Nanostructured Fe–Cr–W Steel Exhibits Enhanced Resistance to Self-Ion Irradiation

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Abstract. This paper presents a study on radiation-induced defect structures in a reactor Fe-14Cr-1W (wt. %) steel with grain sizes of 5 μm and 110 nm. Self-ion irradiation of the steel in both states was carried out with a damage dose of 10 dpa. Microstructure characterization shows that the density of intragranular radiation-induced dislocations is significantly lower in case of the nanostructured material. From the results obtained it follows that microstructure refinement to a grain size of about one hundred nanometers can be effectively used to approach a problem of higher defect production rate in Fe-Cr steels driven by irradiation and to produce alloys with significantly enhanced mechanical performance as well as radiation tolerance.

Ferritic/martensitic steels based on the Fe-Cr system are attractive for nuclear engineering applications due to high strength, low swelling and good thermal stability.[1] Additional capacity to enhance the radiation tolerance together with mechanical performance of engineering alloys can be realized by microstructure design via different approaches to increase the density of internal sinks for radiation-induced point defects.[2,3]

Nanostructuring techniques based on severe plastic deformation are able to produce bulk fine-grained samples of metals and alloys with enhanced multifunctional properties (strength, conductivity, biocompatibility, corrosion resistance, shape memory effect, fatigue properties and so on) [4] making them attractive for innovative applications (for medicine, energy, automotive industries and so on) [5], in particular, for those requiring advanced materials with elevated radiation tolerance.[3]

The aim of this work was to explore the potentiality of this approach to expand the limits of radiation tolerance enhancement of steels of the Fe-Cr system. Recently we showed that in a model Fe-Cr-W alloy it is possible to reduce grain size down to about 100 nm using severe plastic deformation by high pressure torsion, that resulted in a significant enhancement of mechanical performance.[6] One may then expect that such microstructure refinement would also improve the radiation tolerance thanks to enhanced defect annihilation rate provided by drastically increased number of grain boundaries. This is an important task for the alloys of a Fe-Cr system because Cr is known to suppress swelling and at the same time to increase the defect accumulation rate induced by irradiation [7] that provides high radiation strengthening together with significant reduction in ductility of irradiated alloys down to embrittlement at high Cr concentration (18 wt%). [8]

The present paper features the results of a study undertaken to evaluate the effect of ion irradiation in a Fe-14Cr-1W (wt. %) steel with different grain size. As it has been already reported in our previous publication [6], high pressure torsion of a Fe-14Cr-1W steel with an initial grain size of 5 μm provided severe microstructure refinement to a mean grain size of 110 nm with an aspect ratio of about 2 (165×70 nm). The fraction of low angle grain boundaries did not exceed 20%. As a result, the mechanical performance had been dramatically enhanced. The microhardness was notably increased (from 230 Hv to 640 Hv); the yield stress changed from 270 to 1670 MPa and ultimate tensile stress – from 530 to 1885 MPa.[6] In frames of this study the same two states of Fe-Cr-W steel with different grain size were subjected to self-ion irradiation to a damage dose of 10 dpa at a temperature of 400 °C. Following the research by Aydogan et al[9], it is critical to ensure the stability of microstructure under irradiation conditions, otherwise recovery processes of nanostructured state would interfere with accumulation of point defects and lead to faster degradation of the fine-grained specimen. **Figure 1** presents the results of *in-situ* STEM observations on microstructure of nanostructured Fe-14Cr-1W steel subjected to annealing at different temperatures from 300 to 700 °C during ten minutes (Figure 1a-f). It is clear that the nanostructured steel does not exhibit visible changes in grain size and defect configuration after annealing up to 400 °C, while enhanced diffusion near free surface would impact their mobility to make simultaneous contribution to combined thermal and irradiation effects. Slight defect re-arrangement is observed at annealing of 500 °C and after annealing at higher temperatures recrystallization takes place. This is well consistent with our earlier results on the same steel processed under the same conditions published in [6] where it was shown that microhardness of HPT Fe-14Cr-1W steel does not change until annealing at 500 °C for 1 hour. Certain decrease in microhardness value was observed only after annealing for 1 hour at 550 °C. Thus, it is reasonable to suppose that the microstructure of the HPT-produced Fe-Cr-W steel can be considered as stable at the temperature used for the irradiation experiment (400°C).

