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Effect of carbon and nitrogen on grain boundary segregation in irradiated stainless steels

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Abstract

SUS304 stainless steels with carbon contents of 0.052%, 0.019% and 0.004% and SUS316L stainless steels with nitrogen contents of 0.095%, 0.032% and 0.003% were irradiated with 12 MeV Ni ions at 573 K to a dose of 1 dpa at 1 μm depth. Microstructure and grain boundary chemical composition were investigated using a transmission electron microscope with a field-emission-gun (FE-TEM) at the probe size of 0.5 nm. The number density of dislocation loop was higher as the carbon content was higher and was almost independent of nitrogen content. With increasing carbon and nitrogen content, the degree of Cr depletion and Si/Ni segregation was decreased. Both carbon and nitrogen suppressed the Cr depletion and Si/Ni segregation. The suppression effect of carbon was larger than that of nitrogen.

1. Introduction

Irradiation assisted stress corrosion cracking (IASCC) is one of the major concerns on structural materials under neutron irradiation in high temperature water such as light water reactor core components and water cooled first wall components. The recent mechanistic consideration on IASCC has focused on the role of grain boundary segregation and radiation hardening [1–5]. The depletion of chromium at grain boundary due to irradiation is considered to be the most important factor because stress corrosion cracking susceptibility of thermally sensitized stainless steels is determined by the degree of chromium depletion at grain boundary. Kodama et al. reported that the chromium concentration at grain boundary can be correlated to IASCC susceptibility in the irradiated Type 304 stainless steels [2]. The effect of alloying elements on IASCC susceptibility has also been investigated with post-irradiation slow-strain-rate-tensile (SSRT) tests in high temperature water [6–8] and in-core swelling tube test [9,10], and the beneficial effect of Mo, Nb, Ni, C, Si and the deleterious effects of N, P, S, Ti, Nb on IASCC susceptibility have been pointed out. However, the mechanism of these effects has not been clarified and the effect of each elements on microstructural and microchemical evolution has not been well examined. In the present paper the effect of carbon and nitrogen on microstructural and microchemical changes under irradiation was examined to get an experimental basis to understand an inverse effect of carbon and nitrogen on IASCC susceptibility.

2. Experimental

The materials examined were SUS304 (similar to Type 304) stainless steels with carbon contents of 0.052% (HC), 0.019% (LC) and 0.004% (ULC), and SUS316L (similar to Type 316L) with nitrogen content of 0.095% (HN), 0.032% (LN), 0.003% (ULN). The chemical compositions are shown in Table 1. In the case of HC, LC and ULC, nitrogen content was intentionally reduced to avoid its effect. All the materials were solution heat treated at 1323 K for 0.5 h and water cooled. The TEM disc were irradiated with 12 MeV Ni^{3+} ions at 573 K. The dose was 1 dpa at 1 μm depth from the surface. The damage peak depth and Ni ion range peak

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Table 1
Chemical composition of alloys

	C	Si	Mn	P	S	Ni	Cr	Mo	N
304HC	0.052	0.32	0.84	0.017	0.003	13.45	19.00	–	0.0010
304LC	0.019	0.32	0.84	0.017	0.003	13.42	18.90	–	0.0009
304ULC	0.004	0.32	0.88	0.018	0.004	13.47	18.96	–	0.0012
304LN	0.019	0.51	0.91	0.025	0.001	9.90	18.34	–	0.0360
316HN	0.015	0.47	0.88	0.025	0.001	12.26	17.20	2.16	0.0950
316LN	0.017	0.48	0.09	0.026	0.003	12.36	16.90	2.20	0.0320
316ULN	0.014	0.49	0.09	0.025	0.001	12.00	17.04	2.10	0.0030

depth were over 3 μm. After irradiation, the specimen surface was removed by electropolishing to 1 μm and back-thinned for perforation in 10%$HClO_4$ + CH_3COOH solution. Microstructural observation and compositional analysis across grain boundary were conducted using a FE-TEM (TOPCON EM-002BF) with an energy-dispersive X-ray analyzer (EDS). The probe electron beam size for the analysis was 0.5 nm.

