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# Effect of high dose/high temperature irradiation on the microstructure of heat resistant 11Cr ferritic/martensitic steels

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ABSTRACT

Eleven Cr ferritic/martensitic steels with improved high temperature properties (PNC-FMS) were thermally-aged and neutron-irradiated. To understand the thermal-aging and the irradiation effects on their microstructural developments, microstructural observation was made. From the detailed observations and microchemical analyses, the following points were obtained. (1) When irradiated at 400–450 °C to doses up to 94.6 dpa, both dislocation loops and cavities formed in the ferrite phase region. But void swelling was estimated as 0.05% at the most. (2) When irradiated at moderate temperatures of 500–600 °C, $M_{23}C_6$ and $M_6C$ grew and entirely covered the prior austenite grain (PAG) boundaries, suggesting that carbide precipitation on the PAG boundaries contributed to the extended time periods of recovery of martensite laths. (3) When irradiated at high temperatures above 650 °C, formation and growth of equi-axial grains occurred in addition to the complete recovery of martensite laths and the huge growth of carbides.



## 1. Introduction

If ferritic/martensitic (F/M) steels capable of use at higher temperatures could be developed, they would be attractive for fusion power systems and could also be used for core component applications in fast reactors.

Under a fast reactor development project in Japan, 11Cr F/M steels with improved high temperature properties (PNC-FMS) were developed in the 1990s. In previous publications, mechanical properties of the PNC-FMS irradiated with and without fuel conditions were reported [1,2]. These works evaluated the neutron irradiation effects on tensile and transient burst properties of the steels and it was found that no significant degradation occurred in both tensile and transient burst strengths after neutron irradiation to 89 dpa below 600 °C.

Therefore, the present work focuses on microstructure in the PNC-FMS in order to understand the neutron irradiation effects on it.

## 2. Experimental procedures

The chemical composition of the PNC-FMS was 11Cr–0.5Mo–2W–V, Nb in wt%. The composition and the heat treatment conditions are shown in Table 1.

Irradiations were carried out of PNC-FMS cladding tubes at fuel-free condition in the experimental fast reactor (JOYO) at Oarai Research and Development Center (ORDC) and also in the Fast Flux Testing Facility (FFTF). A thermal-aging experiment was also conducted to elucidate thermal effects on the microstructural development. Irradiation and thermal-aging conditions are listed in Table 2.

Microstructural characterization was done with an electron microscope (JEM-4000FX) operated at 400 kV and an energy dispersive spectrum (EDS) device mounted on the electron microscope.

## 3. Results

Numerous micrographs were obtained from microstructural observations and the data on characteristics of the microstructure of as-received, thermally-aged, and irradiated PNC-FMS are summarized in Tables 3 and 4.

The microstructure of the as-received PNC-FMS consisted of martensite laths about 0.3 μm wide and ⩾5 μm long, containing dislocations with a density of $\sim 1.56 \times 10^{14}\ m^{-2}$. The microstructure also included carbide precipitates located on prior austenite grain (PAG) boundaries and packet boundaries, and also ⩽5% of δ-ferrite.

In both microstructures irradiated in FFTF at 405 °C and in JOYO at 451 °C (designated FFTF405 and JOYO451, respectively), fine voids formed in each ferrite region, accompanying the dislocation

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**Table 1**
Chemical composition and heat treatment conditions of PNC-FMS steels (mass%).

| Lot | C | Si | Mn | P | S | Ni | Cr | Mo | W | N | Nb | V | Fe |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| 61FS | 0.10 | 0.07 | 0.54 | 0.002 | 0.002 | 0.32 | 11.05 | 0.45 | 1.89 | 0.04 | 0.06 | 0.21 | Bal. |

Heat treatment conditions: 61FS, Normalized at 1100 °C for 10 min and then tempered at 780 °C for 60 min.

