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Influence of carbon addition on neutron-induced void swelling of Fe–15Cr–16Ni–0.25Ti model alloy

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Abstract

Addition of 0.05 wt% C to a model Fe–15Cr–16Ni–0.25Ti quaternary model alloy leads to a reduction in neutron-induced swelling at 430 °C. The transient regime of swelling is prolonged by carbon addition, most strongly at lower dpa rates. Contrary to the swelling behavior observed in carbon-free Fe–15Cr–16Ni and Fe–15Cr–16Ni–0.25Ti model alloys irradiated in the same experiment, Fe–15Cr–16Ti–0.25Ti–0.05C does not exhibit a strong dependence of swelling on dpa rate. It appears that carbon's role, while not yet well-defined, operates via a solute-based or TiC complex mechanism rather than by a precipitate-based mechanism. A model is proposed whereby carbon stabilizes loop microstructures against unfaulting, where unfaulting is known to be a prerequisite to formation of the glissile dislocation network needed to establish a high swelling rate. This stabilization is proposed to counteract the tendency of loop unfaulting to occur more strongly at low dpa rates.

1. Introduction

In an earlier series of reports by Okita and coworkers it was shown that two simple, annealed austenitic model alloys, ternary Fe–15Cr–16Ni and quaternary Fe–15Cr–16Ni–0.25Ti, when irradiated in the Materials Open Test Assembly in the Fast Flux Test Facility (FFTF–MOTA) during irradiation Cycles 11 and 12 at ~430 °C exhibited a very strong influence of dpa rate on void swelling [1–3]. While the eventual steady state swelling rate of ~1%/dpa was unaffected by dpa rate, the transient regime was strongly affected, with a progressive shortening of the transient duration as the dpa rate decreased, as shown in Fig. 1. At 430 °C the addition of titanium did not change the swelling significantly but there were relatively strong changes in the size distributions and densities of both Frank loops and voids. Boron additions to the ternary alloy also did not alter the total swelling significantly, but did alter the void density somewhat [4].

The counterintuitive dependence of swelling on dpa rate observed in these model alloys was shown to be mirrored in other published neutron experiments conducted on more complex commercial alloys [5–13]. A similar dependence of swelling on dpa rate over a wider range of temperatures was also observed in ion irradiation studies conducted on the same ternary alloy used in the FFTF–MOTA study [14,15].

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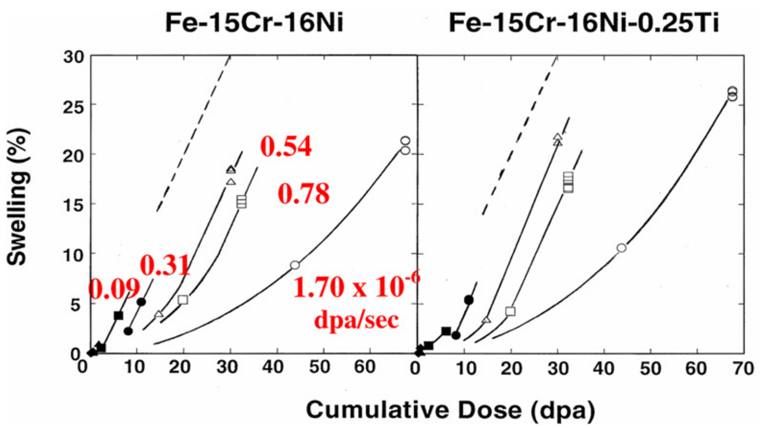

Fig. 1. Swelling of simple model fcc Fe–Cr–Ni alloys in FFTF–MOTA at ~430 °C, as observed by Okita and coworkers [1], showing that the transient regime of swelling increases progressively as the dpa rate increases [1–3].

Okita and coworkers showed that the increased delay in swelling with increasing dpa rate arose primarily from the increased density of smaller Frank faulted loops that developed at higher dpa rates [1–3]. The smaller loops and consequently denser loop ensembles formed at higher dpa rates appeared to be more resistant to unfaulting and subsequent formation of a glissle dislocation network, a condition thought to be critical to the development of a high swelling rate.

Also contained in the FFTF–MOTA experiment was Fe–15Cr–16Ti–0.25Ti–0.05C (wt%), also in the annealed condition and irradiated side-by-side with the ternary and quaternary alloys. Examination of the carbon-added alloy in the current study allows the possibility for investigation of possibly synergistic effects of two important variables, dpa rate and carbon level. This paper addresses the influence of carbon additions on the swelling of this alloy series as observed in specimens irradiated in FFTF Cycles 11 and 12.