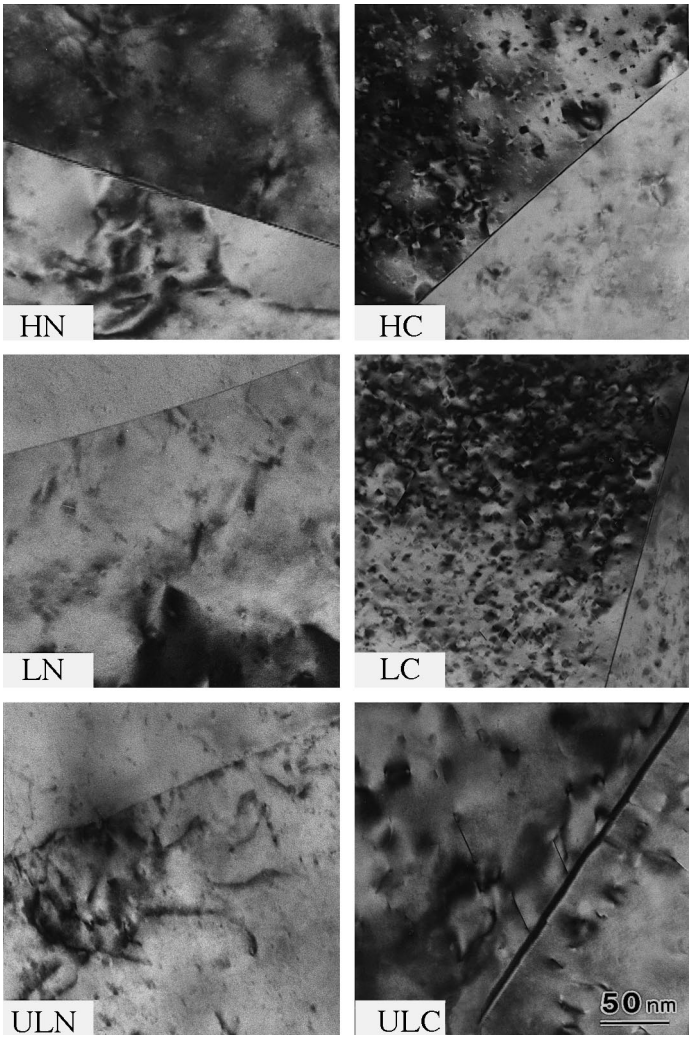

Fig. 1. TEM microstructures after Ni ion irradiation at 573 K to 1 dpa.

3. Results

Fig. 1 shows TEM microstructures after irradiation. Dislocation loops were homogeneously formed in grains. The number density was higher and the size was smaller for higher carbon or nitrogen containing alloys. Nitrogen effect was less remarkable than carbon. No precipitates were observed in grain and at grain boundary after irradiation. Fig. 2 shows compositional profiles measured by EDS across grain boundary. No apparent influence of implanted Ni was observed in the profiles. Fig. 3 shows the depth and width of segregation or depletion as a function of carbon or nitrogen content. The depth (delta element) and the width (element width) are defined as the difference in the concentrations at the grain boundary and at the area far form grain boundary, and the width at the half of the depth at grain boundary, respectively. The depletion of chromium at grain boundary was observed commonly in all alloys. The depletion depth was smaller in the HC and HN alloys and was not linearly dependent on the carbon and nitrogen content. The width of the chromium depletion was sharply increased with decreasing carbon content. The nickel segregation was not detected in the HC and HN alloy. In the alloys containing lower carbon or nitrogen the depth and the width of nickel segregation were increased with the carbon and nitrogen content. Silicon showed clear segregation at grain boundary in the lower carbon or nitrogen alloys. Phosphorus segregation was detected only in the ULC, LN and ULN alloy. No clear phosphorus segregation was detected in the alloys with higher carbon or nitrogen content.