**Table 2**
Neutron irradiation and thermal-aging conditions of PNC-FMS (61FS).

| Specimen ID | Irradiation (thermal-aging) temperature (°C) | Neutron fluence (n/m$^2$) | Displacement damage level (dpa) | Duration (h) | Remarks |
|---|---|---|---|---|---|
| TA410 | 410 | – | – | 24000 | Thermal-aging |
| TA495 | 495 | – | – | 24000 | Thermal-aging |
| TA550 | 550 | – | – | 24000 | Thermal-aging |
| TA605 | 605 | – | – | 24000 | Thermal-aging |
| FFTF405 | 405 | $21.5 \times 10^{26}$ | 94.6 | 19908 | FFTF/MOTA |
| FFTF495 | 495 | $12.8 \times 10^{26}$ | 53.2 | 19594 | FFTF/MOTA |
| FFTF550 | 550 | $22.2 \times 10^{26}$ | 97.2 | 19577 | FFTF/MOTA |
| FFTF605 | 605 | $23.1 \times 10^{26}$ | 101.5 | 19484 | FFTF/MOTA |
| FFTF670 | 670 | $23.4 \times 10^{26}$ | 103.0 | 19567 | FFTF/MOTA |
| JOYO451 | 451 | $15.5 \times 10^{26}$ | 77.5 | 23808 | JOYO/CMIR |
| JOYO493 | 493 | $17.7 \times 10^{26}$ | 88.5 | 19956 | JOYO/CMIR |
| JOYO665 | 665 | $18.3 \times 10^{26}$ | 91.5 | 19956 | JOYO/CMIR |

**Table 3**
Summary of microstructural analyses of the as-received, the aged and the irradiated PNC-FMS steels.

| Specimen ID | Size distribution of prior austenite grain (PAG)[a] (μm) | Average width of martensite laths structure[a] (nm) | Volume fraction of equi-axial recrystallized martensite[b] (%) | Dislocation density[b] (m$^{-2}$) | Remarks |
|---|---|---|---|---|---|
| As-received | 8–15 | 514 | 18.8 | $1.56 \times 10^{14}$ | |
| TA410 | 10–15 | 317 | 35.3 | $1.35 \times 10^{14}$ | |
| TA495 | 10–15 | 403 | 42.9 | $1.15 \times 10^{14}$ | |
| TA550 | 10–20 | 369 | 54.5 | $0.80 \times 10^{14}$ | |
| TA605 | 12–15 | 216 | 71.1 | $0.85 \times 10^{14}$ | |
| FFTF405 | 7–10 | 461 | 47.8 | $0.64 \times 10^{14}$ | Void formation ($\Delta V/V = 0.049\%$) |
| FFTF495 | 7–15 | 464 | 44.4 | $1.21 \times 10^{14}$ | |
| FFTF550 | 6–18 | 472 | 45.0 | $0.62 \times 10^{14}$ | |
| FFTF605 | 12–14 | 426 | 79.5 | $0.51 \times 10^{14}$ | |
| FFTF670 | 14–18 | N.A. | 100 | $1.12 \times 10^{14}$ | |
| JOYO451 | 10–16 | 380 | 46.6 | $2.52 \times 10^{14}$ | Void formation ($\Delta V/V = <0.01\%$) |
| JOYO493 | 9–20 | 410 | 37.0 | $2.23 \times 10^{14}$ | |
| JOYO665 | 13–21 | N.A. | 100 | $0.91 \times 10^{14}$ | |

[a] Area measured was square with $\geqslant 10 \times 10\ \mu m^2$.
[b] Volume was approximately assumed as a rectangular with $10\ \mu m^L \times 10 \mu m^W \times 0.15\ \mu m$th.

structure development. The number density and mean size of voids in both FFTF405 and JOYO451 were $1.0 \times 10^{20}$ and $1.4 \times 10^{19}\ m^{-3}$, and 18.85 and 12.83 nm, respectively. The respective estimated void swellings in these regions, however, were 0.05 and <0.01% (Table 3).

The microstructure of the as-received PNC-FMS and that of specimens thermally-aged or irradiated at moderate temperature are shown in Fig. 1. Comparison of the images showed that existing carbide particles grew and the areas of boundaries wrapped with carbide particles increased due to thermal-aging (Fig. 1(b)) or irradiation. And also the extent of wrapping in the microstructure when irradiated in FFTF (Fig. 1(c)) is quite different from that in JOYO (Fig. 1(d)), indicating the possibility of flux difference effect between FFTF and JOYO on the phase evolution.

Fig. 2 shows microstructural observations obtained from the PNC-FMS specimens thermally-aged at 550 and 605 °C, and from the PNC-FMS specimens irradiated at 550, 605, and 670 °C to around 100 dpa in FFTF. In Fig. 2(a) and (b), it was apparent that the strain within the martensite laths was relaxed and also that the individual precipitates grew with increasing aging temperature. On the other hand, the irradiation at higher temperature significantly affected the microstructural development; in Fig. 2(c), a coalescence of precipitates, mainly carbide particles, occurred homogeneously. When irradiated at 605 °C to 101.5 dpa (Fig. 2(d)), the martensite laths appeared to remain stable locally but heterogeneous growth and spheroidization of precipitates occurred mainly on PAG boundaries. For irradiation at 670 °C, the recrystallized grains nucleated and subsequently grew with precipitate coarsening (Fig. 2(e)).

