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**RADIATION-INDUCED INSTABILITY OF MnS PRECIPITATES AND ITS POSSIBLE
CONSEQUENCES ON IRRADIATION-INDUCED STRESS CORROSION CRACKING OF
AUSTENITIC STAINLESS STEELS***

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RADIATION-INDUCED INSTABILITY OF MnS PRECIPITATES AND ITS POSSIBLE CONSEQUENCES ON IRRADIATION-INDUCED STRESS CORROSION CRACKING OF AUSTENITIC STAINLESS STEELS

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ABSTRACT: Irradiation-assisted stress corrosion cracking (IASCC) is a significant materials issue for the light water reactor (LWR) industry and may also pose a problem for fusion power reactors that will use water as coolant. A new metallurgical process is proposed that involves the radiation-induced release into solution of minor impurity elements not usually thought to participate in IASCC. MnS-type precipitates, which contain most of the sulfur in stainless steels, are thought to be unstable under irradiation. First, Mn transmutes strongly to Fe in thermalized neutron spectra. Second, cascade-induced disordering and the inverse Kirkendall effect operating at the incoherent interfaces of MnS precipitates are thought to act as a pump to export Mn from the precipitate into the alloy matrix. Both of these processes will most likely allow sulfur, which is known to exert a deleterious influence on intergranular cracking, to re-enter the matrix. To test this hypothesis, compositions of MnS-type precipitates contained in several unirradiated and irradiated heats of Type 304, 316, and 348 stainless steels (SSs) were analyzed by Auger electron spectroscopy. Evidence is presented that shows a progressive compositional modification of MnS precipitates as exposure to neutrons increases in boiling water reactors. As the fluence increases, the Mn level in MnS decreases, whereas the Fe level increases. The S level also decreases relative to the combined level of Mn and Fe. MnS precipitates were also found to be a reservoir of other deleterious impurities such as F and O, which could be also released due to radiation-induced instability of the precipitates.

KEY WORDS: austenitic stainless steel, irradiation-assisted stress corrosion cracking, manganese sulfide, transmutation, compositional instability, sulfur, fluorine.

INTRODUCTION

Failures by irradiation-assisted stress corrosion cracking (IASCC) of core internal components in both BWRs and PWRs have increased in recent years after accumulation of relatively high irradiation damage. The general pattern of these failures is that as the neutron fluence increases, nonsensitized austenitic SSs and Ni-base alloys become susceptible to intergranular failure. Although most failed components can be replaced, some safety-significant structural components would be difficult or impractical to replace. Therefore, the structural integrity of these components has been a subject of concern, and it is recognized well that IASCC has potentially large consequences on the reliability and

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safety of long-term operation of LWRs. However, despite many years of investigation since the late 1960s, the mechanism(s) by which IASCC operates are not yet well understood.

One of the frequently mentioned metallurgical processes that might influence IASCC is that of transmutation. In the past, studies of transmutation effects have focused primarily on H, He, and Li, the latter two impurities formed by the $B^{10}(n,\alpha)Li^7$ reaction. Other transmutation processes, however, might also assist IASCC indirectly. One of these previously overlooked processes appears to be the effect of transmutation of Mn to Fe. While the partial loss of Mn and an incremental increase in the concentration of Fe in grain matrices of the steel would not be expected to have direct influence on IASCC, there is an indirect route that might play an important role.

