIM damage profile of 316L implanted with 1.5 MeV He ions (a) and 5 MeV Ni ions (b) at fluence of  $1 \times 10^{14}$  ions. $\text{cm}^{-2}$  compared to positron implantation profile.

### 3. Results and discussion

#### 3.1. Irradiation with light He ions at RT

In this case, metal alloys (316L and D302) were irradiated with 1.5 MeV  $^4\text{He}^{2+}$  at RT up to damage dose between  $1 \times 10^{-4}$  and  $1 \times 10^{-2}$  dpa. Figure 2 (a) shows the average values of S and W parameters of 316L and D302 obtained for positron energy between 20 and 22 keV compared to results obtained on pure Fe irradiated with 1.5 MeV  $^4\text{He}^{2+}$  ( $1 \times 10^{-5}$  to 0.1 dpa) at RT [2]. This energy range is considered to be representative of the annihilation characteristics in the bulk. The error bars are limited in the points and thus are not plotted in this figure ( $\Delta W = \pm 7.5 \times 10^{-4}$ ;  $\Delta S = \pm 13.6 \times 10^{-4}$ ).



**Figure 2.** Variation of low momentum annihilation fraction S as a function of high momentum annihilation fraction W: (a) for irradiated Fe, 316L, and D302 with 1.5 MeV He ions to different damage doses and (b) for 316L and D302 alloys irradiated with 5 MeV Ni ions at 450°C and to two damage doses: 0.5 and 1 dpa. Stars points are the lattice points obtained on virgin samples.

For the metal alloys, we notice different behaviour depending on its composition. For 316L, the S,W points lie at the same “ $V_{\text{Fe}}$  in Fe” line, the single vacancy characteristic line  $V_{\text{Fe}}$  as determined in [1] whatever the irradiation conditions are (low and high dpa, at RT). In the case of D302 alloy, we notice that from  $1 \times 10^{-3}$  dpa, the S,W points are slightly above the “ $V_{\text{Fe}}$  in Fe” line. It could be due to the detection either of small vacancy clusters, or of Stacking Faults Tetrahedral (SFTs) which are typical irradiation induced defects in fcc metals. These types of defects are special arrangements of vacancy defects essentially in 2D morphology leading to annihilation characteristics very different of the ones for 3D arrangement of the same number of vacancies. In fact, as shown in Ni by Kuramoto [6], calculated positron lifetimes for different numbers of vacancy are found strongly lower values for

large number. The size of these clusters observed in D302 alloy is smaller than that observed in pure Fe from the same damage dose ( $1 \times 10^{-3}$ ). It could be related to the different migration properties of vacancy in both fcc and bcc lattices limiting the clustering. In the case of 316L alloy, the migration temperature has been estimated at about 230 to 270°C, compared to  $\sim -53$  to 5°C in the case of pure iron [7]. Moreover in D302 or other fcc materials such as Ni, SFTs are the predominant form of vacancy clusters.

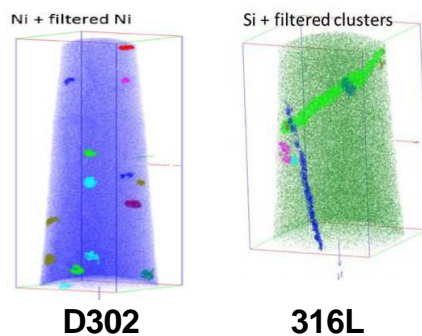
For both alloys and at the highest damage dose, the S and W remain close for an increase of a factor of 10 in damage dose. It suggests that a saturation of vacancy detection is reached or close to be reached. However, for pure Fe such saturation is not reached yet because of 3D- $V_n$  formation and the increase of the size of vacancy clusters with the fluence [2].

