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Radiation-Induced Segregation in Austenitic and Ferritic Steels

Taro TAKEYAMA, Heishichiro TAKAHASHI and Soumei OHNUKI

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Abstract

Void formation and radiation-induced segregation in modified 316 austenitic stainless steels and ferritic steels were investigated by electron and ion irradiations. In austenitic steels modified by Ti and Nb, void swelling was effectively suppressed, particularly the growth rate of voids was remarkably retarded in Nb contained steel. Local composition of solute elements near voids and grain boundaries changed during irradiation. In ferritic steels, significant resistance to void swelling was observed. Radiation-induced segregation and precipitation were confirmed on voids, dislocation loops and grain boundaries. From these results, it was indicated that void formation could be affected due to an effect of solute segregation.

I. Introduction

In alloys, the defect fluxes produced by irradiation could cause segregation of alloying elements to or away from defect sinks such as dislocatins, voids and grain boundaries[1-3]. Radiation-induced segregation(RIS) occurs prominently on materials at a condition of high displacement per atom. Theoretical developemnts have been done for RIS, which are based on misfit strain energy and predict the flow direction of solute atoms. Namely undersized atoms migrate towards and oversized ones away from sinks. For example, in austenitic stainless steels Ni segregates towards and Cr segregates away from defect sinks during irradiation. This RIS occasionally causes solute enrichment which exceeds the solubility limit of alloying elements at the defect sinks, and precipitation of the second phases occurs. Therefore, the RIS produces not only a large change in composition on a local scale but also phase changes or transformation which are not observed under thermal conditions. The non-equilibrium compositional change has also given an important influence on void formation through some mechanisms such as stabilization of void nucleation and recombination. Furthermore, due to the occurrence of the compositional change of alloying elements which were added for a specific purpose, mechanical properties of the alloys such as ductility, toughness will also be altered. Therefore, it is very important to investigate the RIS for development of candidate materials for fusion reactor. In this study, the void formation and RIS in modified 316 stainless steels(PCA) were investigated by electron and ion irradiations, and the segregation behavior and its influence on void formation were clarified.

Metals Research Institute

II. Experimental Procedure

Chemical compositions of the PCA (primary candidate alloy) are shown in Table 1. In the PCA, the amounts of Ti and Nb added for modification were 0.25 and 0.12-0.21wt%, respectively. These PCA were irradiated by a dose of 15 dpa using HVEM (1 MV) in the temperature range of 623-873 K after solution treatment at 1323-1473 K. Post-irradiation compositional analyses were carried out by an energy dispersive X-ray analyzer (EDX).

In case of ferritic steels, irradiation was performed with 200 keV C^+ ions at 798-898 K up to 114 dpa and 1 MV HVEM at 623-873 K up to 10 dpa. Specimens and irradiation conditions were shown in Table 2. Structural observation and micro-chemical analysis were also carried out using HVEM, EDX and EELS.

III. Results and Discussion

III—1. Austenitic Steels

(1) Void Formation in Ti and Nb-modified Steels

When Ti and Ti-Nb modified 316 stainless steels[4] (Ti and Ti-Nb steels) were irradiated, the development of dislocation structures followed the same general pattern of dislocation loop formation following by its growth. A does level greater than approximately 1 dpa was required before voids were observable in the microstructure. However, the behavior of void nucleation in the Ti-Nb steels was different from that in the Ti steel. Fig. 1 and 2 show microstructures of Ti and Ti-Nb steels produced by irradiation to about 10 dpa, respectively. Up to 723 K, the void distribution was similar in both steels, but at higher temperatures above 773 K void nucleation of Ti-Nb steel was distinctly suppressed.

The effect of Nb addition on void growth at various temperatures is illustrated in Fig. 3. For Ti and Ti-Nb steels, the average void size up to 673 K did not differ greatly. However, above 723 K the sizes distinctly decreased in the Ti-Nb steel and this tendency

Table 1. Chemical compositions (wt%).

specimens	Ti steel	Ti-Nb Steels	
Ti	0.24	0.25	0.24
Nb	–	0.12	0.21
Si	0.53	0.53	0.49
Cr	14.6	16.1	16.2
Ni	16.2	16.2	16.2
Mn	1.79	1.55	1.54
Mo	2.37	2.6	2.6
C	0.06	0.05	0.06
P	0.027	0.018	0.016
S	0.009	0.007	0.006
B	0.0035	–	–
Fe	bal	bal	bal

Table 2. Ferritic steels and irradiation.