Electron microscopy examination of microstructure showed that the grain size of the as-received steel did not significantly change during ion irradiation, while for the nanostructured material a slight increase occurred. **Figure 2** displays the results of Electron Backscatter diffraction (EBSD) measurements for the nanostructured Fe-Cr-W steel before (Figure 2a) and after (Figure 2b) irradiation. The derived quantitative data (Figure 2c) reveals that the equivalent grain size grows from 110 nm to 185 nm as a result of irradiation at 400°C.

Results of post-irradiation comparative TEM studies of steel in as-received and nanostructured states are summarized in **Figure 3**. Detailed characterization of radiation-induced defects, such as dislocation loops, in BCC metals requires specific TEM approaches [10], while in this preliminary study we show that the change in dislocation density and configuration after irradiation is striking in as-received and nanostructured materials.

The first results of post-irradiation investigations reported below have rather qualitative but unambiguous character; they require more detailed analysis, also with the help of the other techniques (such as atom probe tomography to account for clustering effects) – this is planned in frames of the future publication activity.

A panoramic image of the as-received Fe-Cr-W (Figure 3b) shows that the irradiation leads to a formation of dislocation networks of high density within the initial grains. The average dislocation density was estimated as 7×10^{14} m^{-2}. This observation is in contrast with the TEM image of un-irradiated area of a coarse-grained alloy (Figure 3a). The microstruture of a hot-extruded alloy contains significant amount of dislocations, however, their density is visibly orders of magnitude less than in an irradiated material and they are mostly situated near grain boundaries.

TEM observations of irradiated nanostructured Fe-Cr-W showed that ion bombardment led to the slight increase in the average grain size (from 110 to about 180 nm) which is in agreement with EBSD data (Figure 2). Figure 3c shows that dislocation pile-ups in the grain interior apparently did not appear. Further high magnification TEM studies revealed an appearance of radiation-induced defects within the nano-scaled grains with the density of about 6×10^{12} m^{-2} (Figure 3d).

These findings are consistent with the earlier data collected for nanostructured stainless[11], low-carbon[12] and ferritic/martensitic[13] steels. Smaller grain sizes promote enhanced

recovery of vacancies and interstitials created by irradiation, and this effect can be more pronounced at elevated temperatures. [14] The increased radiation tolerance of nanostructured steels was confirmed not only by high dose rate ion irradiation experiments, but also by testing of ultrafine-grained steels under neutron irradiation in the research nuclear reactor. [15]
In conclusion, the comparative microstructural study of the ion-irradiated Fe-14Cr-1W (wt. %) steel with grain sizes of 5μm and 110 nm shows that the nanostructured material exhibits a lower tendency to form radiation-induced defects together with a higher mechanical strength. Self-ion radiation of the nanostructured steel led to a slight increase in grain size (from approximately to 110 to 185 nm),while the measured dislocation density was 6×10^{12} m^{-2} against 7×10^{14} m^{-2} in an irradiated coarse grained material (as-received). The study conducted on the example of Fe-Cr-W steel shows that nanostructuring provides substantial reduction in defect production under ion irradiation and can be useful to produce alloys with significantly enhanced mechanical performance as well as radiation tolerance to serve as new advanced materials for nuclear engineering.

Experimental Section

The Fe-14Cr-1W-0.3Mn-0.2Ni-0.3Si (wt.%) steel was chosen as the object of the research. The reference material was produced by CEA LTMEx by powder metallurgy followed by hot extrusion at 1100 °C. The steel was nanostructured by high pressure torsion with 10 revolutions of anvils at a pressure of 6 GPa and a temperature of 350 °C. The produced specimens had a shape of discs 20 mm in diameter and about 0.9 mm in thickness.
The irradiation experiment was carried out using ionic irradiation at 400 °C for 20 hours with Fe^{5+} ions of 10 MeV energy in the "Epiméthée" accelerator of the "JANNUS" facility at the Commissariat for Atomic and Alternative Energy (CEA) in Saclay. The experimental dose and dose rate were 5.0×10^{20} m^{-2} and 7×10^{15} $m^{-2}s^{-1}$. The damage profile was determined based on calculations performed with the "SRIM" program using the Kinchin-Pease approximation.

