Microstructural Characterization of Ferritic-Martensitic Steels by Positron Annihilation Spectroscopy

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Abstract. Positron annihilation (PA) studies are carried on two ferritic/martensitic steels (modified 9Cr-1Mo and EUROFER97) and Fe-9Cr binary alloy. Normalized modified 9Cr-1Mo steel is subjected to isochronal heat treatments between 300 K – 1273 K with PA studies at different intervals. Due to changes in the concentration of positron trapping open volume defects associated, different stages of the microstructural changes are identified. These results are corroborated with scanning electron microscopy studies. In EUROFER97 steel, the relative increase in precipitate number density due to the additional cold-work (after normalization) is brought out. In binary Fe-9Cr alloy, which is the model alloy of 9Cr ferritic/martensitic steels, the effect of dislocations on Cr segregation is brought out by studying alloys with two different initial conditions of varying dislocation densities.

1. Introduction

Ferritic/martensitic steels are considered as important candidate structural materials in fast nuclear reactors pertaining to good void swelling resistance. Void swelling in ferritic steels is around 1% while for the austenitic stainless steels it is 10-28 % for the same fluence of neutron irradiation (18 x 10²² n/cm², E > 0.1 MeV) at 693 K [1]. Ferrite steels (in particular, 9Cr-1Mo steels) have strength higher than 304 austenitic stainless steel up to 973 K. However, the conventional ferritic steels have poorer high temperature creep strength as compared to austenitic steels [2]. The strength and long term performance of ferritic steels critically depend on the initial stable microstructure for the given operating conditions. The microstructure consists of lath structure with a variety of precipitates dispersed [3]. The Fe-9Cr binary alloy is a model system for 9Cr ferritic steels, which could shed light on the nature of Cr segregation, known as α' phase, in Fe-Cr based steels. From a fundamental point of view, the Fe-Cr phase diagram continues to evoke a lot of interest and getting revised with more precise experimental results and ab-initio calculations, as evident from a recent critical review [4]. Earlier positron annihilation spectroscopy (PAS) was extensively employed for characterization of steels [5, 6] and model alloys [5, 7, 8]. In the present work, PAS is employed on modified 9Cr-1Mo steel, EUROFER97 steel and Fe-9Cr binary alloy to find out the different microstructural changes occurring as a function of heat treatment. Electron microscopy studies are used for obtaining corroborative information. The microstructural changes as seen by PAS are compared with previous studies.
2. Experimental Details

The chemical composition of the steels and the binary alloy used in the present work is given in Table-1. Mod. 9Cr-1Mo steel and EUROFER97 steel samples were normalized at 1313 K for 1h followed by heat treatment between 300 – 1027 K with a step size of 50 K and a holding time of 1 h. PAS measurements were carried at selected heat treatment steps. Fe-9Cr model alloys were considered in two different initial conditions viz. (a) heat treatment at 1423 K for 1 h followed by air-quenching (AQ) (b) heat treatment at 1073 K for 2 h (HT). Further details regarding thermomechanical treatments can be found in [8].

| Element | Composition (wt %) | Mod. 9Cr-1Mo | EUROFER97 | Fe-9Cr |
|---------|--------------------|--------------|-----------|--------|
| C       | 0.10               | 0.11         | < 0.0001  |
| Cr      | 8.50               | 8.96         | 9.50      |
| Mn      | 0.40               | 0.49         | -         |
| Si      | 0.25               | 0.04         | -         |
| Mo      | 0.95               | -            | -         |
| W       | -                  | 1.08         | -         |
| V       | 0.22               | 0.20         | -         |
| Ni      | 0.20               | 0.02         | -         |
| Nb      | 0.08               | -            | -         |
| Ta      | -                  | 0.14         | -         |
| N       | 0.01               | 0.021        | -         |
| P       | <0.006             | <0.005       | -         |
| S       | <0.006             | 0.004        | -         |
| Fe      | Bal.               | Bal.         | Bal.      |