Some indication of the complex and interactive microstructural consequences of carbon and titanium additions on void swelling in this alloy series was observed in earlier papers by Sekimura and coworkers that presented results from an irradiation series conducted in FFTF Cycle 10 and/or Cycle 11 [16,17]. Whereas this earlier Cycle 10 study focused on a range of irradiation temperatures, 430–600 °C, at only one dpa rate, the current study conducted in Cycles 11–12 focused on irradiation conducted only at ~430 °C, but at 7 dpa rates.

2. Experimental details

Relatively pure Fe–15Cr–16Ni, Fe–15Cr–16Ni–0.25Ti and Fe–15Cr–16Ni–0.25Ti–0.05C (wt%) with no added solute were prepared by arc melting from high purity Fe, Ni, Cr and Ti. The alloys were rolled to sheets of 0.25 mm thickness, cut into 3 mm diameter disks and then annealed for 30 min at 1050 °C in high vacuum. The final compositions of the three alloys, as measured by the broad-beam EDS technique in a JOEL scanning electron microscope, are presented in Table 1.

Sets of identical specimen groups were placed in sealed, helium-filled packets at each of seven different axial positions of the Materials Open Test Assembly (MOTA), ranging from below the core to above the core of the Fast Flux Test Facility (FFTF). The packets each contained four identical side-by-side specimens of each of the three alloys. The three alloys were located side-by-side in the same packet, with the total of twelve specimens

Table 1
Composition in wt% of alloys as determined by broad-beam EDS analysis

Alloy	C	Ti	Si	Mn	P	S	Cr	Ni	Fe
Fe–15Cr–16Ni	0.012	–	0.004	0.003	–	0.01	16.03	15.01	Bal.
Fe–15Cr–16Ni–0.25Ti	0.017	0.28	–	0.01	–	0.0	16.04	15.46	Bal.
Fe–15Cr–16Ni–0.25Ti–0.05C	0.052	0.27	–	–	–	–	16.00	15.48	Bal.

occupying only 3.0 mm axial height. Two or more identically-loaded packets were placed in each MOTA capsule, with the dpa rate of each capsule dependent on its axial location in MOTA.

With the exception of the below-core capsule, the temperatures in MOTA capsules were actively controlled to ±5 °C of the nominal target, although the nominal target temperatures varied a little from capsule to capsule.

The first irradiation sequence proceeded in Cycle 11 of MOTA-2A for 2.59×10^7 s, and a subset of specimen packets was then removed. The other packets continued in Cycle 12 of MOTA-2B for another 1.71×10^7 s. The dpa rates in the various capsules ranged from 8.9×10^{-9} to 1.7×10^{-6} dpa/s. The dose levels attained by the specimens varied from 0.23 to 43.8 dpa in Cycle 11 and an additional 0.24–24.0 dpa in Cycle 12. Table 2 summarizes the irradiation conditions for the fourteen combinations of temperature, dpa and dpa rate.

The starting and post-irradiation densities were measured using an immersion density technique known to be accurate to ±0.2% change in density. In some cases it was not possible to clearly identify and retrieve all four specimens, but in general there were at least two identical specimens measured from each capsule. Determination of microstructural evolution in the specimens using a transmission electron microscope has been completed for the ternary and quaternary alloys [1–3], but has not been fully completed for the carbon-doped alloy from Cycle 12. Both the recently measured density change data and the earlier microscopy data are presented in Figs. 2–4.

3. Results

Fig. 2 presents some limited microscopy of the three model alloys at the two highest dpa levels attained in this experiment. Although Ti addition to the ternary alloy does not significantly change the overall swelling, it does significantly coarsen the void ensemble. Addition of carbon to the quaternary alloy clearly reduces the swelling, however, leading to a lower mean void size in particular. These micrographs illustrate that electron microscopy is not suitable for accurate swelling determinations at such high swelling values with high levels of void intersection with the foil surface. The use of density change measurements to determine the swelling is necessary for accurate swelling values in excess of 5–10%.

It is considered to be particularly important that no significant precipitation was observed by microscopy as a result of carbon addition at these high swelling levels, implying that most of the carbon was retained in solution or existed as sub-visible clusters of TiC.

