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Journal of Nuclear Materials 271&272 (1999) 316–320

journal of nuclear materials

Microstructures of type 316 model alloys neutron-irradiated at 513 K to 1 dpa

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Abstract

Solution-annealed, high-purity type 316 stainless steel and its heats doped with C, Ti, Si, P and S alone or together were irradiated at 513 K to a dose level of 1 dpa in the Japan Research Reactor No. 3 at Japan Atomic Energy Research Institute. After irradiation, transmission electron microscopy was carried out. In all alloys, Frank loops were mainly developed. Addition of Mo decreased the number density and the average diameter of Frank loops. Addition of C made the density increase and the diameter decrease, while addition of Si made the density and the diameter decrease.

1. Introduction

Type 316 stainless steel (SS) will be used as the blanket and first wall structural material of the International Thermonuclear Experimental Reactor [1]. This austenitic SS is known to have a susceptibility to stress corrosion cracking (SCC) in high-purity water under irradiation. This cracking was termed irradiation assisted stress corrosion cracking (IASCC).

IASCC is caused by the irradiation-induced changes of microstructure, microchemistry in the material and water chemistry. Recently much attention has been focused on the changes of grain boundary microchemistry and microstructure [2]. The change of grain boundary microchemistry is due to radiation-induced segregation (RIS) which then degrades the corrosion resistance of grain boundaries. The RIS, especially Cr depletion at grain boundaries, is considered to be one of the important mechanisms for IASCC [3]. Kodama et al. [4] reported the IASCC susceptibility in a nonoxidizing environment, which suggests another mechanism beyond the active corrosion path of Cr depleted grain boundaries. This observation indicates that RIS is not the only key factor for IASCC.

The effect of microstructural changes on mechanical properties due to the change of microscopic deformation mechanism is also important. Bruemmer et al. [5] reported that higher irradiation hardened SSs had higher IASCC susceptibility. Was et al. [6] suggested localized plastic deformation preferentially within or near grain boundaries. Since the matrix was hardened by radiation-induced defects, then matrix deformation was retarded until a higher stress. Intergranular deformation or deformation in narrow regions which were free of the radiation-induced defects were relatively promoted.

These changes of microstructure and microchemistry are known to be influenced by alloying elements and impurities. In this study, the effects of minor elements on microstructure in neutron-irradiated type 316 model alloys were investigated.

2. Experimental

A high-purity Fe–17Cr–13Ni–2.5Mo and its heats doped with C, C/Ti, C/Ti/Si, C/Ti/P, C/Ti/S and C/Ti/Si/P/S were used for this study. The chemical compositions and notations are shown in Table 1. A high-purity Fe–18Cr–12Ni was also used in order to compare the effect of Mo addition. These alloys were solution-annealed at 1273 and 1398 K for 0.5 h. The specimens irradiated in this study were disks of 3 mm diameter and about 0.25 mm thickness.

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0022-3115/99/$ – see front matter
PII: S0022-3115(98)00717-X

Table 1
Chemical compositions of irradiated stainless steels (wt%)

	C	Si	Mn	P	S	Cr	Ni	Mo	Ti	Al	N	Fe
HP316	0.004	0.02	1.40	<0.001	0.0010	17.21	13.50	2.50	0.01	0.10	0.0020	Bal.
HP316/C	0.061	0.03	1.40	0.001	0.0014	17.28	13.50	2.49	0.01	0.09	0.0026	Bal.
HP316/C/Ti	0.062	0.04	1.39	0.001	0.0014	17.05	13.47	2.48	0.29	0.11	0.0026	Bal.
HP316/C/Ti/Si	0.065	0.70	1.39	<0.001	0.0014	17.16	13.53	2.44	0.30	0.09	0.0033	Bal.
HP316/C/Ti/P	0.061	0.05	1.40	0.019	0.00015	16.95	13.53	2.48	0.29	0.11	0.0032	Bal.
HP316/C/Ti/S	0.061	0.03	1.41	0.001	0.0370	17.82	13.60	2.47	0.30	0.12	0.0020	Bal.
HP316/C/Ti/Si/P/S	0.063	0.76	1.42	0.018	0.0370	17.32	13.56	2.43	0.30	0.10	0.0022	Bal.
HP304	0.003	0.01	1.36	0.001	0.0014	18.17	12.27	–	0.01	0.16	0.0014	Bal.