One of the major roles of Mn in austenitic stainless steels is to tie up S in MnS precipitates and thereby keep it off grain boundaries where it is known to exert a strong deleterious role in weakening the boundary. Sulfide ions dissolved in water are also well known to exacerbate susceptibility of sensitized austenitic stainless steels to intergranular stress corrosion cracking. Therefore, it seems important to understand the stability of MnS precipitates and the behavior of S in steels under irradiation to understand IASCC. Stability of MnS-type precipitates under LWR conditions may be influenced because of the combined action of cascade mixing, strong transmutation, and the inverse-Kirkendall effect. In this paper, therefore, we have focused our attention to (a) the compositional stability of MnS-type precipitates and (b) behavior of S and other impurities (such as F and O) known to be deleterious or implicated in IASCC. Fluoride ions in water or F contamination in non-irradiated weldments or some irradiated Type 304 SS neutron absorber tubes^{1,2} have been reported to exacerbate susceptibility to intergranular stress corrosion cracking. Higher O levels in steels have been also implicated to higher susceptibility to IASCC.¹⁻³ In view of this, the partitioning behavior of S, F, and O in MnS-type precipitates in unirradiated and irradiated steels was examined by Auger electron spectroscopy (AES), which is sensitive to these nonmetallic elements. A consequence of irradiation-induced destabilization of MnS precipitates would be the release of S and other deleterious elements back into the alloy matrix where they could diffuse, perhaps in a radiation-enhanced manner, to grain boundaries.

MECHANISMS LEADING TO INSTABILITY OF MnS

Cascade mixing of atoms on both sides of the interface of a precipitate is a well-known process that might incrementally release S, but in itself is probably not strong enough to contribute substantially to IASCC. Manganese, however, is a fast diffusing element in stainless steels and is known to migrate strongly up vacancy gradients established near microstructural sinks during irradiation. If the sink has an incoherent boundary with the matrix, then the operation of the inverse-Kirkendall effect can be even stronger. Figure 1 shows the schematic operation of this process.

Added to these two processes is the fact that Mn has only one isotope, Mn^{55} , with a large cross-section (13.3 barn) for transmutation by the reaction of $Mn^{55}(n,\gamma)Mn^{56}$. Mn^{56} then decays to Fe^{56} by emitting β^- particles with energies of 2.06 (50%), 1.10 (30%), and 0.82 MeV (20%) over a half-life of 2.58 h. Unlike MnS, FeS is resistant to decomposition. Table 1 shows the calculated net change in original elements in Type 316 SS for a PWR baffle bolt for an irradiation dose of 100 displacements per atom (dpa). The percentage of transmutation depends on not only the local thermal neutron flux but also the total neutron exposure. As shown in Fig. 2, the neutron spectrum can change from one position

to another, especially when the thermal-to-fast neutron ratio is examined. For the examples shown in the figure, this ratio (T/F ratio) changes by a factor of about 2 between the two spectra. Based on the PWR baffle bolt spectrum shown in Fig. 2, the expected percentage transmutation of Mn has been calculated as a function of time assuming a 75% duty factor for a PWR reactor. The result is shown in Fig. 3.

Fig. 1.

Schematic illustration of inverse Kirkendall effect operating on an incoherent precipitate surface. Manganese (fast diffuser) will be driven back to matrix from MnS precipitates by this effect.

Table 1. Solid transmutation products (as percentage of original element) formed in Type 316 stainless steel after irradiation to 100 dpa in PWR baffle bolt position.

Element	Transmutation Product	Net Decrease in Original Element (%)
Fe	Mn ⁵⁵	0.40
	Co ⁵⁹	0.08
	Ni ⁶⁰	0.07
Mn	Fe ⁵⁶	46.00
Cr	V ⁵¹	2.00
Mo	Tc ⁹⁹	2.10
	Ru ¹⁰¹	0.50
Si	p ³¹	0.02
P	p ³²	0.10
S	Cl ³⁵	0.03
	Cl ³⁶	0.02

Therefore, the purpose of this study was to investigate experimentally the stability of MnS-type precipitates contained in austenitic SSs after irradiation in BWRs. Because it is impossible to make a comparison of an identical precipitate before and after irradiation to observe shrinkage and compositional change, such evidence must be found by analyzing group of precipitates in several heats of SSs before and after irradiation. If indeed the inverse-Kirkendall effect is acting as a strong pump to export Mn from an irradiation-destabilized precipitate, it should be possible to demonstrate the Mn-to-Fe ratio that should decreases with increasing fluence.

Fig. 2.

Comparison of normalized neutron flux spectra (thermal-to-fast flux ratio, T/F ratio) for PWR in-core and baffle bolt positions

Fig. 3.

