

Effect of the Initial Microstructure on Defect Evolution in Neutron Irradiated Fe–Cr–C Alloys

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The irradiation-induced evolution of vacancy type defects in various iron-chromium model alloys and high chromium ferritic/martensitic steels have been studied using coincidence Doppler broadening spectroscopy. Specimens were neutron irradiated to 0.11 dpa at two different temperatures, 290 °C and 450 °C. It has been found that the microstructure (ferrite vs. ferrite/martensite), more precisely distribution of dissolved carbon within the matrix, is one of the key factor that affect response of the materials to neutron irradiation. Presence of dissolved carbon within the matrix leads to formation of stable and immobile carbon-vacancy complexes which act as traps for irradiation induced vacancies and therefore, leading to increased formation of vacancy clusters. Impact of carbon-vacancy complexes on defects evolution during neutron irradiation is relevant only for certain irradiation temperatures.

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1. Introduction

Ferritic/martensitic (F/M) high-Cr steels are candidate structural materials for the construction of several components of future Generation IV (GEN IV) reactors, because they are more resistant to irradiation than stainless steels, while offering good thermal and thermal-mechanical properties. Still, despite accumulated research [1–4], the perception on the role that the different alloying elements and their amount have on the mechanical performance of these steels under irradiation is limited. Moreover, the impact of the initial microstructure of steels and alloys on the defect properties formed after irradiation, and their overall contribution to the degradation of the mechanical properties, is not yet fully understood. Initial microstructure is directly related to the amount of dissolved carbon in matrix and its distribution [5]. Carbon easily segregates at dislocations and grain boundaries as well as it binds to neutron irradiation induced defects such as vacancy and interstitial clusters and precipitates [6]. These nanometric complexes obstruct dislocation motion, thereby inducing the hardening and consequently causing embrittlement.

In this study, the Fe–Cr–C alloys with different Cr and C concentrations are investigated to study the influence of the interplay between ferritic and ferritic/martensitic phases to the defect properties in these alloys after neutron irradiation.

2. Materials preparation and experimental technique

Fe–Cr–C alloys were fabricated by vacuum induction furnace melting of industrial Fe (containing carbon) and

appropriate amount of various solutes (added as pure elements) required to reach desired chemical composition. The impurity level is kept below 100 ppm. Besides Fe–Cr alloys, two 9Cr steels were investigated. The commercially available ferritic/martensitic steel T91 and the European Reduced Activation Ferritic Martensitic (RAFM) steel EUROFER97 (E97). E97 was delivered to SCK-CEN from FZK (Germany) and the T91 from CEA/Saclay (France) [7]. Chemical composition of all materials is given in Table 1.

Specimen preparation consisted of surface polishing to a mirror finish with 1 μm diamond paste and chemical etching by $\text{HF} + \text{H}_2\text{O}_2 + \text{H}_2\text{O}$ solution to remove deformed surface layer (≈ 0.05 mm).

Neutron irradiation was performed in the Belgian nuclear reactor 2 (BR2) of SCK-CEN in Mol. The fluence for all samples is calculated to correspond to 0.11 dpa.

The PAS experiments were performed with the coincidence Doppler broadening spectrometer (CDB). The CDB spectra were measured using two Ge detectors. Details of the setup are described elsewhere [8].

3. Results and discussion

Measured materials could be divided into 3 groups according to initial microstructure: specimens Fe, Fe–5Cr–NiSiP, Fe–9Cr (F), Fe–9Cr–NiSiP, Fe–14Cr–NiSiP are ferritic Fe–Cr–C alloys, specimen Fe–9Cr (F/M) is ferritic/martensitic Fe–Cr–C alloy and specimens E97 and T91 are ferritic/martensitic steels. Structure of these dual-phase materials consists of ferrite matrix containing martensitic laths that are created during quenching in prior austenitic grains.

3.1. Non-irradiated

The results of the CDB measurements for non-irradiated materials are given in Fig. 1a. This figure

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Chemical composition of the alloys and steels [wt%].