The implantation peak is located about 2 μm above the surface, and the samples to be studied by TEM were cut from the area, where the damage dose was estimated to be about 10 dpa. TEM studies of microstructure in the as-received state of a material were conducted using the JEOL JEM 2100 microscope at an accelerating voltage of 200 kV. Samples for post-irradiation TEM studies were prepared using a focused ion beam (FIB) on a two-beams FEI Strata 400S. The observations were carried out using the NanoMegas ASTAR Automated Crystal Orientation Mapping (ACOM) system on the Philips Tecnai F20ST @ 200kV, operating in the μp-STEM mode. Electron backscatter diffraction (EBSD)data were obtained with a SEM Zeiss XB540 from the Genesis platform. As an EBSD detector, the EDAX Digiview camera was used. Grain size was calculated as the equivalent grain size determined from grain surface assuming that they are spherical. *In-situ* TEM experiments were conducted on a JEOL ARM 200CF microscope from the Genesis platform operated at 200kV. Thin foils were prepared by electropolishing and observed in a double tilt heating holder (Gatan 652 MA). Images were recorded in scanning mode (STEM) using a bright field (BF) detector. The dislocation density was determined by counting the number of dislocations intersections with random lines of known length (secant method) and using the equation: $\rho=2N/Lt$, where ρ is the dislocation density, N is the number of intersections, L is the length of lines and t is the sample´s thickness. The thickness of the sample foil was measured from the electron energy loss spectrum and was about 60-70 nm (via a standard procedure in Gatan Digital Micrograph). We determined the dislocation density from five images of the samples structure.

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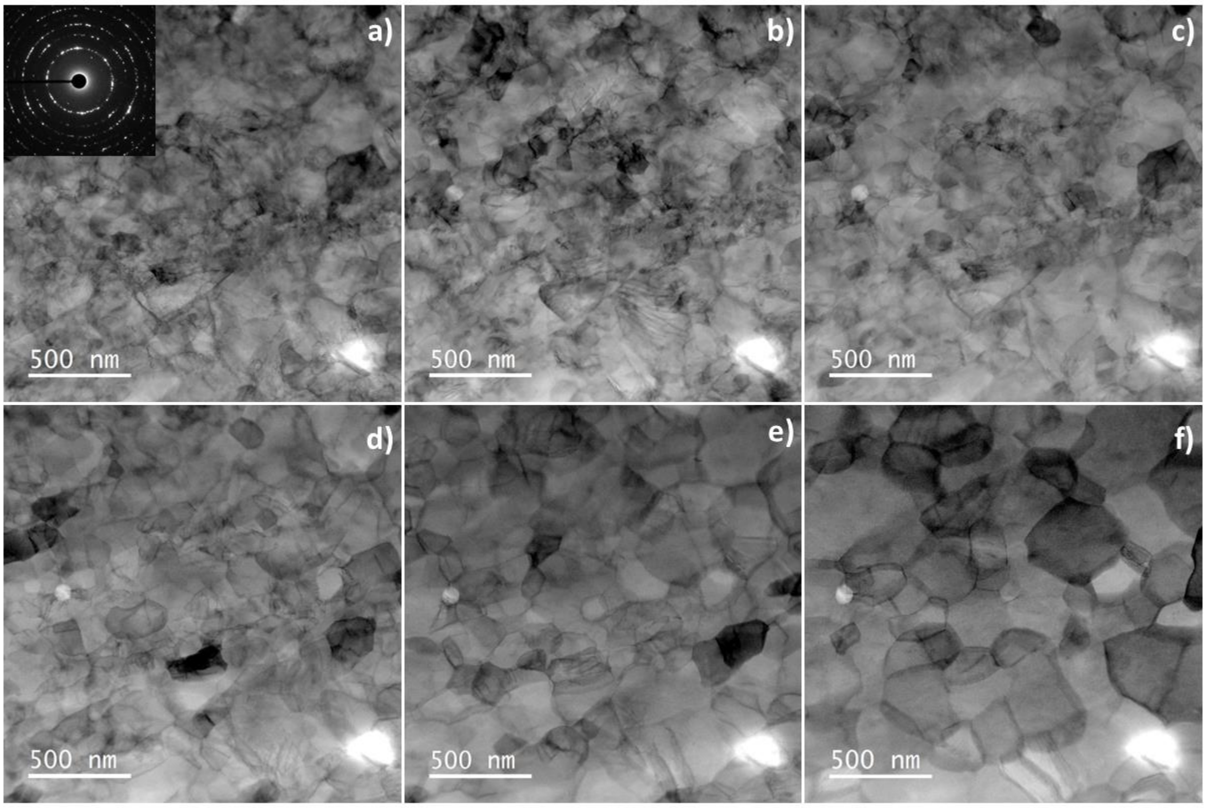
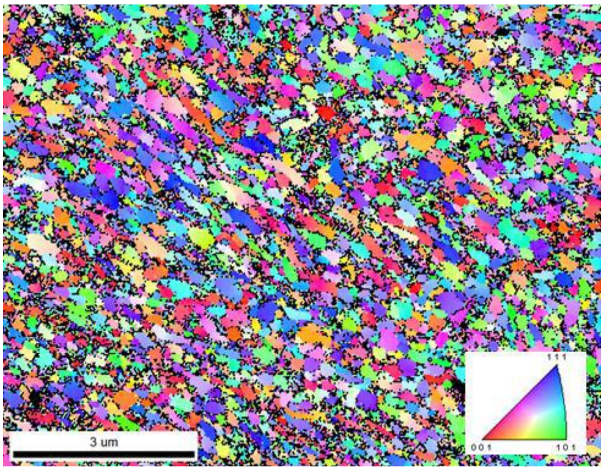
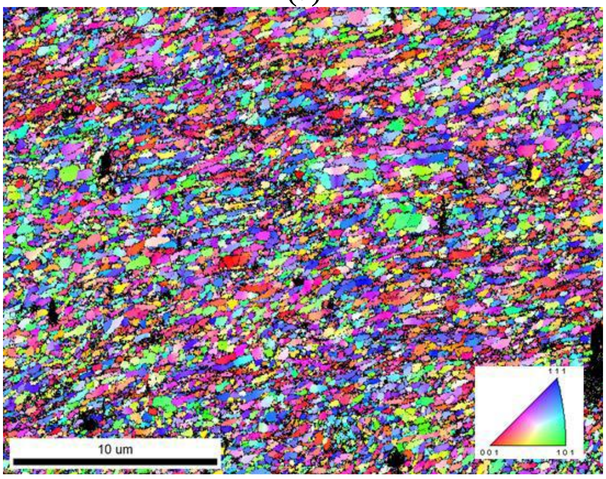