Neutron irradiation was performed at about 513 K to a dose level of about 1 dpa in the Japan Research Reactor No. 3 at Japan Atomic Energy Research Institute. After the irradiation, transmission electron microscopy was carried out using a HF-2000 microscope.

3. Results

Examples of weak-beam dark-field images of HP304, HP316, HP316/C and HP316/C/Ti/Si/P/S are shown in Fig. 1. In all alloys, Frank loops and small defect clusters were the dominant microstructural features, while neither precipitates nor cavities were observed. Well-developed defect-free zones along grain boundaries [7] were also not observed. Fig. 2 shows the size distributions of Frank loops in all alloys. The number densities and the average diameters of Frank loops in all alloys are listed in Table 2. The densities and the diameters were influenced by either alloying elements or impurities.

As seen in Fig. 2, two high-purity alloys, both HP304 and HP316, had relatively larger Frank loops which reached a diameter up to 25 nm. The number density and the average diameter in HP316 were smaller than those in HP304. Chemical compositions between these alloys were slightly different except for molybdenum content, so that an addition of Mo decreased the average diameter and the number density of Frank loops (NFL). The number density of small defect clusters in HP316 seemed to be lower than that in HP304, as seen in Fig. 1.

By addition of C in HP316, NFL drastically increased and the average diameter decreased. The diameter of the largest Frank loop was reduced to about 15 nm. By further addition of Ti in HP316/C, NFL decreased and average diameter increased slightly. The diameter of the largest Frank loop in HP316/C/Ti was almost equivalent to that in HP316/C. No TiC-like precipitate was detected in diffraction patterns of HP316/C/Ti.

Addition of P in HP316/C/Ti made NFL increase and the average diameter decrease, but the changes of NFL and the average diameter were not remarkable. Larger Frank loops up to about 15 nm were observed in this P-doped alloy as well as in HP316/C. An addition of S in HP316/C/Ti did not change NFL, the average diameter, or the size distribution. Decreases of NFL and the average diameter were observed in HP316/C/Ti/Si. The

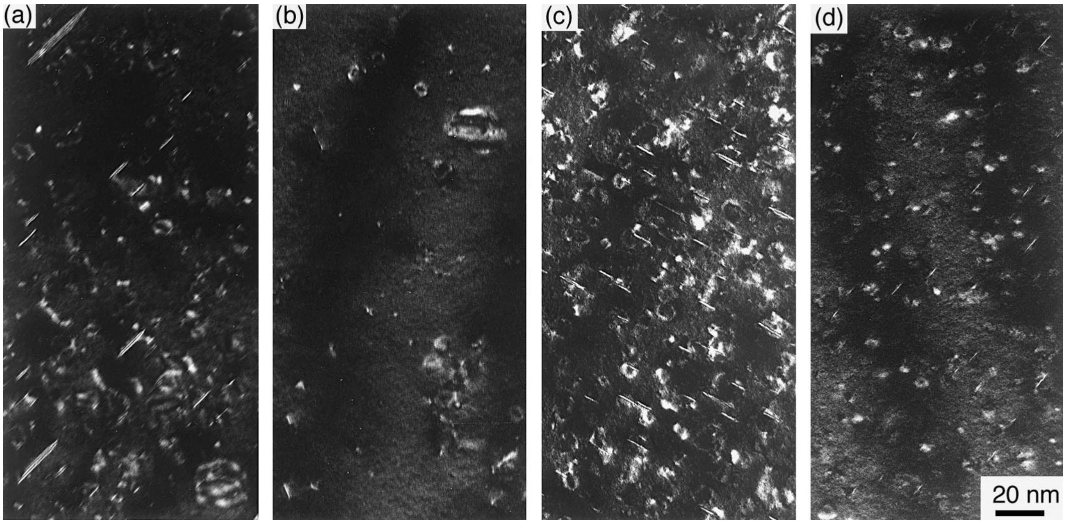

Fig. 1. Typical transmission electron micrographs of (a) HP304, (b) HP316, (c) HP316/C and (d) HP316/C/Ti/Si/P/S.

