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Characterization of neutron-irradiated ferritic model alloys and a RPV steel from combined APT, SANS, TEM and PAS analyses

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ABSTRACT

Understanding the behavior of reactor pressure vessel (RPV) steels under irradiation is a mandatory task that has to be elucidated in order to be able to operate safely a nuclear power plant or to extend its lifetime. To build up predictive tools, a substantial experimental data base is needed at the nanometre scale to extract quantitative information on neutron-irradiated materials and to validate the theoretical models. To reach this experimental goal, ferritic model alloys and French RPV steel were neutron irradiated in a test reactor at an irradiation flux of 9×10^{17} nm^{-2} s, doses from 0.18 to 1.3×10^{24} nm^{-2} and 300 °C. The main goal of this paper is to report the characterization of the radiation-induced microstructural change in the materials by using the state-of-the-art of characterization techniques available in Europe at the nanometre scale. Possibilities, limitations and complementarities of the techniques to each other are highlighted.

1. Introduction

The application of experimental techniques to the microstructural characterization of neutron-irradiated ferritic model alloys of increasing complexity has contributed to the mechanistic understanding of irradiation embrittlement of reactor pressure vessel (RPV) steels [1]. Simultaneously, modeling in this field has been characterized by the evolution from empirical models of prediction of the ductile to brittle transition temperature (DBTT) shift [2], via mechanistically-based correlations (MBC) [3,4] to multi-scale multi-physics (MSMP) models [5,6]. The latter aim at being sufficiently reliable to be safely extrapolated to never tested conditions, especially high doses. The availability of models of this type will also help reducing the amount of experiments needed, thereby reducing the need to produce, handle, test and store radioactive materials. To be applied to irradiation embrittlement, dedicated experiments on ferritic model alloys are required to identify the basic mechanisms responsible for embrittlement and to constitute a thorough experimental validation of the submodels at the appropriate time and space scale. These models are supposed to be developed fully based on physical considerations, without fitting. The validation provides thus an indication of whether all relevant mechanisms have been understood and introduced or not. In this context, the European PERFECT project was initiated [7] to bring together the knowledge gained in Europe and abroad from the various disciplinary involved in the phenomena of radiation effects on the mechanical performance of reactor pressure vessel steels. The approach adopted was to investigate Fe-base materials of increasing complexity irradiated in a test reactor. The main goal of this paper is to report on the nanometer-scale characterization of these materials.

Among the experimental techniques able to detect the irradiation-induced microstructural changes at this scale, atom probe tomography (APT), small-angle neutron scattering (SANS), transmission electron microscopy (TEM) and positron annihilation spectroscopy (PAS), play a particular role. It turned out that, because of the complexity of the problem as well as particular strengths and weaknesses of the individual techniques, there is no single method capable of solving all the related issues. Therefore, combinations of two or more techniques were applied to the materials in order to get a more complete picture including composition, morphology

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and distribution of the irradiation-induced features [8–13]. Few investigations in the literature make use of a synergistic combination of the results obtained from different methods (e.g. [9]). The aim is to demonstrate the complementarity of different techniques as well as synergisms while focusing on combinations between APT, SANS, TEM and PAS.

These methods as well as the compositions and the irradiation conditions of materials [14] are briefly introduced in Section 2. Section 3 is devoted to the results obtained by each individual technique (APT, SANS, TEM and PAS). They are individually described in Refs. [15–18]. The whole set of results is exploited in Section 4 in order to obtain a coherent picture of irradiation damage in the present case and of the effects of dose and of the alloying elements, mainly Cu, Mn and Ni.

2. Experimental details

2.1. Materials and irradiation conditions

Fe-base alloys with increasing complexity were studied: Pure iron, low copper Fe–0.1 Cu (wt.%), high copper Fe–0.3 Cu, copper-free Fe-1.2 Mn–0.7 Ni, Fe–0.1 Cu–1.2 Mn–0.7 Ni and a 16MND5 RPV steel. The materials were prepared using argon-arc melting and zone refinement methods, starting from electrolytic iron. The resulting ingots were cold-worked after austenization tempering. A final heat treatment at 1075 K for 1 h was performed to release the stresses and to get well-recrystallized materials. The resulted model alloys were essentially composed of ferrite grains having a size ranging from 50 to 200 μm when going from the quaternary alloy (FeCuMnNi) to pure Fe. The average initial dislocation density was very similar in all alloys of about 5×10^{13} m^{-2}.