specimens	conditions
Fe-13%Cr (wt%) Fe-13%Cr-1%Si Fe-13%Cr-1%Ti Fe	200 keV C^+ 114 dpa 700-900 K
Fe-10%Cr (wt%) Fe-10%Cr-0.03%C Fe-0.1%Ti (at%) Fe-0.2%Ti Fe-1%Ni Fe-1%Mn Fe-1.8%Mo	1 MV HVEM 10 dpa 623-873 K

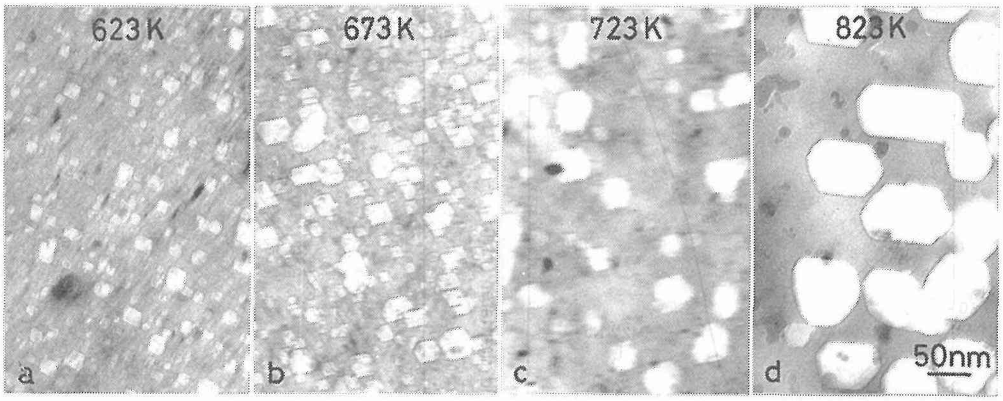


Fig 1. Void distribution for Ti steel irradiated to 10 dpa at various temperatures.

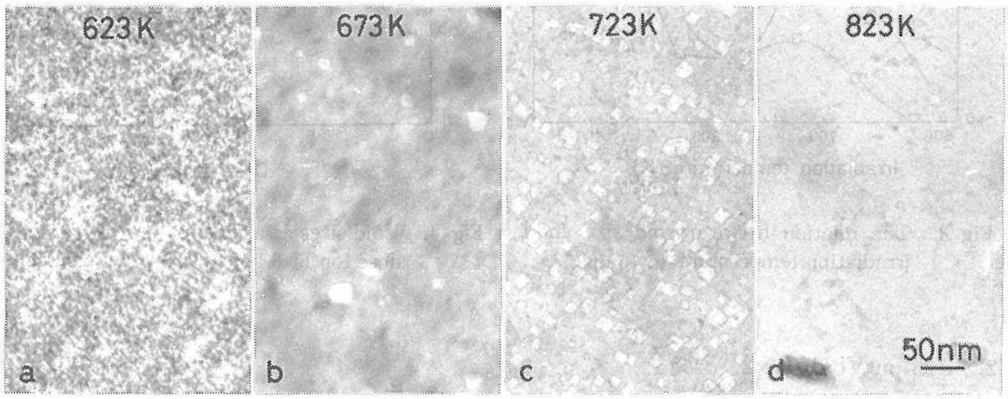


Fig 2. Void distribution for Ti-0.21% Nb steel irradiated to 10 dpa at various temperatures.

in void size was more markedly observed in a higher temperature range and for high Nb contained steel.

The quantitative data on void growth is given in Fig. 4 for the Ti-Nb steels. It can be seen that the void growth is remarkably influenced due to containing a small amount of Nb, i.e. the growth rate is retarded by Nb addition and this trend appears strongly in the high Nb concentration steel.

The void swelling as a function of temperature for a given dose of 10 dpa is shown in Fig. 5. In case of the Ti steel the double peaks of swelling were recognized at 723 and 823 K. Especially the swelling at 823 K was very high. On the other hand, the Ti-Nb steels showed only one peak at 723 K and no swelling peak appeared at the higher temperature. Furthermore, void swelling of Ti-Nb steel was lower at all irradiation temperatures. This swelling suppression effect of Nb addition directly contributed to void nucleation retardation but not to void growth.