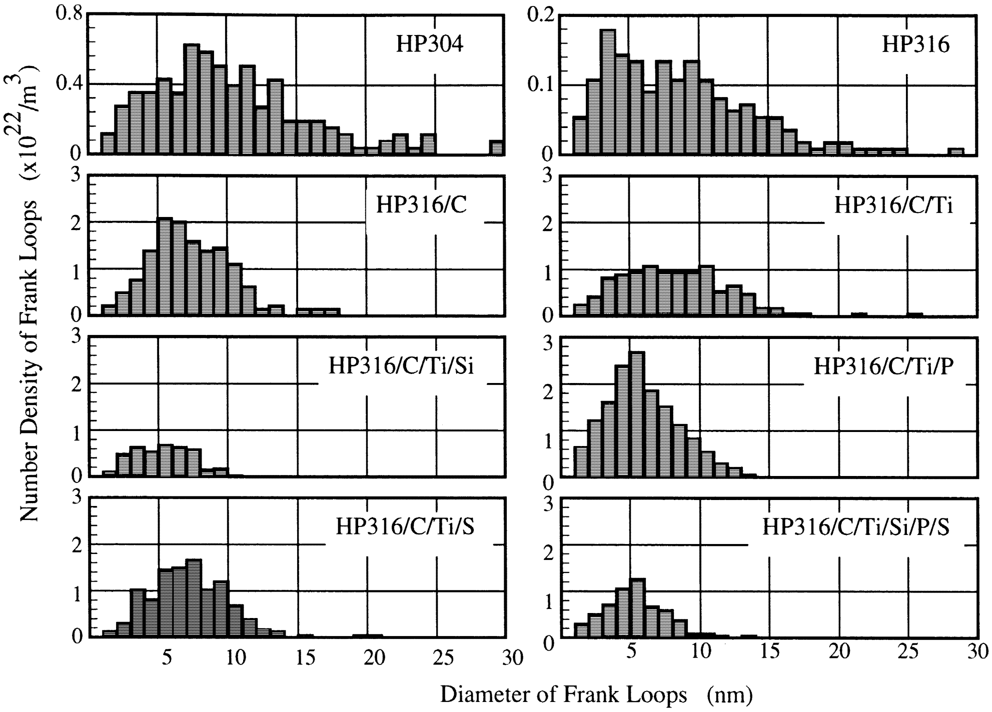

Fig. 2. Frank loop size distributions in grain interior.

Table 2
Summary of the number density and the average diameter of Frank loops

	Number density (10^{23} m^{-3})	Average diameter (nm)
HP316	0.17	9.2
HP316/C	1.3	7.9
HP316/C/Ti	1.1	8.7
HP316/C/Ti/Si	0.39	5.8
HP316/C/Ti/P	1.5	6.4
HP316/C/Ti/S	1.1	7.7
HP316/C/Ti/Si/P/S	0.57	5.9
HP304	0.66	11.2

largest diameter of Frank loops reduced to about 10 nm. Similar size distributions and number density of Frank loops were observed in all the elements doped alloy, HP316/C/Ti/Si/P/S.

4. Discussion

4.1. Effect of molybdenum

Addition of Mo decreased NFL and the average diameter of Frank loops, resulting in a decrease of dislocation density. Since these Frank loops cause the increase of irradiation hardening via the interaction with moving dislocations [8], Mo addition in high-purity austenitic SS seemed to suppress the increase of irradiation hardening. Tsukada et al. [9] reported the slow strain rate tensile (SSRT) test results on those alloys in oxygenated high-temperature water. The increase of apparent yield stress in HP316 was smaller than that in HP304. Therefore addition of Mo was effective to suppress the increase of irradiation hardening by suppressing the nucleation and growth of Frank loops. Shigenaka et al. [10], however, reported that there is no influence of Mo on the nucleation of dislocation loops in a high-purity austenitic SS under ion irradiation in the range of 250–450°C. It is speculated that this different influence of Mo between under neutron and under ion irradiation is caused by the difference of dose rates and/or primary knock-on atom energy spectra.