Positron lifetime measurements were carried out at room temperature with a fast-fast lifetime spectrometer having a time resolution of 260 ps (FWHM), using a $^{22}$Na source. Source lifetime and intensity were deduced using annealed Fe as a reference sample. For each measurement, more than $10^6$ total counts were accumulated and the measured lifetime spectra were analyzed using the LT program [9]. In the present experiments, only a single mean lifetime is obtained for all the measurements over the entire annealing temperature range. Doppler broadening annihilation line shape measurements were carried out at room temperature using a HPGe detector having energy resolution of 1.29 keV at 662 keV. The defect sensitive S-parameter is defined as the ratio between the area under annihilation peak energy region of 511 ± 1 keV and the total area under the region of 511 ± 10 keV. Scanning electron microscopy (SEM) was carried out using a Carl Zeiss FE SEM with an INCA EDS analyser (M/s. Oxford) in secondary emission mode. Samples subjected to the same heat treatment procedures as described earlier were used. These samples for electron microscopy were prepared by standard metallographic methods of grinding and polishing.

3. Results and Discussion

The normalized ferritic/martensitic steel consists of martensitic lath structure with high concentration of dislocations. Martensitic steel in this state also contains vacancies and vacancy-carbon complexes as explained previously in reference [10]. Figure-1 shows the Doppler broadening S-parameter.
obtained for normalized sample as a function of heat treatment. It also presents positron lifetime values for corresponding heat treatments from previous work [10]. The results can be understood as three stages of microstructural changes i.e., (i) the S-parameter and lifetime show decrease, as compared to values in a normalized sample, upto 673 K (ii) an increase and decrease during heat treatment between 773 - 1073 K (iii) increase beyond 1073 K.

![Graph](image1.png)

**Figure 1.** Doppler S-parameter and lifetime as a function of temperature in modified 9Cr-1Mo steel. Lifetime results are from reference [10]. The changes seen between 773 K – 1073 K correspond to precipitation.

![Image](image2.png)

**Figure 2.** SEM micrograph of as-normalized modified 9Cr-1Mo steel. A similar microstructure is observed in 673 K annealed sample.

In the first stage, as a function of heat treatment the S-parameter decreases till 673 K indicating defect (dislocations and/or vacancy complexes) annealing. While the PAS is sensitive to these changes, other techniques such as hardness and ultrasonic velocity did not show sensitivity [10]. A SEM micrograph of the normalized sample is shown in Figure-2. It is found to be similar up to 673 K [10]. Increase in positron lifetime above 773 K corresponds to the nucleation and growth of the metal carbide/nitrides precipitates with majority of the precipitates being M23C6 [3, 11]. With the increase in the number density and the size of precipitates, the associated precipitate-matrix interface area increases and hence, the interfacial open volume defects increases. It is possible that the increase in
lifetime could also be due to vacancy defects inside the precipitates. It is known from earlier calculations that positron lifetime in metal vacancy is higher than the corresponding perfect metal carbide (or nitride) lattice [12]. However, the present experiments are inadequate to identify the exact defect site. Nevertheless, these results confirm that the sites are associated with precipitates.

Figure 3. SEM micrographs of modified 9Cr-1Mo steel samples treated at (a) 873 K and (b) 1073 K. Magnified images are shown on the right side. In the 873 K treated sample, large concentration of precipitates with mean separation of ~150 nm are seen. In the 1073 K sample, the precipitate concentration decreases while the mean separation increases to > 0.5 µm.