Burnout of Mn in PWR baffle bolt spectrum as a function of operating years.

EXPERIMENTAL PROCEDURE

The material type, fabrication source (i.e., laboratory or commercial heat), fast neutron fluence, and chemical composition of the austenitic SSs investigated in this study are given in Table 2. All of these heats were solution-annealed and water-quenched materials. Standard-size needle-like specimens for analysis by Auger electron spectroscopy (AES), approximately 2.5 mm in diameter and 20 mm in length, were machined and notched before charging with hydrogen and fracture in a scanning Auger microscope (SAM).

Both unirradiated and irradiated specimens were charged with hydrogen for ≈ 48 h at $\approx 60^\circ\text{C}$ in a solution of 100-mg/L NaAsO_2 dissolved in 0.1-N H_2SO_4 at a current density of ≈ 500 mA/cm². Each hydrogen-charged specimen was fractured by repeated bending at $\approx 23^\circ\text{C}$ in-situ in the ultrahigh vacuum ($\approx 3 \times 10^{-7}$ Pa) of the SAM. Microchemistries of precipitates, grain boundaries, and grain matrices of the specimens were analyzed with a JEOL-JAMP10 shielded SAM. Auger electron spectroscopy is sensitive to nonmetallic

elements and superior to other techniques for determining compositions of nonmetallic trace impurities and many metallic elements.

In a typical AES analysis, five to eight relatively large precipitates were selected. Most of the precipitates were located on ductile portion of the fracture surface, although some were on intergranular fracture surface. Most of the precipitates were sulfides (MnS or CuS), although some were carbides. Typically, the MnS-type precipitates selected for AES analysis were spherical or ellipsoidal and 2-3 μm in diameter. The beam size was kept constant at $\approx 1 \mu\text{m}$, and the beam was focused carefully at the center of the precipitate. Under this condition, virtually all of the detected Auger electrons originated from the precipitate, and Auger electrons originating in the matrix was insignificant.

Table 2. Material type, chemical composition (in wt.%), and fast fluence ($E > 1 \text{ MeV}$) of austenitic stainless steel specimens.

Heat ID No.	Fabrication	Steel Type	Composition (wt.%)									Service Reactor	Fluence (10 ²¹ n·cm ⁻²)
			Cr	Ni	Mn	C	N	Si	P	S	Other		
63	Laboratory	304L	18.23	9.24	1.27	0.019	0.103	0.70	0.007	0.002	—	—	0
625-S	Laboratory	316	17.25	11.70	0.92	0.012	0.064	0.72	0.007	0.002	Mo 2.39	—	0
HP304-CD	Commercial	304L	18.58	9.44	1.22	0.017	0.037	0.02	0.002	0.003	—	BWR-B ^a	1.4
CP304-A	Commercial	304	16.80	8.77	1.65	0.08 ^b	0.052	1.55	0.045 ^b	0.030 ^b	—	BWR-Y ^c	0.7
CP348a	Commercial	348	17.40	11.50	1.56	0.074	0.042	0.34	0.007	0.009	Nb+Ta 0.81	BWR- ^{pd}	1.5
HP348b	Commercial	348	17.70	11.10	1.65	0.041	0.008	0.19	0.002	0.007	Nb+Ta 0.76	BWR- ^{pd}	3.5

^aHigh-purity neutron absorber tubes; composition measured before service.

^bRepresents maximum value in the specification; actual value not measured.

^cCommercial-purity absorber tubes; composition measured after service.

^dSwelling mandrel tube irradiated in 7 x 7 fuel assembly in BWR KKP-1.

RESULTS

Figures 4-7 show examples of the derivative AES spectra $[dN(E)/dE]$ that were obtained from MnS-type precipitates in the unirradiated and irradiated materials listed in Table 1. In each figure, morphologies of the in-situ-produced fracture surface and the MnS-type precipitate from which the $dN(E)/dE$ spectra were obtained are also shown.