Tsukada et al. [9] reported that these high-purity type 316 SSs had less susceptibility for IASCC than high-purity 304 SSs. HP316 failed by ductile fracture, but HP304 failed by intergranular SCC. Microstructure of HP316 after irradiation is not remarkably different from that of HP304. It is speculated that addition of Mo has a chemical influence on IASCC.

4.2. Effect of carbon

Addition of C in HP316 decreased the average and maximum diameter of Frank loops, but increased NFL. This influence of C on the development of Frank loops was also observed in type 304 SSs [11]. It is expected that the increase of NFL by C addition gives rise to the increase of dislocation density, resulting in the increase of irradiation hardening. Tsukada et al. reported that a large increase of irradiation hardening was observed in HP316/C [9], as well as in the C-doped high-purity type 304 SS [11]. In high-purity type 304 SS, fracture mode changed from intergranular SCC in C free alloys to transgranular SCC in C-doped alloys [9]. It is expected that the large increase of irradiation hardening due to the addition of C retards the onset of plastic deformation in the matrix and then may lead to the change of plastic deformation mode. Cole et al. [12] found the occurrence of dislocation channels in ion-irradiated and very slowly deformed type 304L SS and the development of small Frank loops in diameter of 5–30 nm. Similar-sized Frank loops also developed in our neutron-irradiated type 316 SSs. They suggested that the increase of stacking fault energy should tend to make dislocation channeling more likely. Suzuki et al. [13] reported that the formation of dislocation channelling related to the density and size of the irradiation-induced loops in proton-irradiated Mo. Dislocation channelling was observed in Mo where high-density small-size loops developed. Addition of C increased the density and decreased the size of Frank loops in this study and in high-purity type 304 SSs [11]. Addition of C in austenitic SSs also increases the stacking fault energy [14]. It is speculated that the higher likelihood of heterogeneous deformation such as dislocation channelling is increased by addition of C. Therefore addition of C in austenitic SSs might affect the deformation mechanism after irradiation.

Since Frank loops act as trapping sites for point defects, the flow of point defects, especially inflow of interstitials, from grain interior to grain boundaries was expected to be reduced by addition of C. Consequently, RIS at grain boundaries in C-doped alloys might be mitigated more than that in C free alloys. Type 304 SSs with high C contents failed by transgranular SCC, while type 304 SSs without C contents failed by intergranular SCC [11]. In these alloys, any precipitate was not observed [11]. It is speculated that addition of C may reduce the susceptibility of intergranular SCC in irradiated SSs until the formation of radiation-enhanced $M_{23}C_6$ precipitates at grain boundaries. However, there was no SCC in neutron-irradiated HP316 or HP316/C [9]. In type 316 SSs, the influence of C on SCC morphology was obscured by Mo addition, although the influence of C on the development of Frank loops and the irradiation hardening was not obscured by Mo addition.

4.3. Effect of titanium

Yoshida et al. [15] reported Ti had no strong influence on interstitial loop formation in a Ti-doped, high-purity Fe–16Cr–17Ni under either neutron or electron irradiation. Following the addition of Ti in HP316/C presented in this study, a weaker influence of Ti on the development of Frank loops was observed. Ti was added in order to affect the function of C on microstructural development. The amount of doped Ti was enough to trap C by TiC formation in all Ti-doped alloys. These Ti-doped alloys were irradiated without using stabilization treatment, so that TiC was not formed before irradiation. By forming TiC and carbide former complexes (Ti–C etc.) during irradiation, the suppression of not only void swelling but also vacancy migration was intended [16]. However, TiC precipitates were not observed after irradiation, since the irradiation dose was not enough to form those precipitates [17]. It is considered that Ti is dissolved in all Ti-doped alloys and that the dissolved Ti does not affect the function of C on the development of Frank loops at 513 K and to 1 dpa.