The precipitates were identified based on the EDS analyses for the microstructure (except for specimens irradiated in FFTF for which there were no such data) and on selected diffraction pattern analyses for the microstructure of all specimens. These results are summarized in Table 4. The principal and most stable carbide formed in the PNC-FMS was $M_{23}C_6$ though $M_6C$ was often found in the same specimens. In addition, Laves phase formation containing W and Mo was identified for the microstructure aged at $\geqslant$550 °C, and for those irradiated at $\geqslant$605 °C.

**Table 4**
Summary of precipitates of the as-received, the aged and the irradiated PNC-FMS steels.

| Specimen ID | Volume fraction of precipitate within laths and sub-grains[a],% | Area fraction of precipitate occupied PAG[b],% | Precipitates | | |
|---|---|---|---|---|---|
| | | | Within laths or sub-grains | On laths or PAG boundaries | Metal elements in precipitates |
| As-received | 0.94 | 41.3 | $M_{23}C_6$ or $M_6C$ | $M_{23}C_6$ or $M_6C$ | FeCrW |
| TA410 | 1.45 | 33.8 | $M_{23}C_6$ or $M_6C$ | $M_{23}C_6$ or $M_6C$ | FeCrWMoSi |
| TA495 | 1.29 | 88.0 | $M_{23}C_6$ or $M_6C$ | $M_{23}C_6$ | FeCrWMo |
| TA550 | 5.44 | 49.7 | $M_{23}C_6$ or $M_6C$ | $M_{23}C_6$ or $M_6C$ and Laves | FeCrWMoSi and FeCrWMo |
| TA605 | 12.01 | 68.2 | $M_{23}C_6$ or $M_6C$ | $M_{23}C_6$ or $M_6C$ and Laves | FeCrWMoSi and FeCrWMo |
| FFTF405 | 2.9 | 44.0 | $M_{23}C_6$ or $M_6C$ | No precipitate | N.A. |
| FFTF495 | 2.54 | 47.0 | $M_{23}C_6$ or $M_6C$ | No precipitate | N.A. |
| FFTF550 | 14.37 | 100 | $M_{23}C_6$ or $M_6C$ | $M_{23}C_6$ | N.A. |
| FFTF605 | 8.38 | 55.3 | $M_6C$ | Laves | N.A. |
| FFTF670 | 8.92 | 32.3 | $M_{23}C_6$ or Laves | Laves | N.A. |
| JOYO451 | 1.36 | 76.7 | MC | MC | FeCrNb |
| JOYO493 | 1.14 | 88.1 | $M_{23}C_6$ | $M_{23}C_6$ or $M_6C$ or MC | FeCrNiNbMo and FeCrNb |
| JOYO665 | 6.26 | 69.4 | $M_{23}C_6$ | Laves | FeCrNbWMo |

N.A.: No data available.
[a] Volume was approximately assumed as a rectangular with $10\ \mu m^L \times 10 \mu m^W \times 0.15 \mu m^{th}$.
[b] Area measured was square with $\geqslant 10 \times 10\ \mu m^2$.