The composition of the MnS precipitates in the unirradiated heats of Type 304 and 316 SSs is nearly stoichiometric and relatively free of other impurities (Figs. 4 and 5). These two heats were fabricated by a multiple vacuum-arc melting process using an electrolytically produced Fe ingot. The three Mn peaks (i.e., Mn⁵⁴², Mn⁵⁸⁹, and Mn⁶³⁶; numbers in superscript being energies in eV) are distinctively visible in the MnS contained in these relatively clean steels. Oxygen (O⁵¹⁰) and iron (Fe⁶⁰¹, Fe⁶⁵¹, and Fe⁷⁰³) peaks are very low, whereas fluorine (F⁶⁰⁵ and F⁶²⁵) peaks are absent.

MnS-type precipitates in irradiated specimens of a commercial-purity heat of Type 304 SS [Fig. 6] and high-purity heat of Type 348 SS [Fig. 7] were significantly lower in Mn and richer in Fe, Cr, F, O, and Ca. The higher levels of O, F, and Ca are believed to be associated with alloy melting and fabrication processes of the commercial SS components (deoxidizing process and use of CaF₂ as a flux additive). The S content in MnS precipitates in the irradiated specimens also seems to be lower than that in unirradiated specimens.

Figure 8 shows that the Mn content in MnS decreases for increasing fluence. The relative content of Mn was measured by the peak height of Mn⁵⁴² which is influenced by neither the Cr nor Fe peaks. The decrease in Mn peak intensity is accompanied by a concomitant increase in the Fe peak (Fe⁷⁰³) intensity. This is shown in Fig. 9.

Fig. 4.

AES spectra and morphology of MnS contained in unirradiated Type 304 SS (Heat 63). Size of MnS precipitate analyzed (denoted by arrow in fracture surface) was $\approx 1.7 \mu\text{m}$ (beam size $\approx 1 \mu\text{m}$).

Fig. 5.

AES spectra and morphology of MnS contained in unirradiated Type 316 SS (Heat 625-S). Size of MnS precipitate analyzed (denoted by arrow in fracture surface) was $\approx 2.6 \mu\text{m}$ (beam size $\approx 1 \mu\text{m}$).

The combined results of Figs. 8 and 9 show that the composition of manganese sulfides are unstable under irradiation, which is in qualitative agreement with the prediction based on the combined action of transmutation and the inverse Kirkendall effect. However, further analysis is necessary to confirm quantitative aspect of the prediction. For example, concentration gradients of Mn and Fe could be measured across the precipitate-matrix

Fig. 6.

AES spectra and morphology of MnS contained in Type 304 SS BWR neutron absorber tube irradiated to a fluence of $\approx 0.7 \times 10^{21} \text{ n cm}^{-2}$. Size of MnS precipitate analyzed (#10 in fracture surface) was $\approx 2 \mu\text{m}$ (beam size $\approx 1 \mu\text{m}$).

Fig. 7.

AES spectra and morphology of MnS contained in high-purity Type 348 SS tube specimen irradiated to a fluence of $\approx 3.5 \times 10^{21} \text{ n cm}^{-2}$ in a BWR. Size of MnS precipitate analyzed (#5 in fracture surface) was $\approx 2.7 \mu\text{m}$ (beam size $\approx 1 \mu\text{m}$).

interface and compared with the predicted profile. As shown in Figs. 6 and 7, the composition of the MnS contained in the commercial stainless steel components irradiated in BWRs was in general complex and differed much from that of MnS contained in the unirradiated stainless steels (e.g., Figs. 4 and 5). As a result of the modification of chemical composition, the solubility of MnS (e.g., in BWR water) could be also modified.

Fig. 8.

AES peak intensity of Mn^{542} from Mn sulfides in austenitic stainless steels irradiated in BWRs as function of fluence.

Fig. 9.

AES intensities of Mn^{542} vs. Fe^{703} peaks, showing that decrease in Mn in sulfides is accompanied by increase in Fe content as fluence increases.