Beyond 873 K, the lifetime decreases indicating decrease in positron trapping defects. Above 873 K, the precipitates coarsen at the expense of small precipitates resulting in less concentration of precipitates having bigger size. After heat treatment at 1073 K, the mean distance between precipitates increases to ~1 µm. The positron diffusion length being about 100 nm in metals and alloys, the fraction of positrons trapped at precipitates decreases with the increase in the mean separation length of the precipitates. Figure-3 shows the precipitate microstructure of 873 K and 1073 K heat treated samples at different magnifications. In the 873 K heat treated sample the precipitates are found to be high in concentration and small in size, while the sample heat treated at 1073 K shows lower concentration of precipitates of larger size. Hence, the microstructures at 873 K and 1073 K indicate growth and coarsening stages respectively. The third stage beyond 1073 K (Figure-1) is a mere reproduction of the microstructure similar to the initial condition of the normalized sample. This is because, heat treatment above 1073 K and subsequent quenching results in martensitic structure. However, there could be differences in the size of prior austenitic grain boundaries that would not be able to influence positron annihilation parameters significantly.

In summary, the microstructural changes in terms of quenched-in defects annealing below 673 K, the growth and the coarsening of precipitates between 773 K – 1073 K and the formation of martensitic phase around 1173 K are distinguished using positron annihilation. Our previous studies using ultrasonic velocity and hardness techniques [10] were found to be insensitive to the defect annealing stages below 673 K. While these techniques show sensitivities for the changes in lath structure and the associated precipitation stages, they show monotonic changes for both, growth and coarsening stages, indicating they cannot distinguish the precipitation stages. However, the martensitic phase formation is duly detected by ultrasonic velocity and hardness.

Lifetime studies were also carried out on EUROFER97 samples and they exhibit similar stages of defect annealing, precipitation growth and coarsening. Figure-4 shows the mean positron lifetime during the growth and the coarsening stages, with one of the samples further cold worked to 10 %, upon normalization, to increase the nucleation sites in the form of dislocations. As can be seen, the positron lifetime in the cold-worked sample is longer as compared to only normalized sample, throughout the range, indicating more positron traps in the cold worked sample. Since the positron
lifetimes are almost the same before precipitation in both samples, the increase in trapping is expected to be associated with the variation in precipitate associated defects. Hence, the increase in positron lifetime is due to an increase in the number density of precipitates. As a summary, this study brought out the variation in precipitate concentrations using positron lifetime technique.

Figure 4. Selected temperature range in EUROFER97 steel showing the precipitation stage, under two different initial conditions. Due to cold-work the precipitate number density increases, resulting in an increased lifetime.

Figure 5. Positron lifetime in Fe-9Cr alloys with two different initial conditions (AQ & HT), showing the effect of dislocations on precipitation between 823 K – 973 K [8]. The onset of precipitation is correlated with dislocation annealing in the cold-worked (CW) pure Fe sample.

Figure-5 shows results of Fe-9Cr samples in comparison to cold-worked 99.99% pure Fe samples. AQ samples quenched from elevated temperature (FCC phase) contains random dislocations and they are found to be annealed out by 773 K [8]. Upon further heat treatment, they showed a longer lifetime between 823 K – 973 K while, the dislocation free HT sample showed no change in lifetime in the corresponding temperature range. Annealing of the majority of dislocations by 773 K in pure Fe
sample clearly indicates that the Cr segregation in Fe-Cr sample is induced by dislocation annealing, indicating that the Cr segregation is driven by dislocations. Transmission electron microscopy confirmed the existence of precipitates at 900 K and their dissolution by 1073 K [8]. A similar kind of Cr segregation upon helium implantation was reported previously [13]. Further, the nature of precipitates is found, indicatively, as Fe-Cr intermetallic.

4. Summary
PAS studies were carried out on two different ferritic steels and a Fe-9Cr binary alloy to investigate the microstructural changes as a function of heat treatment. The effect of dislocations on Cr precipitation in Fe-9Cr alloys is brought out. The effect of cold work on the precipitation in EUROFER97 steel is presented. The growth and coarsening stages in Modified 9Cr-1Mo steels are distinguished using PAS and the results are corroborated with SEM studies.

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