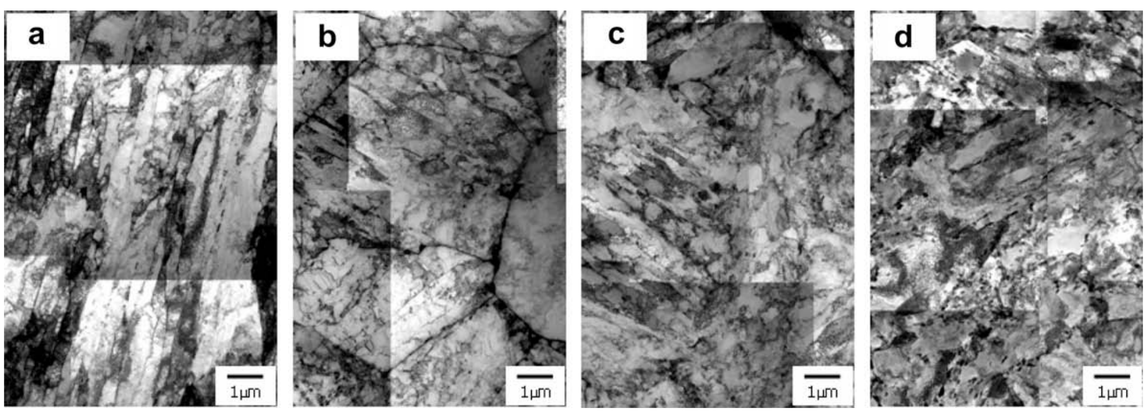


**Fig. 1.** Microstructure of PNC-FMS specimens: (a) as-received, (b) thermally-aged at 495 °C, (c) irradiated in FFTF at 495 °C–53.2 dpa and (d) in JOYO at 493 °C to 88.5 dpa.

## 4. Discussion

Considerable studies on irradiation effects of F/M steels have been made since they were considered to be prospective materials not only for fast reactors but also for fusion reactors. Recently, helpful knowledge and raw data on the F/M steels including the irradiation effects on the mechanical properties and the microstructures were collected from various sources and were reviewed for their practical use [3]. Therefore, the effect of high dose/high temperature irradiation of the PNC-FMS should be discussed with comparable data considered.

HT9 with the composition of 12Cr–1MoVW in wt% is very similar to the PNC-FMS. The compositional differences are in Cr, Mo, and W contents. As stated above, the mechanical properties of the HT9 irradiated in JOYO at 420–550 °C to doses up to ~42.5 dpa were investigated to compare them directly with those of the PNC-FMS [2]. In that work, the difference in their tensile and transient burst strengths was attributed to martensite laths stability which came from a balance of Mo and W contents.

The low-swelling character of the PNC-FMS was demonstrated in this work. The fact that the radiation-induced void swelling at 405 °C to 94.6 dpa was ≅0.05% was thought to be consistent with the result that the HT9 irradiated in FFTF to over 200 dpa at 400–420 °C was <2% [4,5]. As indicated in previous studies on void swelling of 12Cr F/M steels including the HT9 [3–10], it can be deduced that peak void swelling of the PNC-FMS was lying in the temperature range of 400–425 °C or that of lower side [11,12].

In the medium temperature ranges, the mechanical properties of the F/M steels are considered to be closely associated with martensite laths structural stability as well as with radiation-induced precipitate change. Fig. 3 shows histograms of martensite laths width measured from all images in which the microstructure was large enough for statistical comparison (the region with $7.5 \times 7.5\ \mu m^2$ per one specimen at each condition was used for the analysis); this excluded specimens irradiated at temperatures of ⩾665 °C in which martensite laths completely disappeared and recrystallized grains grew. From this analysis and the results on volume fraction of equi-axial recrystallized martensite in Table 3, it was clearly indicated that martensite laths with a broad range of width produced by the initial normalizing and tempering treatments became spheroids due to thermal-aging and irradiation effects, and that the extent of recrystallization significantly depended on the temperature conditions examined.

Additionally, two important changes on precipitation were simultaneously progressing for this temperature range, that is, the Laves phase formation and carbide coarsening. As summarized in Table 4, the Laves phase formation was confirmed as a plate-like shape in the 550 °C-aged microstructure and with blocky shapes in all of the specimens aged or irradiated at temperatures of >600 °C. In addition, $M_{23}C_6$ and/or $M_6C$ carbides were observed to grow preferentially along martensite laths and PAG boundaries where the main diffusion paths for metal alloying elements should be found, suggesting that carbide precipitation on the PAG boundaries contributed to prolongation of recovery of martensite laths. Table 4