In view of recent reports with regard to the deleterious effects of F^{1,2} and O¹⁻³, the partitioning and dissolution behavior of these impurities in association with irradiation-induced instability of Mn sulfides is of particular importance. Although spectra such as those in Figs. 6 and 7 provide qualitative evidence that the O level was relatively higher in MnS sulfides contained in irradiated commercial heats than in MnS sulfides in unirradiated laboratory heats, it is difficult to determine the partitioning behavior of O quantitatively because of the uncertainties associated with contamination by O from the vacuum environment of the SAM.

Fluorine analysis by AES was conducted on several types of BWR-irradiated components, as well as on a Type 304 SS weld specimen (composition unknown) sectioned from an irradiated field component. The AES signals of F in steels can be easily overlooked because the primary $\text{dN(E)}/\text{dE}$ peak at ≈ 650 eV is hidden behind the strong Fe peak at ≈ 651 eV. However, F gives rise to the relatively weak secondary peak at ≈ 625 eV, which is

characteristic of F. At the same time, the peak height at ≈ 650 eV (F plus Fe) should increase proportionately with increased peak height at ≈ 625 eV (F). To analyze these characteristics more quantitatively, nonirradiated standard samples of FeF_2 and pure Fe were examined to obtain standard AES spectra.

In Fig. 10, the $dN(E)/dE$ spectra of Auger electrons, obtained from an unirradiated standard of FeF_2 compound and Type 304 SS weld, respectively, are shown for comparison. Fluorine in stainless steels could not be detected from the integral-energy spectra. However, in the derivative-energy spectra $dN(E)/dE$, F gives rise to a weak secondary peak at ≈ 625 eV. Therefore, for increasing F content in Fe, the peak height at ≈ 625 eV (F only) should be linearly proportional to the peak height at ≈ 651 eV (Fe plus F). Such data in Fig. 11 were obtained from Type 304 SS neutron absorber tubes, a control blade sheath, and Type 348 SS expanding-mandrel tubes, and they are compared with those from the irradiated Type 304 SS weld and the FeF_2 standard. As expected, the peak height at ≈ 650 eV (Fe plus F) increased linearly with increasing peak height at ≈ 625 eV in a manner consistent with the standard spectra obtained from the unirradiated FeF_2 . This provides a positive identification of the ≈ 625 eV peak as indeed being the secondary peak of F in the BWR components.

Fig. 10.

$dN(E)/dE$ spectra from unirradiated standard FeF_2 (A) and irradiated Type 304 SS weld of BWR component (B).

Peak height of F 625-eV signal is plotted as a function of peak height of 651-eV peak (F + Fe) in Fig. 11 for several types of precipitates contained in different heats, i.e., MnS- and (Ca,Mn)S-type sulfides, and spinel-type (FeCr_2O_4) oxides. The figure indicates that F contents in precipitates and grain boundaries are relatively higher than those in the grain matrices of (unwelded) base metals. The results indicate also that relative F content in the weld specimen is significantly higher than those in the other solution-annealed BWR components. Fluorine 625 eV signals from most grain-matrix spots were comparable to background noise or were too low to be identified unambiguously; therefore, only those grain-matrix signals distinctively higher than the noise level were plotted in Fig. 11.

Formation of Ca-rich sulfides in Heat 348a could be associated with use of a CaAl alloy as a deoxidizer in making the steel, because a relatively high level of Al was also detected

in the specimen. It is also possible that Ca originated from fluorspar ($\approx 75\% \text{CaF}_2$), which is frequently used as flux material in iron- and steelmaking processes. The F signals from sulfides and oxides are significantly higher than those from ductile fracture surfaces (grain matrices). However, F enrichment in carbides seemed to be negligible. Because these precipitates are typically formed during fabrication, it is likely that F enrichment in the sulfides and oxides also occurred by a thermal process.

Fig. 11.

Relative intensities of Auger electrons of F at ≈ 625 eV and F plus Fe at ≈ 651 eV from ductile and IG fracture surfaces and precipitates found in irradiated base metal and welds.