### 3.2. Irradiation with heavy Ni ions at HT

Under high temperature conditions, metal alloys have been irradiated with 5 MeV  $\text{Ni}^{2+}$  at 450°C, and to 0.5 or 1 dpa damage doses. Figure 2 (b) shows the variation of S parameter versus W parameter, obtained for positron energy between 16 and 20 keV which correspond to a depth zone also observed by APT and TEM. First of all, we notice that the defect concentration in 316L is drastically lower than in D302. Moreover for 316L, only one type of defect is detected: single vacancy (V), independently of damage dose (0.5 or 1 dpa) like it was observed under RT irradiation conditions, while in the case of D302, vacancy clusters seem to be the major defect detected (bulk points are lying above the “ $V_{\text{Fe}}$  in Fe” line). The size of clusters is smaller than that observed in the case of pure iron. In addition, for D302 we notice a lower defect concentration at 1 dpa dose compared to 0.5 dpa dose: decreasing of S parameter and increasing of W parameter. Such difference in defect concentration can be explained by an annealing effect of the induced defects during the irradiation which is two times longer for 1 dpa compared to 0.5 dpa (same flux, but fluence (irradiation time) is two times higher).

A. Volgin has performed APT and TEM analyses for 316L and D302 irradiated at 450°C and to 1 dpa damage dose [1]. APT shows, in all bulk samples irradiated at high temperature, the formation of Cottrell clouds. These clouds were enriched in Ni and depleted in Cr (Size: 5 nm;  $N_d = (6.8 \pm 1.3) \times 10^{22} \text{ m}^{-3}$ ) in the case of D302 alloy, and in Ni, Si, and P in 316L. In the latter case, the Cottrell clouds are along linear dislocation lines (disl. density:  $(2.7 \pm 0.2) \times 10^{14} \text{ m}^{-2}$ ), and the presence of some small objects (clusters and clouds) NiSiP-rich also is noticed (Figure 3). TEM observations show the formation of Frank loops for both alloys D302 and 316L. The mean size of loops is however different, the diameter of loops is bigger in the D302 alloy, 15.3 nm compared to 6 nm in the case of 316L. Frank loops were distributed homogeneously in D302 alloy while they were preferentially located in the vicinity of the dislocation network in the 316L. SFTs are also detected in D302 but not in 316L. Their number density ( $N_d$ ) is  $(2.8 \pm 0.6) \times 10^{22} \text{ m}^{-3}$  with mean size of 4 nm (450°C, 1 dpa). These SFTs could correspond to the clusters detected by SPBDBS from 0.5 dpa dose. Neither cavities, nor precipitates are detected in both alloys [1].

To explain this difference observed between 316L and D302, especially as regarding the absence of vacancy clusters in the case of 316L, it was suggested that the presence of Si in 316L could play a role. In fact, it is known that the addition of silicon in pure nickel, Ni-Cr alloys, and Fe-Ni-Cr alloys, raises the diffusivity of each of the alloy components [8]. The resultant increase in the effective vacancy diffusion coefficient causes large reductions in the nucleation rate of voids during irradiation. The concept of existing a correlation between the suppression of void formation and the presence of fast-diffusing solute or solvent elements initially proposed by Venker, Ehrlich, and Giesecke [9, 10] appears to be an alternative to the concept that defect trapping at solute elements reduces void formation. The latter possibility has been proposed and analyzed by several authors [11]. Indeed, the trapping of interstitials and/or vacancies at solute atoms or impurities enhances the probability of recombination, and thereby lowers the supersaturation of vacancies. Silicon in 316L was observed by APT after irradiation to be especially segregated along linear dislocation lines. The dislocations as known are a major sink of defects; this can be added to the idea of existing Si-interstitial complexes and can contribute in the recovering of the alloy.



**Figure 3.** APT 3D reconstruction of typical volumes of D302 and 316L implanted with Ni ions: 1 dpa, 450°C. Detected elements are filtered and imaged in colour; in this paper we only show the Ni and Si enrichment in D302 and 316L, respectively [1].

#### 4. Conclusions

The principal results obtained show that only single vacancies have been observed in the 316L alloy independent of the irradiation conditions studied in this work (low and high dpa, at RT or HT), while vacancy clusters seem to be formed in the D302 alloy under HT irradiation conditions and from  $1 \times 10^{-3}$  dpa at RT. The size of clusters is smaller than that observed in the case of pure iron. The difference observed between 316L and D302 alloys could be linked to a role played by the alloying elements such as silicon on the nature of created defects.

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