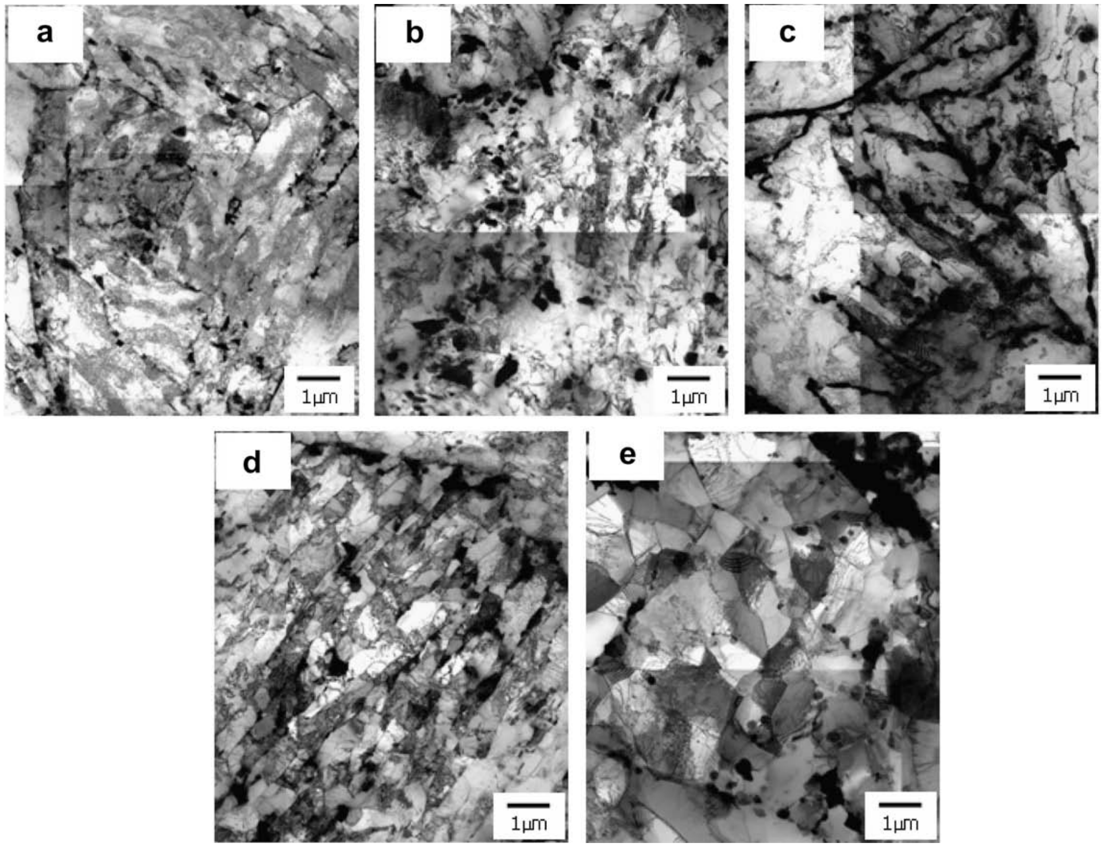


**Fig. 2.** Microstructure of PNC-FMS specimens thermally-aged (a) at 550 °C and (b) at 605 °C, and irradiated in FFTF (c) at 550 °C to 97.2 dpa and (d) at 605 °C to 101.5 dpa and (e) at 670 °C to 103.0 dpa.