DISCUSSION

There is clear evidence presented in this study that a progressive compositional modification of MnS precipitates occurs with increasing exposure to neutrons in LWRs. As fluence increases, the Mn level in MnS sulfides decreases relative to the S level, whereas the Fe level increases. The S level decreases relative to the combined level of Mn and Fe as fluence increases. This compositional modification seems to be consistent with the operation of the mechanisms proposed in this study, i.e., transmutation of Mn to Fe, cascade-induced disordering, and inverse Kirkendall effect. It is therefore reasonable to assume that S is also being released from Mn sulfides into grain matrices during irradiation. To confirm this directly, however, it is necessary to obtain more quantitative evidence, e.g., line profiles of Mn, Fe, and S across sulfide-matrix interfaces as a function of fluence.

The increased instability of MnS-type precipitates and the concomitant release of S and F into grain matrices with increasing fluence will be most likely deleterious from the standpoint of susceptibility to IASCC. In particular, these processes that occur on or near grain boundaries are believed to be more deleterious, because S and F released on the grain boundaries of an advancing intergranular crack can be dissolved readily into the water in the crack tip. The rugged three-dimensional morphology of the predominantly intergranular fracture surface of the BWR components, produced either during a hot-cell slow-strain-rate tensile test or service in the reactor, was examined by the technique of stereo scanning electron microscopy (SEM). The results showed that the depth of the intergranular

fractures perpendicular to the direction of the overall crack propagation were as much as ≈ 20 times the average grain size. Under this situation, the ratio of the surface area of the material to the volume of the water in the crack tip is very large, and hence, the effect of the dissolution of S and F on the crack-tip water chemistry could be significant.

The higher F and O levels in the sulfide precipitates and on grain boundaries in the irradiated commercial heats appear to be consistent with the very low solubility of F and O in SSs, because to reduce the total free energy of the system, F and O will segregate by thermal processes to local sites such as matrix-precipitate interfaces, grain boundaries, and stacking faults. As shown in Figs. 6 and 7 as examples, higher level of F in MnS in the irradiated commercial heats was frequently observed in association with higher level of Ca. This seems to indicate that F and Ca originated from fluorspar ($\approx 75\%$ CaF_2) which is frequently used as flux material in iron and steelmaking processes. Furthermore, it seems to indicate also that F and Ca were trapped in MnS by a thermal process during fabrication (i.e., before irradiation) rather than by irradiation-induced segregation. However, the exact mechanism(s) that lead to higher level of F and O in the MnS-type precipitates in the irradiated commercial heats are not clear at this time, and further investigation is necessary.

CONCLUSIONS

- (1) Compositional modification of MnS-type precipitates and gradual release of S into grain matrices are predicted on the basis of combined effects of strong transmutation of Mn to Fe in highly thermalized neutron spectra, cascade-induced disordering, and the inverse Kirkendall effect.
- (2) There is clear evidence that a progressive compositional modification of MnS precipitates occurs with increasing exposure to neutrons in BWR-irradiated austenitic stainless steels. As fluence increases, Mn level in MnS precipitates decreases, whereas Fe level increases. The sulfur level decreases relative to the combined level of Mn and Fe. This compositional modification seems to be consistent with the operation of the proposed mechanisms. It is therefore reasonable to assume that S is also being released from Mn sulfides into grain matrices during irradiation. To confirm this directly, however, it is necessary to obtain more quantitative evidence.
- (3) Fluorine and oxygen levels in irradiated commercial heats were relatively higher on MnS-type precipitates, grain boundaries, and welds than in grain matrices of base metal. This appears to be consistent with the very low solubility of F and O in austenitic stainless steels, indicating that they are likely to segregate to MnS precipitates and grain boundaries by thermal processes. A higher level of F in MnS precipitates in the irradiated commercial heats was frequently observed in association with higher level of Ca. This seems to indicate that F and Ca originated from fluorspar ($\approx 75\%$ CaF_2 , which is frequently used as flux material in iron and steelmaking processes) and that F and Ca were trapped in MnS by a thermal process during fabrication.
- (4) The increased instability of MnS-type precipitates and the concomitant release of S and F into grain matrices at higher fluence should be deleterious from the standpoint of susceptibility to IASCC.

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