4. Discussion

Nakata et al. have reported formations of a higher loop number density in a Type 304 stainless steel than in a Type 304L stainless steel and a higher density in a Type 316NG stainless steel than in a Type 316L stainless steel after irradiation to 2.5×10^{25} n/m^2 at 573 K [11]. It was considered from the present study that carbon and

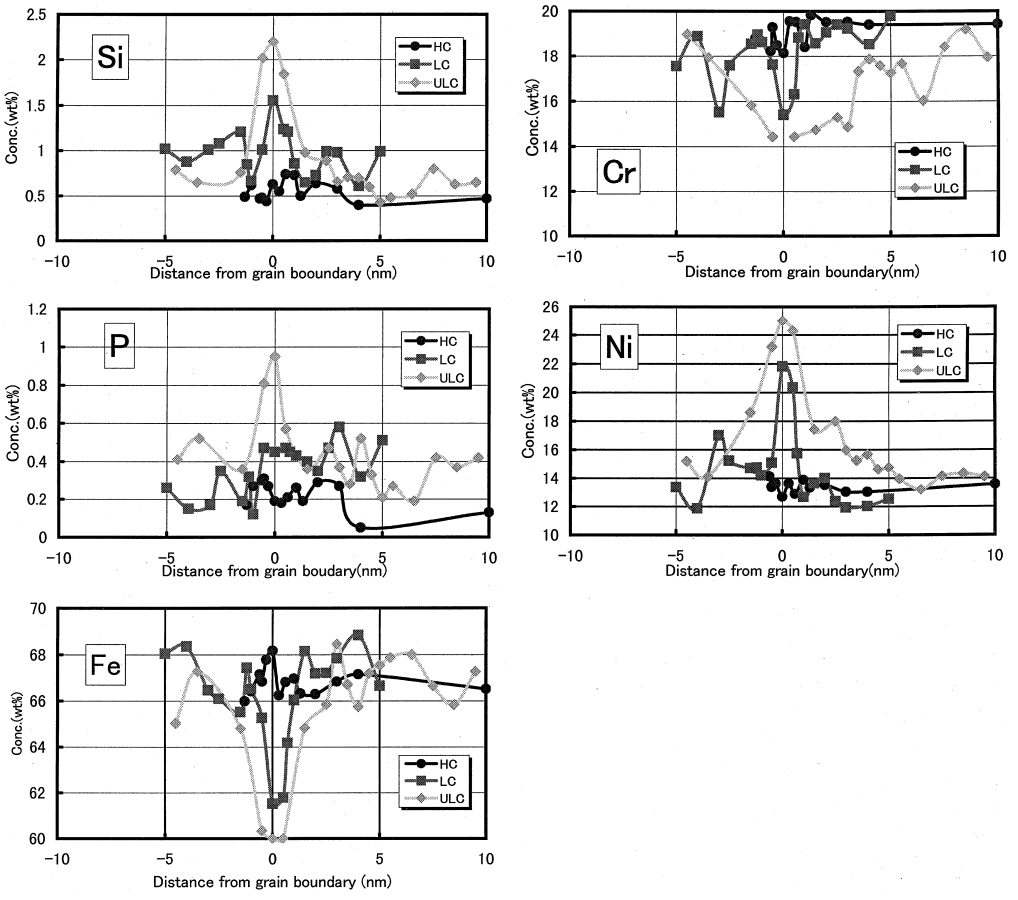

Fig. 2. Profiles of chromium, nickel, silicon, phosphorus, iron and molybdenum across grain boundary after Ni ion irradiation at 573 K to 1 dpa.