Figure 1. STEM-BF observations of changes in microstructure evolution during in situ annealing of nanostructured Fe-14Cr-1W steel. Initial state (a) after 3 min at 300 ˚C (b), 10 min at 400 ˚C (c), 20 min at 500 ˚C (d), 15 min at 600 ˚C (e), 15 min at 700 ˚C (f). Same location on all images, the position was tracked by following the small hole at the bottom right of the image (bright contrast).



(a)



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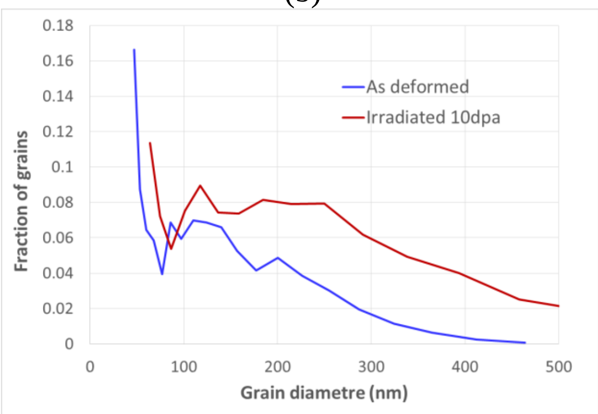

(c)

Figure 2. Radiation-induced grain growth in a nanostructured Fe-14Cr-1W steel as revealed by EBSD examination (raw data are presented): as-deformed state (a), as-deformed state after irradiation (b) and comparative plot for the grain size distribution in both states.