TABLE I

Material	C	Cr	N	Si	P	Ni	S	Al
Fe*	< 0.005	0.002	< 0.005	0.001	0.003	0.007	< 0.005	0.023
Fe-5Cr-NiSiP		4.9		0.219	0.033	0.097		0.026
Fe-9Cr (F)		9.1		0.004	0.003	0.009		0.027
Fe-9Cr-NiSiP		9.1		0.212	0.032	0.092		0.028
Fe-14Cr-NiSiP		14.4		0.194	0.031	0.087		0.025

Material	C	Cr	N	Si	P	Ni	V	Mn	S	Ti	Al	O
Fe-9Cr (F/M)	0.02	8.4	0.015	0.09	0.012	0.07	0.002	0.03	0.0007	0.0034	0.0069	0.066

Material	C	Cr	N	Si	P	Ni	V	Ta	W	Mn	Mo
E97 (F/M)	0.12	8.96	0.016	0.07	< 0.005	0.07	0.19	0.13	1.1	0.43	–
T91 (F/M)	0.1	8.32	0.03	0.32	0.02	0.24	0.24	–	< 0.01	0.43	0.96

indicates that steels exhibit somewhat higher S parameter and lower W parameter compared to the Fe-Cr-C alloys, i.e. containing more vacancy type defects. This is probably due to the fact that they have more complex chemical composition and higher dislocation density. Another factor that could affect the S parameter is the microstructure of the materials, as could be seen in Fig. 1a, where all three materials with ferritic/martensitic microstructure exhibit higher values of the S parameter compared to ferritic materials.

3.2. Irradiation at $T = 290^\circ\text{C}$

All materials irradiated at 290°C (Fig. 1b), exhibit an increase of the S parameter and a decrease of the W parameter compared to the non-irradiated condition. In general, the S parameter can be affected by both the number density and the size of vacancy-type defects [9], so this enhancement of the S parameter indicates that positrons are trapped and annihilate at vacancy-rich complexes induced by neutron irradiation.

The most interesting observation is the change of the S parameter for specimens Fe-9Cr (F) and Fe-9Cr (F/M) after being irradiated at 290°C (Fig. 1b) compared to the non-irradiated state (Fig. 1a). In the non-irradiated case, F/M Fe-9Cr exhibits more open volume defects than Fe-9Cr with pure ferritic microstructure. In the contrary, after irradiation at 290°C opposite behavior occurs and specimen Fe-9Cr (F) has significantly more open volume defects than Fe-9Cr (F/M). This results indicates that initial microstructure of alloys, in particular dissolved carbon distribution, plays an important role in terms of defects evolution after neutron irradiation. It is known from accumulated research that carbon and vacancies strongly interact and form stable carbon-vacancy (CVa) complexes such as CVa, C_2Va , C_4Va_2 and bigger ones. These complexes act as traps for gliding interstitial dislocation loops and vacancies, thereby preventing them from reaching sinks (grain boundaries and dislocations) [10–12]. Internal friction (IF) and magnetic after-effect (MAE) studies revealed that, as manifestation of the different initial microstructure, C atoms were distributed differently within the matrix of the pure ferritic vs. ferritic/martensitic alloys [5]. Namely, while in

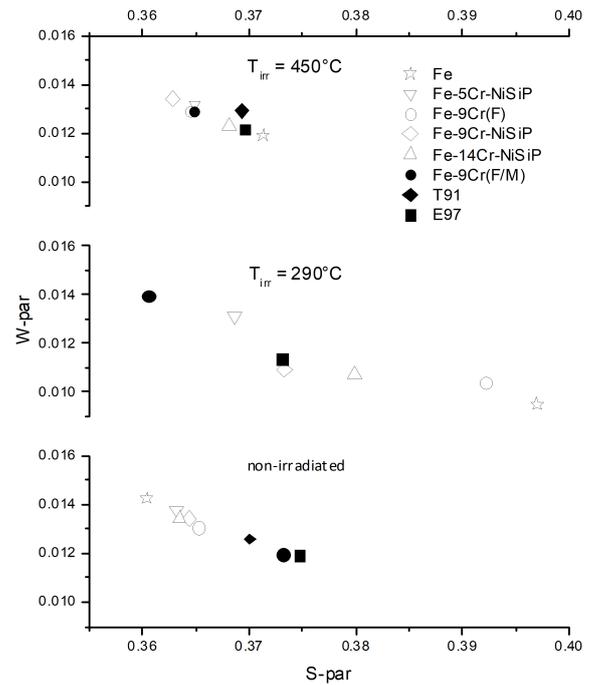


Fig. 1. W parameter as function of the S parameter for the non-irradiated state, irradiation at 290°C and irradiation at 450°C .