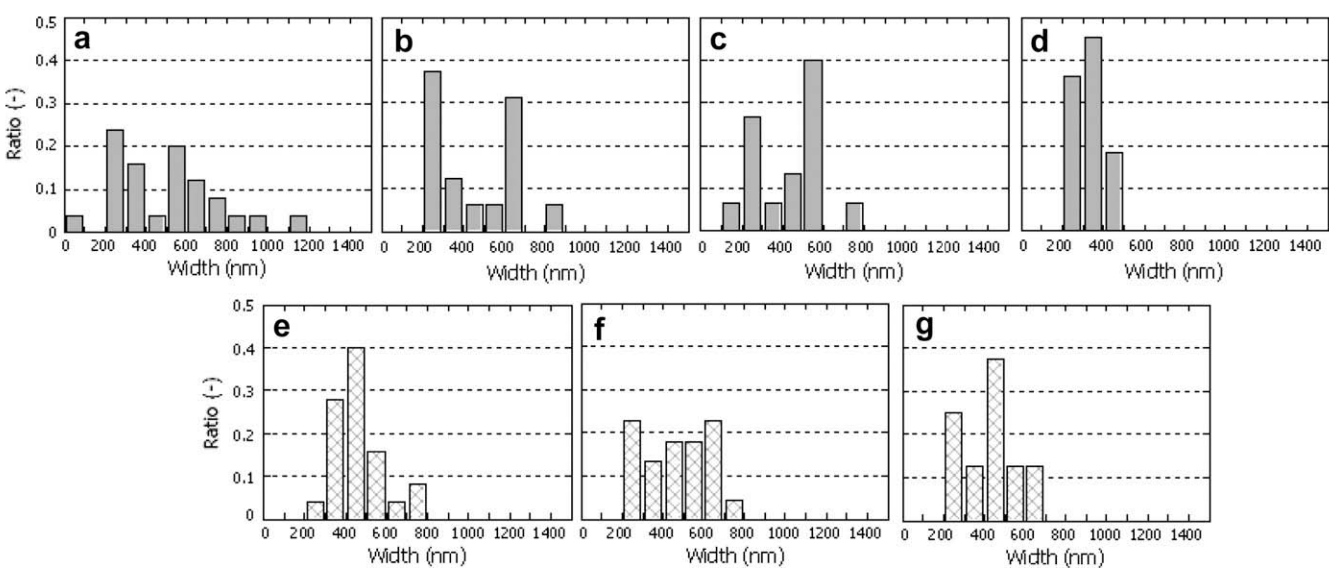


**Fig. 3.** Histograms for martensite laths width: (a) as-received; (b), (c) and (d) thermally-aged at 495, 550, 605 °C; (e), (f) and (g) irradiated in FFTF at 495 °C to 53.2 dpa, at 550 °C to 97.2 dpa at 605 °C to 101.5 dpa.

shows data on how much of the PAG boundaries were occupied by precipitate at each condition. Of particular concern, but of little surprise, was the finding that the peak temperature of PAG boundaries occupation by precipitate in the thermal-aging specimens was likely to be lower than that in the irradiation specimens. This was attributed to the belief that the irradiation at low temperatures enhanced the growth of precipitates due to irradiation-assisted diffusion. For the practical use of the PNC-FMS for nuclear applications, further irradiation studies are needed.

## 5. Conclusion

Microstructural investigations of heat resistant 11Cr ferritic/martensitic steels (PNC-FMS) which were thermally-aged and which were irradiated in both JOYO and FFTF were conducted. The following conclusions about dependence on irradiation temperature conditions were obtained.

(1) When irradiated at 400–450 °C to doses up to 94.6 dpa, both dislocation loops and cavities less than 30 nm in diameter formed in the region of ferrite phase. Estimated void swelling was 0.05% at the most.
(2) When irradiated at moderate temperatures of 500–600 °C, $M_{23}C_6$ and $M_6C$ grew and entirely covered the PAG boundaries. This suggested that carbide precipitation on the PAG boundaries played an important role in prolongation of recovery of martensite laths.
(3) When irradiated at elevated temperatures above 650 °C, formation and growth of equi-axial grains occurred in addition to the complete recovery of martensite laths, and there was extensive growth of carbides. This microstructural change was considered to be inevitable and would be responsible for a severe degradation in the mechanical properties.

## References


[1] Y. Yano, T. Yoshitake, S. Yamashita, N. Akasaka, S. Onose, H. Takahashi, J. Nucl. Mater. 367&370 (2007) 127.
[2] Y. Yano, T. Yoshitake, S. Yamashita, N. Akasaka, S. Onose, S. Watanabe, H. Takahashi, J. Nucl. Sci. Technol. 44 (2007) 1535.
[3] R.L. Klueh, D.R. Harries, High-Chromium Ferritic and Martensitic Steels for Nuclear Applications, American Society for Testing and Materials, West Conshohocken, PA, 2001.
[4] D.S. Gelles, J. Nucl. Mater. 122&123 (1984) 207.
[5] D.S. Gelles, J. Nucl. Mater. 212&215 (1994) 714.
[6] C.Y. Hsu, D.S. Gelles, T.A. Lechtenberg, in: F.A. Garner, N.H. Packan, A.S. Kumar (Eds.), Radiation-Induced Changes in Microstructure – 13th International Symposium (Part I), ASTM STP 955, American Society for Testing and Materials, Philadelphia, 1987, p. 545.
[7] J.J. Kai, R.L. Klueh, J. Nucl. Mater. 230 (1996) 116.
[8] M.B. Toloczko, F.A. Garner, C.R. Eiholzer, J. Nucl. Mater. 212–215 (1994) 604.
[9] M.B. Toloczko, F.A. Garner, J. Nucl. Mater. 233&237 (1996) 289.
[10] F.A. Garner, M.B. Toloczko, B.H. Sencer, J. Nucl. Mater. 276 (2000) 123.
[11] A.M. Dvoriashin, S.I. Porollo, Yu.V. Konobeev, F.A. Garner, J. Nucl. Mater. 329&333 (2004) 319.
[12] N.I. Budylkin, E.G. Mironova, V.M. Chernov, V.A. Krasnoselov, S.I. Porollo, F.A. Garner, J. Nucl. Mater. 375 (2008) 359.