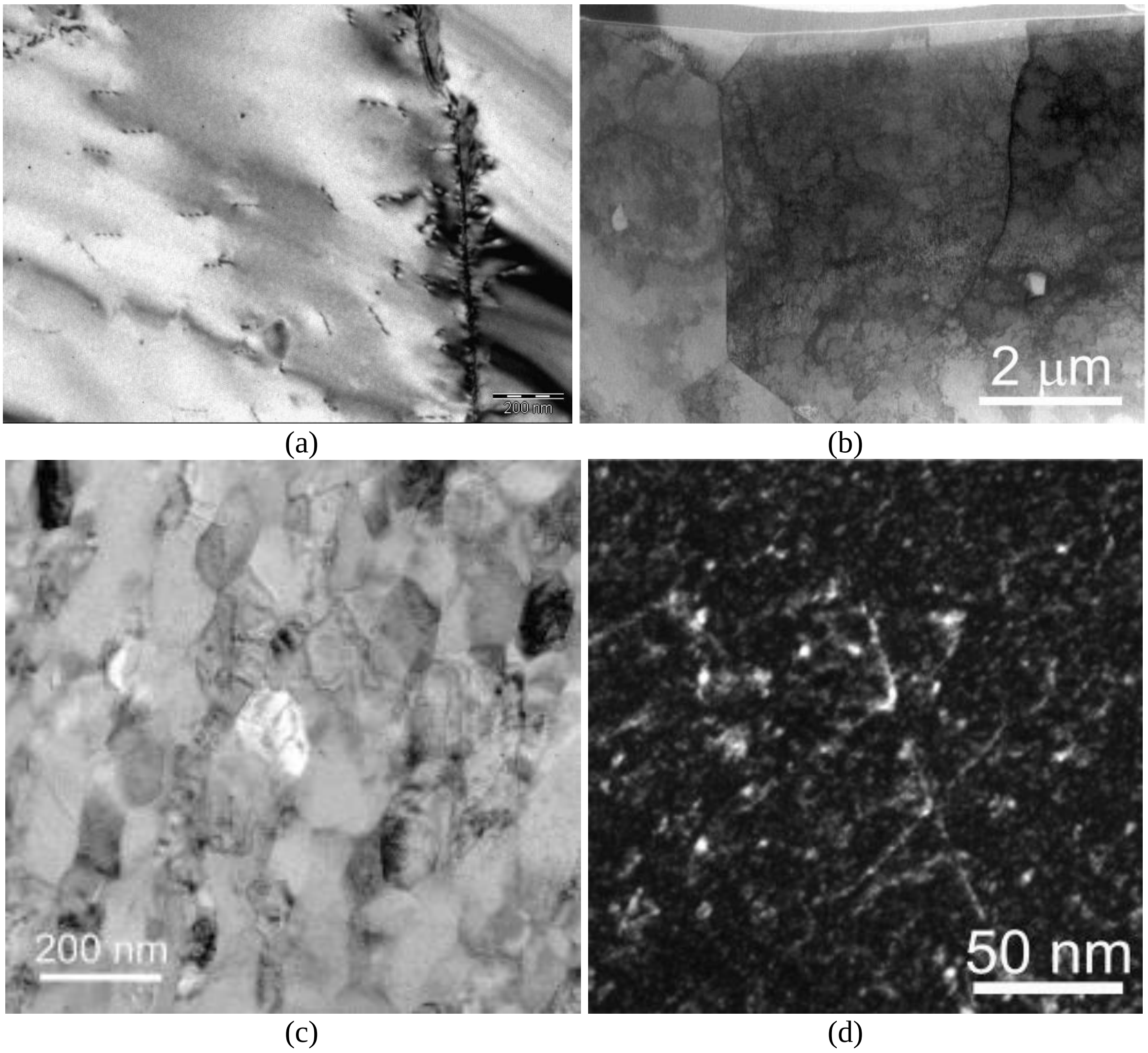

Figure 3. TEM images showing microstructure of as-received Fe-Cr-W before (a) and after irradiation (b); as well as microstructure of the Fe-Cr-W in the nanostructured state after irradiation (c). Higher magnification dark-field (in a weak beam) TEM image of the nanostructured Fe-14Cr-1W steel after irradiation showing radiation-induced intragranular dislocations (d).

This paper shows that nanostructured Fe-14Cr-1W (wt. %) steel with a grain size of about 110 nm exhibits notably higher resistance to self-ion irradiation to a damage dose of 10 dpa than the steel with the grain size of 5 µm. After ion bombardment the nanostructured material contains intragranular dislocations with the density lower by about two orders of magnitude than the as-received steel.

Keywords radiation resistance, ferritic/martensitic steel, nanostructured materials, defect structure

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