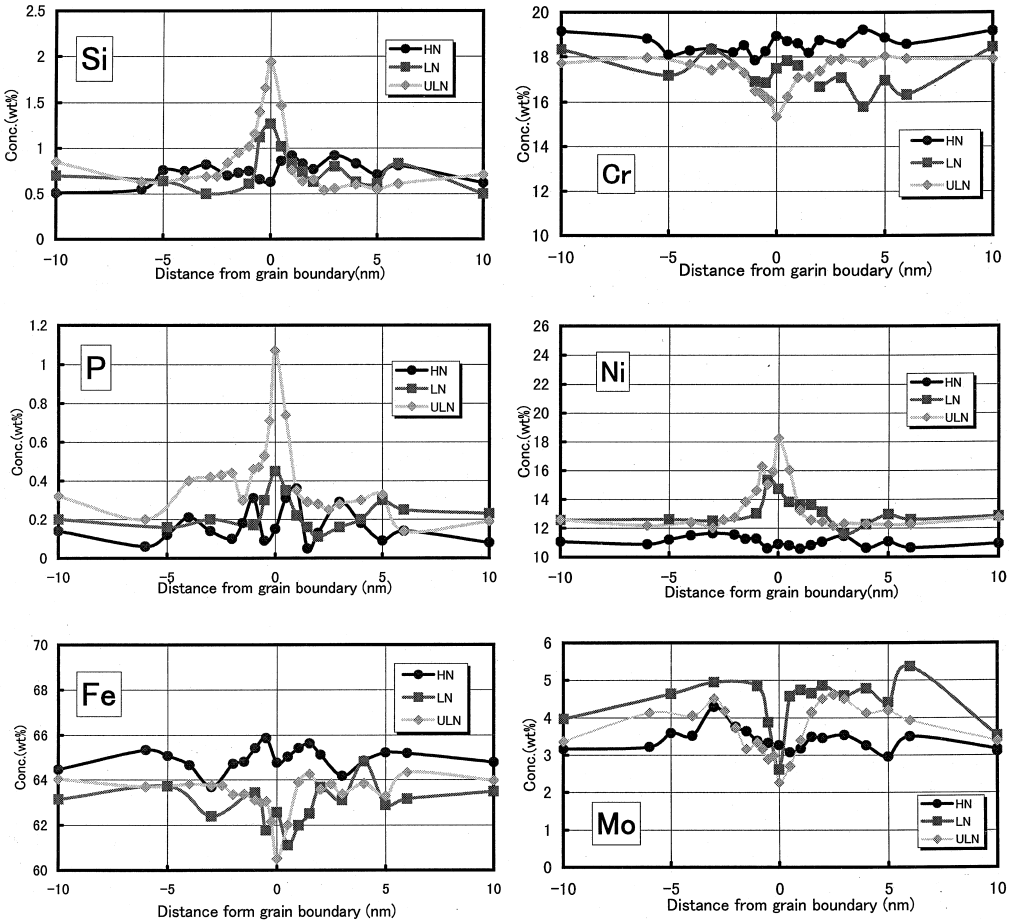

Fig. 2. Cont.

nitrogen act to stabilize defect clusters and small dislocation loops, resulting in higher loop density. As the sink strength becomes higher in the alloys with higher carbon and nitrogen, the grain boundary segregation during irradiation was restrained. Similar effect of substitutional elements such as phosphorus, silicon was reported [12,13].

The present results showed that both carbon and nitrogen have a suppressive effect on radiation induced segregation at grain boundary. In the case of carbon the suppressive effect on chromium depletion is considered to be one of the mechanisms for the beneficial effect of carbon on IASCC susceptibility. In the case of nitrogen, however, the deleterious effect on IASCC susceptibility reported on neutron-irradiated type 304 and 316L stainless steels [9,14,15] seems not to be explained by the idea that IASCC susceptibility is controlled by chromium depletion at grain boundary. Further investigations on microstructural and microchemical effects of alloying elements are important to understand IASCC susceptibility of stainless steels.