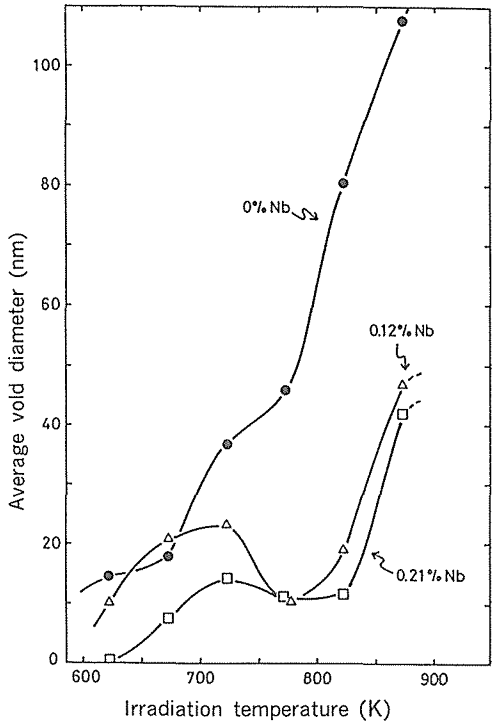


Fig 3. The relation between void size and irradiation temperature to 10 dpa.

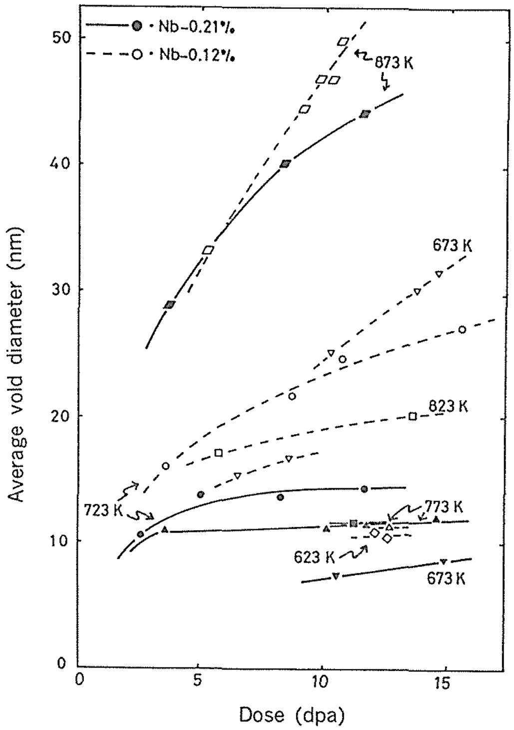


Fig 4. Void sizes as a function of irradiation dose for Ti-0.12 and 0.21 wt% Nb steels.

(2) RIS on Void

To examine the effect of RIS on void formation, composition analysis around voids of the Ti steel was performed by EDX. Fig. 6 indicates the concentration profiles for alloying elements between two voids after irradiation to 11 dpa at 823 K as a function of distance from void center. The concentration was calculated on the basis of Kα X-ray intensity. It is clear that Ni concentration near voids is higher than that in the matrix. Conversely, Cr tends to deplete near voids. The segregation of Ni and Cr showed difference of more than several percent. A similar concentration change on voids was recognized for minor solute elements, in which Si and Ti tended to segregate and Mo concentration was slightly lower than that in the matrix. Similar concentration profiles, though not as large as at 823 K, were obtained after irradiation at 723 K. However, no significant concentration change of solutes could be observed around voids for Nb containing steels because of retardation of voids and/or small voids formation.

The temperature dependence of RIS on the voids is shown in Fig. 7.The RIS of the elements except Ti was recognized conspicuously at 823 K where the maximum swelling occurred presumably due to acceleration of void growth. However, Ti showed maximum RIS at 723 K, at which is corresponding to the temperature of the second swelling peak, where fine precipitates caused by RIS will enhance the void nucleation.

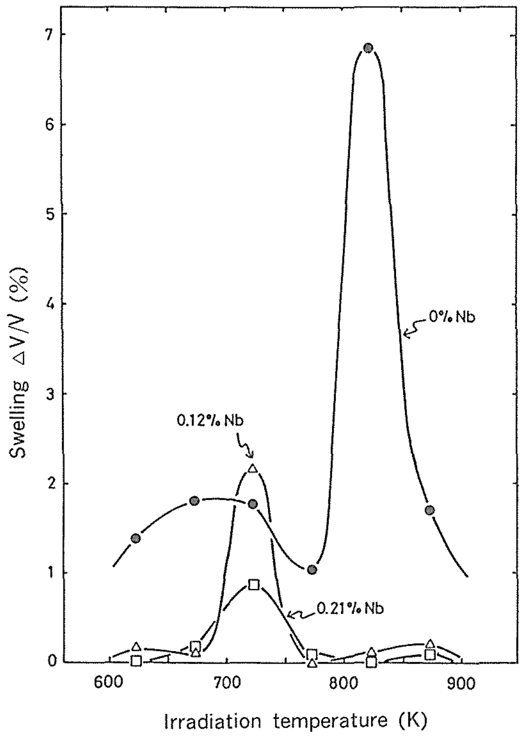


Fig 5. Temperature dependence of void swelling for each steel after irradiation to 10 dpa.