There are a number of major results observed in the swelling behavior when carbon was added to the quaternary alloy. First, the maximum swelling at the highest dose level and 430 °C is reduced from

Table 2
Irradiation conditions in FFTF Cycles 11 and 12 (MOTA-2A and MOTA-2B)

Dose rate (dpa/s)		Dose (dpa)		Temperature (°C)		Symbols
# 11	#12	#11	#11 and #12	#11	#11 and #12	
1.7×10^{-6}	1.4×10^{-6}	43.8	67.8	427	408	▼
7.8×10^{-7}[a]	9.5×10^{-7}	20.0[a]	32.4	390	387	▲
5.4×10^{-7}	8.4×10^{-7}	14.0	28.8	430	424	♦
8.2×10^{-7}	–	21.1	–	430	–	■
3.2×10^{-7}[b]	3.5×10^{-7}	8.22[b]	13.1	373	373	•
3.1×10^{-7}[c]	3.0×10^{-7}	8.05[c]	11.1	411	410	▷
1.5×10^{-7}	1.3×10^{-7}	3.87	6.12	430	431	◁
9.1×10^{-8}	2.1×10^{-7}	2.36	6.36	430	431	▽
4.6×10^{-8}	4.2×10^{-8}	1.18	1.91	434	437	△
2.7×10^{-8}	6.6×10^{-8}	0.71	1.87	434	437	◇
1.4×10^{-8}	1.4×10^{-8}	0.37	0.61	436	444	□
8.9×10^{-9}	2.2×10^{-8}	0.23	0.61	436	444	○

Note that in three of the seven cases the specimens irradiated in both cycles did not experience conditions completely identical with those of single cycle packages.

Note: the swelling data of the underlined irradiation conditions come from TEM observation, while the others are density measurements.

[a] 6.0×10^{-7} dpa/s and 15.6 dpa for #11 in 2 cycle irradiation specimens.

[b] 2.7×10^{-7} dpa/s and 6.90 dpa for #11 in 2 cycle irradiation specimens.

[c] 2.2×10^{-7} dpa/s and 5.69 dpa for #11 in 2 cycle irradiation specimens.

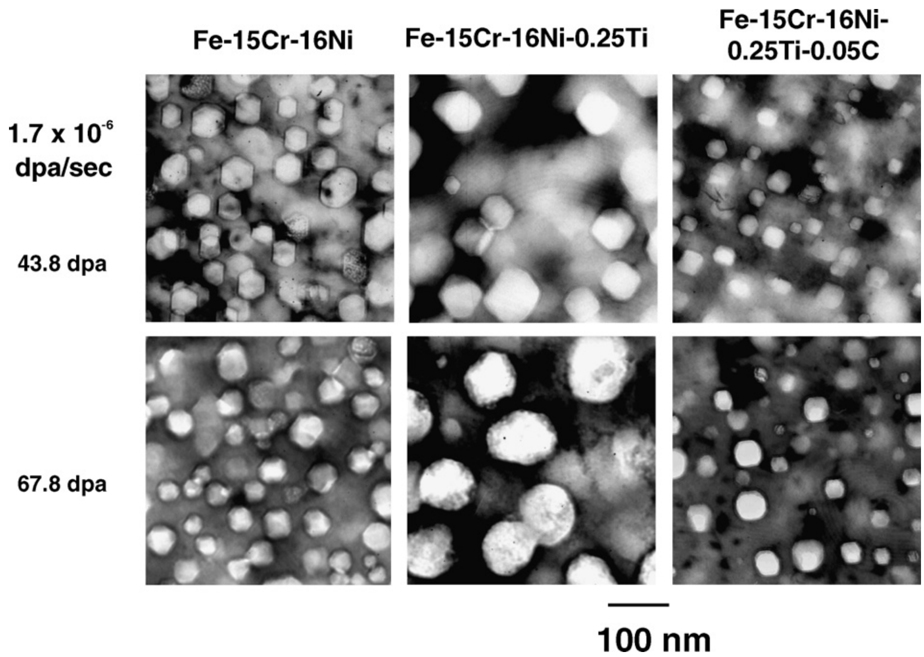

Fig. 2. Void microstructures observed in the three model alloys irradiated in this experiment at ∼430 °C for the two highest dpa rates.