4.4. Effect of phosphorous

It was reported by Watanabe et al. [18] that the interstitial type loop density in Fe–Cr–Ni–P alloys was considerably higher than that in pure Fe–Cr–Ni ternaries under electron irradiation. Addition of P in HP316/C/Ti presented in this study, slightly increased NFL, but decreased the average diameter. The yield stress of HP316/C/Ti/P was slightly higher than that of HP316/C/Ti [9]. It is considered that the increase of yield stress in a P-doped alloy was caused by the increase of NFL.

4.5. Effect of sulphur

Addition of S in HP316/C/Ti did not change the number density, the average diameter or the size distribution of Frank loops. Fukuya et al. [19] reported a similar effect of S on the loop nucleation in high-purity type 304 SS under electron irradiation. It is considered that there is no difference in yield stress between HP316/C/Ti and HP316/C/Ti/S because of no difference of Frank loops. Tsukada et al. [9] reported that the apparent yield stress of HP316/C/Ti/S was as high as that of HP316/C/Ti.

The S-doped alloys, both HP316/C/Ti/S and HP316/C/Ti/Si/P/S, failed by transgranular SCC in SSRT tests after neutron irradiation [9]. On the other hand, addition of S enhanced intergranular SCC in neutron irradiated type 304 SSs [20]. It is known that S is a deleterious impurity, because S makes sulphide inclusions such as TiS and MnS which enhance the initiation of cracking. Either Mn or Ti was doped enough to form those sulfides in these alloys, but neither MnS nor TiS particles in HP316/C/Ti/S were observed before or after irradiation. It is considered that S seemed to be dissolved in the alloy, and this sulphur affects intergranular and/or transgranular SCC under SSRT testing.

4.6. *Effect of silicon*

Addition of Si drastically decreased the number density and the average diameter of Frank loops. The maximum size of Frank loops was also reduced from about 15 nm in HP316/C/Ti to about 10 nm in HP316/C/Ti/Si. This effect of Si on the development of Frank loops was also observed in type 304 SSs [11]. Since the decrease of NFL and the average diameter was also observed in HP316/C/Ti/Si/P/S, this effect of Si did not appear to be obscured by the other impurities such as P and S. The different effect of Si on the loop nucleation in high-purity austenitic SSs under electron [19] or ion irradiation [10] has been reported. Under ion or electron irradiation, Si addition promoted loop nucleation. It is speculated that the dose rate might change the effect of Si on the suppression of NFL.

Addition of Mo, as well as Si, decreased NFL and the diameter in this study. However an addition of Mo did not reduce the maximum size of Frank loops. Shigenaka et al. [10] reported that Mo addition suppressed the effect of Si addition to Fe–18Cr–16Ni under ion irradiation. Therefore different processes between Mo and Si on the development of Frank loops might be operating.

5. Conclusions

A high-purity type 316 SS and its heats doped with C, C/Ti, C/Ti/Si, C/Ti/P, C/Ti/S and C/Ti/Si/P/S were irradiated at 513 K to a dose level of 1 dpa in Japan Research Reactor No.3. The following conclusions were drawn through TEM observations.

1. In all alloys, Frank loops and small defect clusters developed, but neither voids nor precipitates were observed.
2. Addition of Mo decreased the average diameter and the number density of Frank loops.
3. Addition of C decreased the average diameter of Frank loops, but increased the number density of Frank loops.
4. Addition of Si decreased the average diameter and the number density of Frank loops.
5. Other alloying elements and impurities such as Ti, P and S had a weaker influence on the development of Frank loops than either C or Si.

Acknowledgements

The authors would like to thank Drs S. Jitsukawa and T. Sawai and Mr Kita for helpful discussion and support, and the staff of the Japan Atomic Energy Research Institute Hot Laboratories for performing TEM observations.

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