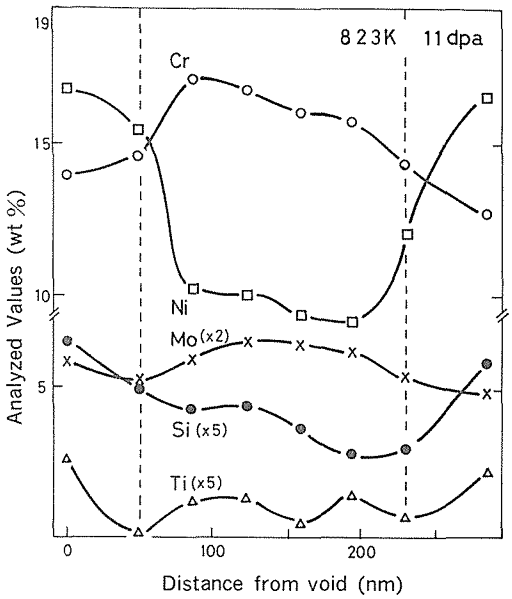


Fig 6. Concentration profiles as a function of distance from void center for Ti-Nb steel at 823 K.

When the equivalent concentration of Nb and Ti is higher than carbon and/or nitrogen impurities, Nb and Ti will exist in solution in addition to the precipitates. Therefore, it would be explained by the following two effects for the void behavior. One of the effects will enhance point defect recombination by solutes in solution[5] and the other will be the role of the precipitates for the nucleation[6].

From the study of composition analysis, it is suggested that the swelling peak at 823 K for Ti steel is contributed to the segregation effects on voids through the acceleration of void growth[7]. However, Nb addition may retard these effects due to segregation as a result of the stabilization of fine precipitates which occur uniformly in the matrix even under high tempererature irradiation, and enhances recombination due to the increase of free Nb and causes void swelling suppression.

(3) RIS on Grain Boundary

Figure 8 shows the results of grain boundary irradiation in Ti steel. At lower temperatures (<720 K), voids were observed uniformly in the matrix, however, at higher tempertures (>770 K), the void size became larger and the voids tended to be formed on the grain boundary. With the increase in dose, the voids grew and joined together, as a result a line of voids was formed on the grain boundary. At the same time, grain boundary migration

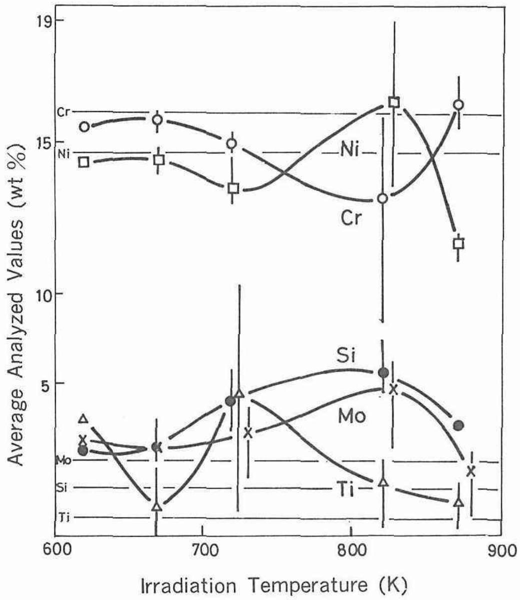


Fig 7. Temperature dependence of solute concentration on voids in Ti steel electron-irradiated to about 10 dpa.