the ferritic alloy most of the C atoms were distributed uniformly within the matrix, in ferritic/martensitic alloy the matrix was virtually free of C, where most of it had segregated at the martensite lath boundaries and grain boundaries. So, in the case of Fe-9Cr (F/M) alloy irradiation induced defects, especially vacancies, easily glide towards sinks such as grain boundaries and lath boundaries. While in the case of Fe-9Cr (F) alloy, these irradiation induced vacancies stick to C atoms, which are uniformly distributed in the matrix and ready to interact with irradiation defects, creating very strong and stable CVa defects with high dissociation energies, e.g. as established from the DFT calculations for a vacancy-carbon pair it is 1.12 eV. Because of formation of these CVa complexes, which prevent irradiation induced vacancies from

gliding and reaching the sinks, combined with relatively low migration energy of a single vacancy (≈ 0.64 eV from DFT calculations) [13] compared to migration energy of CVa complexes, new vacancies are easily attached and therefore promoting vacancy cluster to grow. Therefore this might be the explanation for the relatively high increase of the S parameter in Fe–9Cr (F) compared to Fe–9Cr (F/M).

In general, the lowest value of the S parameter is observed in Fe–9Cr (F/M) alloy, while alloys with comparatively same amount of Cr, but with pure ferritic microstructure (Fe–9Cr (F), Fe–9Cr–NiSiP) exhibit higher values of the S parameter. Ferritic alloys Fe–5Cr–NiSiP, Fe–9Cr–NiSiP and Fe–14Cr–NiSiP exhibit lower values of the S parameter which means that they contains less open volume defects than other ferritic alloy Fe–9Cr (F). Decrease of the S parameter occurred because of more complex chemical composition of the alloys Fe–5Cr–NiSiP, Fe–9Cr–NiSiP and Fe–14Cr–NiSiP, containing more solute atoms than Fe–9Cr (F) which act as additional sinks for irradiation induced vacancies to recombine.

3.3. Irradiation at $T = 450^\circ\text{C}$

The results of the CDB measurements for alloys irradiated at 450°C are given in Fig. 1c. As could be seen from the figure, values of the S parameter practically decreased to level of non-irradiated alloys. Also the significant difference in S parameter of Fe–9Cr (F) alloy and Fe–9Cr (F/M) alloy from Fig. 1b has vanished and both exhibit almost identical values of the S parameter. This general decrease of the S parameter and equalling the values of S parameter for Fe–9Cr (F) and Fe–9Cr (F/M) alloys after irradiation at high temperatures may present another confirmation of the theory that the evolution of open volume defects after neutron irradiation is highly dependent on the initial microstructure, since as reported by various authors CVa complexes dissolve at $400\text{--}430^\circ\text{C}$ [10, 14]. If irradiation is performed above this temperature, dissociation of highly stable and immobile CVa complexes occurs and irradiation induced vacancies are not trapped therefore could easily migrate towards the sinks and disappear — no vacancy clustering occurs.

4. Summary and conclusion

In this work, neutron irradiated Fe–Cr–C alloys with various Cr concentration (≈ 5 , ≈ 9 , and $\approx 14\%$ Cr) and different initial microstructure (pure ferritic and ferritic/martensitic) which is characterized by a different distribution of C atoms in the matrix have been investigated by CDBS measurements. It turns out that values of the S parameter, which corresponds to number density/size of the open volume defects, is higher for the alloys with pure ferritic than alloys with ferritic/martensitic initial microstructure after the irradiation to 0.11 dpa at 290°C . Based on the results, an important correlation between initial microstructure, in particular dissolved carbon distribution, and evolution of vacancy type defects after neutron irradiation could be

highlighted. The presence of C atoms in a ferritic microstructure promotes the formation of vacancy clusters in the investigated alloys due to the formation of stable and immobile CVa complexes which act as traps for irradiation induced vacancies and prevent them from reaching the sinks, therefore these vacancies could coalesce and create vacancy clusters. On the contrary, alloys with ferritic/martensitic initial microstructure exhibit lower S parameter values suggesting suppressed formation of vacancy clusters due to the absence of C atoms in the matrix (C atoms are segregated at lath/grain boundaries) and inability to create CVa complexes. This theory is also supported by the CDBS results from alloys irradiated to 0.11 dpa at 450°C , where all alloys independently of initial microstructure exhibit S parameter values comparable to non-irradiated condition caused by the dissociation of stable CVa complexes at such high irradiation temperature. This suggest that the presence of C atoms in the matrix may counteract the positive effect of Cr in terms of swelling suppression for neutron irradiation at temperatures below $\approx 400\text{--}430^\circ\text{C}$. At this temperature, dissociation of CVa complexes occurs and C does not play role in terms of void formation anymore.

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