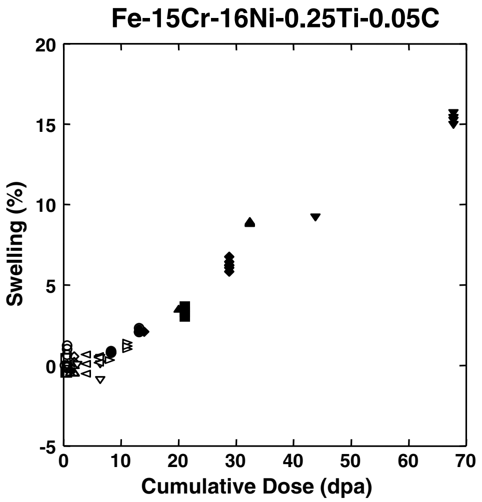

Fig. 3. Swelling of simple model fcc Fe–15Cr–16Ni–0.25Ti–0.05C irradiated in FFTF–MOTA Cycles 11 and 12 at ∼430 °C, showing that the swelling is relatively independent of dpa rate. There were two to four identical specimens for each irradiation condition. See Table 2 for symbol identification of dpa rates and reactor cycles for each data point.

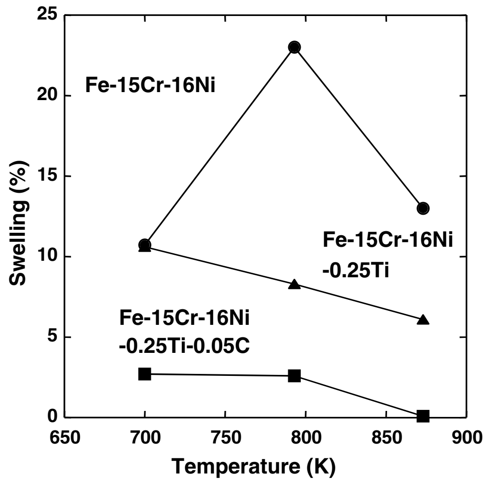

Fig. 4. Cavity volume fraction determined by Sekimura and Ishino using microscopy of three simple austenitic alloys after irradiation in FFTF–MOTA-2A at three different temperatures. In the first publication the dpa level was estimated to be ∼36 dpa, but the reported doses in the second reference were reevaluated to be ∼43 dpa at all three temperatures [16,17].

∼26% to ∼15%, as shown in Fig. 3. Second, the trends of microscopy determinations of swelling agree reasonably well with values and trends of density determinations. Third, and most importantly, the swelling of the carbon-added alloy at ∼430 °C appears to show no obvious influence of the dpa rate whereas the swelling behavior of the carbon-free ternary and quaternary alloys shown in Fig. 1 exhibits a very pronounced dependence on dpa rate. Finally, it is particularly noteworthy that the carbon-added alloy never reached the terminal swelling rate of ∼1%/dpa observed in the carbon-free alloys at most lower dpa rates. The swelling rate was still increasing at the end of the experiment, never exceeding ∼0.3%/dpa. This implies that the transient regime is still in progress.

As was observed earlier in the simple ternary and quaternary alloys, the range of swelling between identical specimens irradiated side-by-side is relatively small, especially at higher dpa exposures, indicating the overall reproducibility of the swelling phenomenon. However, when the data at lower dpa and dpa rates are examined more closely, a somewhat larger amount of scatter is observed in the swelling values, with some measurements indicating that a net densification may have occurred.

4. Discussion

A minor complication of this experiment was the fact that while the target capsule temperatures were maintained within ±5 °C they varied somewhat (373–444 °C) from capsule to capsule as shown in Table 2. In earlier papers on the carbon-free alloys Okita and coworkers addressed the possibility that variations in capsule target temperatures might obscure or overwhelm the effect of differences in dpa rate [2]. However, it was easy to group the various data sets into groups such that two or more capsules operated at nearly identical temperatures but at greatly different dpa rates. In each group the strong effect of dpa rate was obvious and overwhelmed any effect of temperature differences.

There are five major features of these results. First, carbon addition clearly delays somewhat the onset of swelling in Fe–15Cr–16Ni–0.25Ti at ∼430 °C. Second, carbon addition suppresses the early termination of the transient regime, especially at lower dpa rates where the carbon-free alloys exhibited very short durations of the transient. Third, the carbon-induced suppression looks to be less effective at higher dpa rates. Fourth, the addition of carbon introduces more specimen-to-specimen scatter than observed in the carbon-free alloys at low dpa and dpa rates. Finally, there does not appear to be any significant precipitation of titanium carbides, at least in the higher dose and dose rate specimens.