5. Summary

Ni ion irradiation at 573 K to 1 dpa and subsequent FE-TEM analysis on SUS304 stainless steels with different carbon contents showed that carbon enhances dislocation loop nucleation and suppresses segregation at grain boundary. Nitrogen in SUS316L has a similar but less remarkable effect as carbon.

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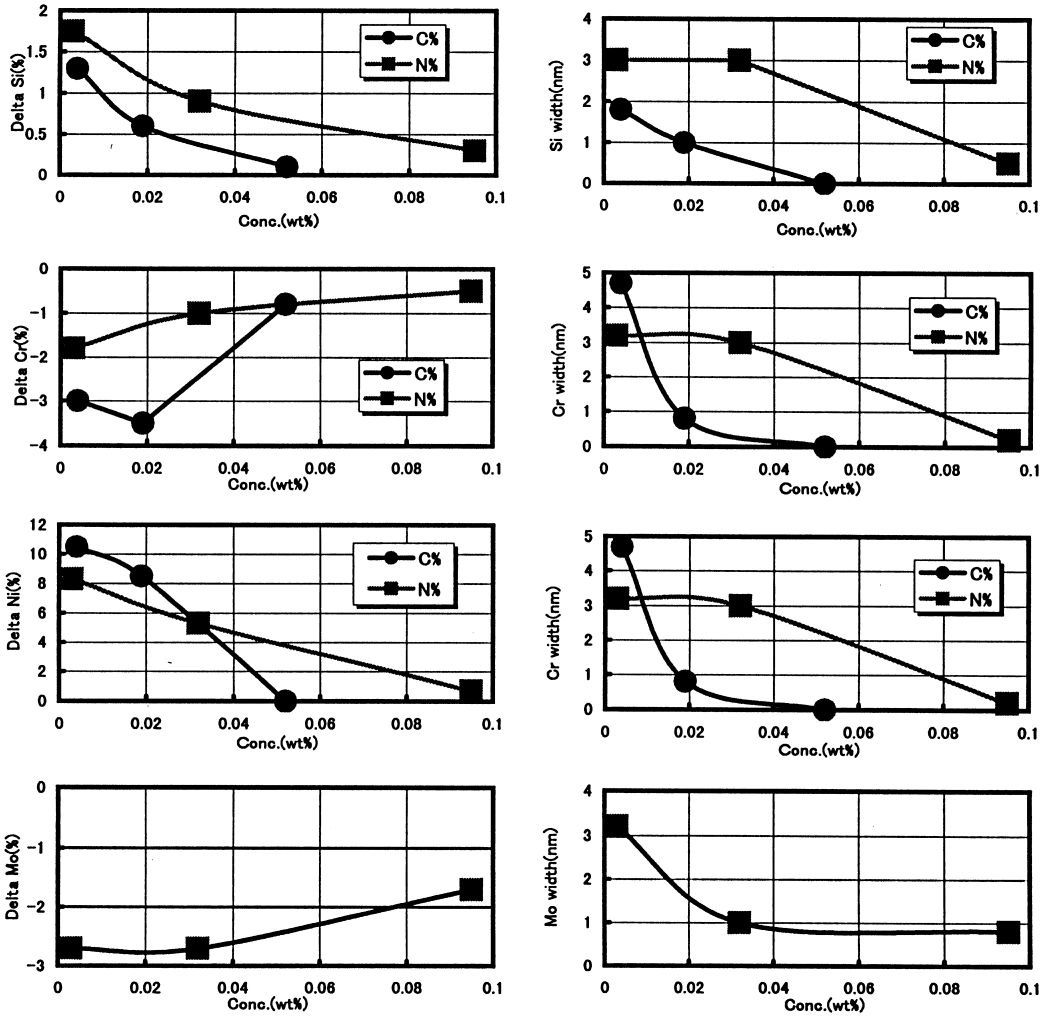

Fig. 3. Depth and width of segregation of chromium, nickel, silicon and molybdenum as a function of carbon and nitrogen content.

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