The nominal compositions of the fabricated materials were controlled by chemical analysis (CA). The results are given in Table 1. They were performed at EDF R&D (France) by ICP/MS (Induced Coupled Plasma/Mass Spectrum), except for the free carbon within the matrix, measured by internal friction at SCK-CEN (Belgium). The compositions were checked by APT analysis at the University of Rouen (France) before irradiation in the Fe–0.1Cu, FeMnNi, FeCuMnNi model alloys and in the RPV steel. CA and APT measurements performed in the Fe–0.1Cu and FeMnNi alloys are in good agreement. In the FeCuMnNi alloy, the APT measurements gave lower values than CA. The difference is most probably due to the non-homogeneous distribution of the alloying elements in the whole produced ingots. While in the case of the RPV steel, the observed depletion in Mn and C is certainly due to the presence of carbides, observed by TEM. Furthermore, the APT analyses were used to check the initial distribution of the solutes known to precipitate under irradiation (Cu, Mn, Ni and Si). The statistical χ^2 test confirmed their homogeneous distribution at the nanometer scale before irradiation.

The neutron irradiation was conducted at 300 °C and 150 bars in the CALLISTO loop of the BR2 test reactor at SCK-CEN (Mol, Belgium) to mimic the temperature and pressure of RPV steels in PWR reactors. The materials were wrapped tightly in steel capsules to avoid their contact with the cooling water and to ensure a high thermal conductivity in the whole capsule. The average temperature measured by the numerous thermometers (more than 14 per capsule) was (300 ± 5) °C. The specimens were exposed to a constant neutron flux of 9×10^{17} nm^{-2} s^{-1} ($E > 1$ MeV). The reached neutron doses were determined via the analysis of the multiple flux monitors that were inserted in each capsule. Four irradiation campaigns have been performed to accumulate increasing doses ranging from 0.18 to 1.3×10^{24} nm^{-2} ($E > 1$ MeV). In terms of displacement per atom (dpa) and by using the widely accepted cross-section of 1500 barns for neutrons of energy higher than 1 MeV, these conditions correspond to a dose rate of about 1.4×10^{-7} dpa s^{-1} and to four doses (0.025, 0.05, 0.1 and 0.2 dpa). It is worth mentioning that 0.1 dpa corresponds to about 40 years of operation of pressurized water reactors. A more detailed description of the materials including exact material compositions, irradiation conditions and mechanical characterization before irradiation can be found in Ref. [14].

The investigation by means of the four microstructural characterization methods involved was not conducted for the whole set of materials. For the sake of clarity, the conditions studied by every characterization technique are gathered in Table 2.

2.2. Atom probe tomography (APT)

The kinetic of solute clustering after irradiation was followed by APT [19]. This technique is known to be a very efficient tool for the chemical analyses of solute-enriched clusters. Their characteristics – number density, size and composition – as well as the matrix composition are accurately determined in the volume accessible. Analyses were performed at set-up developed at the University of Rouen (France). To reduce the energy spread of emitted ions, they were conducted with an energy compensating device (a reflectron lens). Furthermore, to avoid the preferential evaporation of copper, the experiments were carried out at a cryogenic temperature of 50 K and with an electrical pulse fraction of 20% of the standing voltage. All the experiments were performed with a pulse rate limited to 0.03 atom/pulse to reduce the risk of failure of the needle-shape sample. The analyzed volume was typically $15 \times 15 \times 100$ nm^3 for each sample. More details about the treatment of the data and how to get the essential information out of them can be found in Ref. [15].

Table 1
Nominal compositions of the ferritic alloys and of the RPV steel obtained by chemical analyses (CA) and AP measurements. AP measurements in the 16MND5 RPV steel revealed also the presence of Mo, Al, Cr and Co with a respective content of 0.39 ± 0.04, 0.02 ± 0.01, 0.24 ± 0.01 and 0.03 ± 0.01 at.% in agreement with the literature [55–57].

Material	at.%	Cu	Mn	Ni	C	P	Si
Pure iron	CA	<0.004	0.007	<0.005	<0.01	0.01	0.009
Fe–0.1Cu	CA	0.079	0.010	<0.005	<0.01	0.011	0.01
	AP	0.085 ± 0.006	–	–	–	0.0045 ± 0.001	–
Fe–0.3Cu	CA	0.28	0.006	<0.005	<0.01	0.014	<0.009
FeMnNi	CA	<0.005	1.11	0.71	<0.01	0.009	<0.01
	AP	–	1.12 ± 0.02	0.73 ± 0.01	–	0.0045 ± 0.001	–
FeCuMnNi	CA	0.092	1.11	0.68	<0.01	0.009	<0.01
	AP	0.068 ± 0.006	0.98 ± 0.02	0.57 ± 0.02	–	0.0034 ± 0.0015	–
16MND5	CA	0.056	1.31	0.71	0.65	0.013	0.385
	AP	0.05 ± 0.01	1.07 ± 0.06	0.6 ± 0.05	0.048 ± 0.01	0.008 ± 0.006	0.48 ± 0.04