The latter observation was confirmed at comparably high dpa rates in the results of the earlier Cycle 10 and/or Cycle 11 study of Sekimura and Ishino [16,17]. They showed that TiC precipitates were only occasionally present after irradiation at ∼430 °C but were not a dominant feature of the microstructure in carbon-bearing specimens. Therefore, a direct precipitate role in the swelling behavior can not be invoked and we must assume that a large fraction of the carbon must still have been in solution or existed in sub-visible TiC clusters, at least at the higher dpa rates.

Based on the current results alone, however, it can not be assumed that precipitation did not occur at the lower dpa rates, since no microscopy was performed at the lower dpa conditions. Kawanishi and Ishino, however, conducted similar irradiations on Fe–15Cr–16Ni–0.3Ti–0.06C alloys at lower doses and dpa rates in the JOYO fast reactor at ∼400 °C [18,19]. They showed that carbon additions led to a longer transient regime of swelling and that visible TiC carbide precipitates were not formed during irradiation.

Microstructural observations of the carbon-free alloys irradiated in both Cycle 11 and Cycle 12 specimens showed that the flux sensitivity of the transient regime arose primarily from the flux sensitivity of Frank loop evolution [1–3]. Higher dpa rates produced higher densities of smaller loops which were more resistant to unfaulting and network formation, thereby delaying the development of a dislocation network. Attainment of a glissile dislocation network was found to be coincident with the termination of the transient regime in these carbon-free alloys [1–3].

In the Sekimura and Ishino studies the loop microstructure could not be accurately assessed because an off-normal shutdown and cooldown sequence occurred in Cycle 10 and resulted in addition of a dense population of small Frank loops in all alloys studied [16,17].

Kawanishi and Ishino, however, showed that the addition of carbon and titanium significantly altered the faulted loop morphology, producing highly irregular-shaped or 'crenulated' loops. Carbon addition also changed the loop distribution such that their interaction and unfaulting was delayed [18,19]. Kawanishi and Ishino also noted that TiC complexes form easily and act to retard loop unfaulting.

Garner and Gelles demonstrated that sub-visible precipitates or complexes encountered by growing loops in carbon-containing alloys create the irregular boundaries characteristic of 'crenulated' loops. They also demonstrated that the irregular periphery of such loops indeed changes the growth rate and stability of individual loops and loop ensembles [20].

While the above arguments appear to be plausible at 430 °C over the investigated rates of dpa rates, the swelling behavior observed in Cycle 10 by Sekimura and Ishino (Fig. 4) indicates that carbon also suppresses swelling at higher temperatures, even though the effect of titanium on swelling becomes stronger with increasing temperature [16,17]. Remember that these specimens were identical to those of the current experiment. Note that in agreement with the current study the influence of Ti addition was very small at ~430 °C, but increased at higher temperatures.

Garner compiled a summary of data examining the effect of carbon on swelling of commercial austenitic stainless steels [21]. At temperatures near 430 °C the effect of carbon is usually to delay or reduce swelling, but at higher temperatures the effect is reversed to produce increased swelling. This latter behavior is not observed in the simple model alloys shown in Figs. 3 and 4. In commercial alloys the presence of other solutes leads to significant precipitation of carbides and intermetallic phases at higher temperatures, while such precipitation can not occur in the model alloys.

Redistribution of carbon during irradiation frequently produces a small net densification in irradiated stainless steels [21]. It appears in this study that densification occurs during irradiation in this experiment but densification does not require discrete precipitates to form. Associated with this densification appears to be a somewhat larger amount of data scatter in identical specimens than observed in carbon-free alloys.

5. Conclusions

The addition of 0.05% carbon to Fe–15Cr–16Ni–0.25Ti leads to a reduction of neutron-induced swelling at ~430 °C, with the reduction being largest when the irradiation is conducted at relatively low dpa rates. Another consequence of carbon addition is that the strong influence of the dpa rate observed in the carbon-free alloy completely disappears in the carbon-doped alloy.

Earlier discussions of the effect of dpa rate to determine the onset of swelling at high rate focused on the effect of dpa rate to influence the development of a glissile dislocation microstructure by stabilizing or destabilizing Frank loop ensembles against unfaulting.

Carbon appears to stabilize loop microstructures against unfaulting, thereby possibly counteracting the tendency of loop unfaulting to occur strongest at lower dpa rates. It is speculated that perhaps this mechanism accounts for the disappearance of the dose rate effect in carbon-bearing alloys.

It appears that carbon's role, while not yet well-defined, operates via a solute-based or TiC complex mechanism rather than by a precipitate-based mechanism.

Acknowledgements

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References

[1] T. Okita, N. Sekimura, F.A. Garner, L.R. Greenwood, W.G. Wolfer, Y. Isobe, in: E.P. Ford, G. Was, J.L. Nelson, (Eds.), Proceedings of 10th International Conference on Environmental Degradation of Materials in Nuclear Power Systems – Water Reactors, 2001, issued on CD format, NACE International, also in Fusion Materials Semiannual Progress Report for Period Ending June 30, 2001, vol. 30, p. 148.

[2] T. Okita, N. Sekimura, T. Sato, F.A. Garner, L.R. Greenwood, J. Nucl. Mater. 307–311 (2002) 322.

[3] T. Okita, W.G. Wolfer, F.A. Garner, N. Sekimura, Philos. Mag. 85 (18/21) (2005) 2033.

[4] T. Okita, W.G. Wolfer, F.A. Garner, N. Sekimura, J. Nucl. Mater. 329–333 (2004) 1013.

[5] J.L. Seran, J.M. Dupouy, in: H.R. Brager, J.S. Perrin (Eds.), The 11th International Symposium, ASTM-STP 782, American Society for Testing and Materials, 1982, p. 5.

[6] J.L. Seran, J.M. Dupouy, in: The Proceedings Conference on Dimensional Stability and Mechanical Behavior of Irradiated Metals and Alloys, vol. 1, BNES, 1983, p. 25.

[7] G.M. Bond, B.H. Sencer, F.A. Garner, M.L. Hamilton, T.R. Allen, D.L. Porter, in: The Proceedings of the 9th International Conference on Environmental Degradation of Materials in Nuclear Power Systems – Water Reactors, 1999, p. 1045.

[8] F.A. Garner, N.I. Budylkin, Yu. V. Konobeev, S.I. Porollo, V.S. Neustroev, V.K. Shamardin, A.V. Kozlov, in: The Proceedings of the 10th International Conference on Environmental Degradation of Materials in Nuclear Power Systems – Water Reactors, 2003, p. 647.

[9] F.A. Garner, M.B. Toloczko, J. Nucl. Mater. 251 (1997) 252.

[10] V.S. Neustroev, V.K. Shamardin, Z.E. Ostrovsky, A.M. Pecherin, F.A. Garner, in: M.L. Hamilton, A.S. Kumar, S.T. Rosinski, M.L. Grossbeck (Eds.), The 19th International Symposium, ASTM-STP 1366, American Society for Testing and Materials, 2000, p. 792.

[11] O.P. Maksimkin, K.V. Tsai, L.G. Turubarova, T. Doronina, F.A. Garner, J. Nucl. Mater. 329–333 (2004) 625.
[12] O.P. Maksimkin, K.V. Tsai, L.G. Turubarova, T.A. Doronina, F.A. Garner, J. Nucl. Mater., these Proceedings, doi:10.1016/j.jnucmat.2007.03.170.
[13] F.A. Garner, B.J. Makenas, Paper A302-PV1, in: Proceedings of Fontevraud 6 International Symposium on Contributions to Materials Investigations to Improve the Safety and Performance of LWRs, SFEN French Nuclear Energy Society, 2006.
[14] T. Okita, N. Sekimura, T. Iwai, F.A. Garner, in: E.P. Ford, G. Was, J.L. Nelson (Eds.), Proceedings of 10th International Conference on Environmental Degradation of Materials in Nuclear Power Systems – Water Reactors, 2001, issued on CD format, NACE International.
[15] T. Okita T. Sato, N. Sekimura, T. Iwai, F.A. Garner, J. Nucl. Mater., these Proceedings, doi:10.1016/j.jnucmat.2007.03.061.
[16] N. Sekimura, S. Ishino, J. Nucl. Mater. 179–181 (1991) 542.
[17] N. Sekimura, K. Hamada, S. Ishino, in: A.S. Kumar, D.S. Gelles, R.K. Nanstad, E.A. Little (Eds.), The 16th International Symposium, ASTM STP 1175, American Society for Testing and Materials, 1994, p. 992.
[18] H. Kawanishi, S. Ishino, J. Nucl. Mater. 155–187 (1988) 806.
[19] H. Kawanishi, S. Ishino, J. Nucl. Mater. (1991) 534.
[20] F.A. Garner, D.S. Gelles, J. Nucl. Mater. (1988) 286.
[21] F.A. Garner, Materials Science and Technology: A Comprehensive Treatment, VCH Publishers, 1994, vol. 10A, p. 419 (Chapter 6).