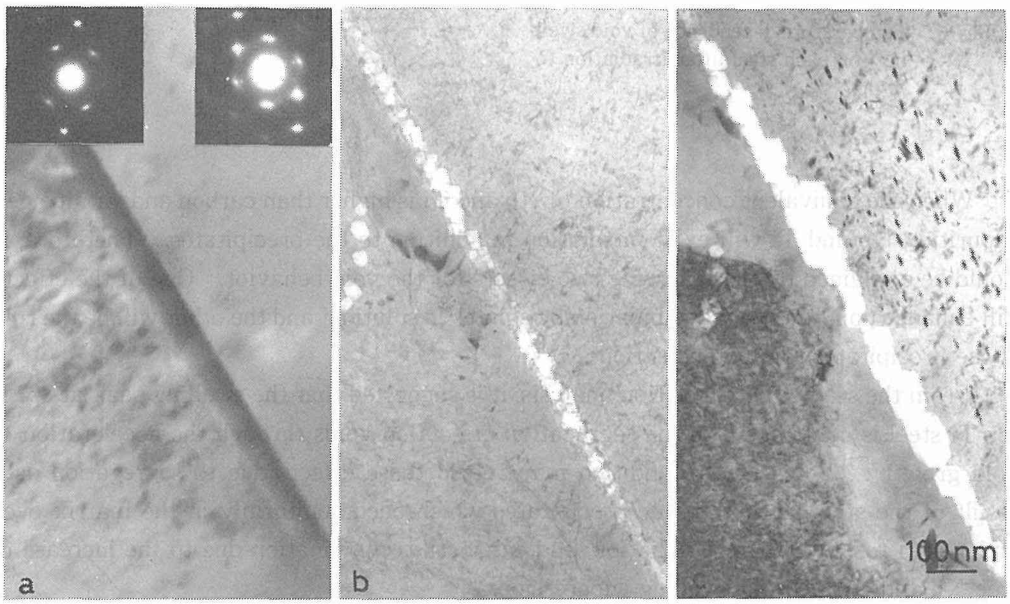


Fig 8. An example of grain boundary and void structures during electron-irradiation at 822 K. (a) before irradiation, (b) 2.7 dpa and (c) 6 dpa.

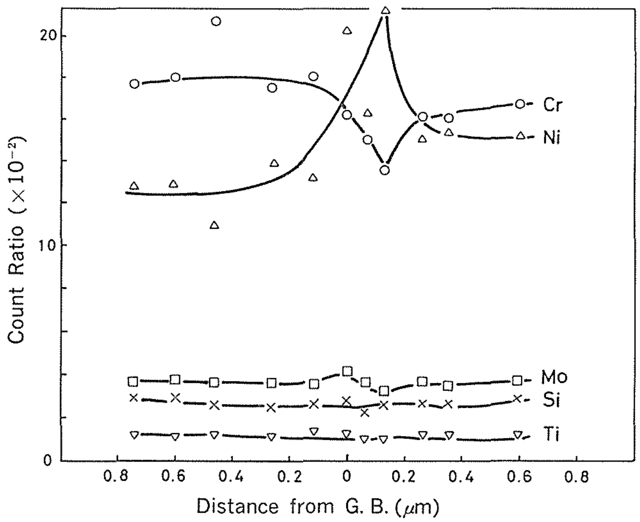


Fig 9. Segregation profiles of elements near grain boundary in Ti steel electron-irradiated to 5.4 dpa at 789 K.

was observed. RIS was also recognized on and near the irradiated grain boundary. As shown in Fig. 9, the results of EDX analysis indicated that Ni, Si and Ti were enriched, but Cr and Mo tended to be depleted. The RIS depended usually on the size effect of the solute elements except for Ti of a carbide former. The maximum segregation appeared at 823 K, where the void formation on grain boundary was clearly observed.

These results indicate that the remarkable segregation on the grain boundary offer a preferential void nucleation site at higher temperatures. Thus, it seems that the grain boundary would not act as neutral sink for point defects. Moreover, it is suggested that these remarkable segregations and the formation of voids on the grain boundary could contribute to reduction of the grain boundary strength.

III—2. **Ferritic Steels**

(1) Fe-Cr and Fe-Cr-X Alloys

On the C^+ ion irradiated Fe-Cr alloys[8], precipitates and small voids nucleated and grew with the increase of dose. Voids could be observed by electron microscopy after irradiation above 30 dpa. After irradiation to 114 dpa, rod-shaped precipitates were formed in the matrix and on the grain boundary, but they were not observed on the unirradiated specimens of thermal aging. The mean size was 0.2-1 μm and the number density was 3 -9x10^{19}m^{-3}. From EDX and EELS analyses, the precipitates were found to be enriched in chromium and carbon, and it was identified as $M_{23}C_6$. Fig. 10 shows the voids structures in Fe-Cr alloy irradiated to 114 dpa at three different temperatures. Voids grew with the increasing irradiation temperature, and their number densities decreased. At 750 and 800 K, voids were formed almost homogeneously, but at higher temperatures large voids were seen located on rod-shaped precipitates and the void swelling was 1%. The voids structure

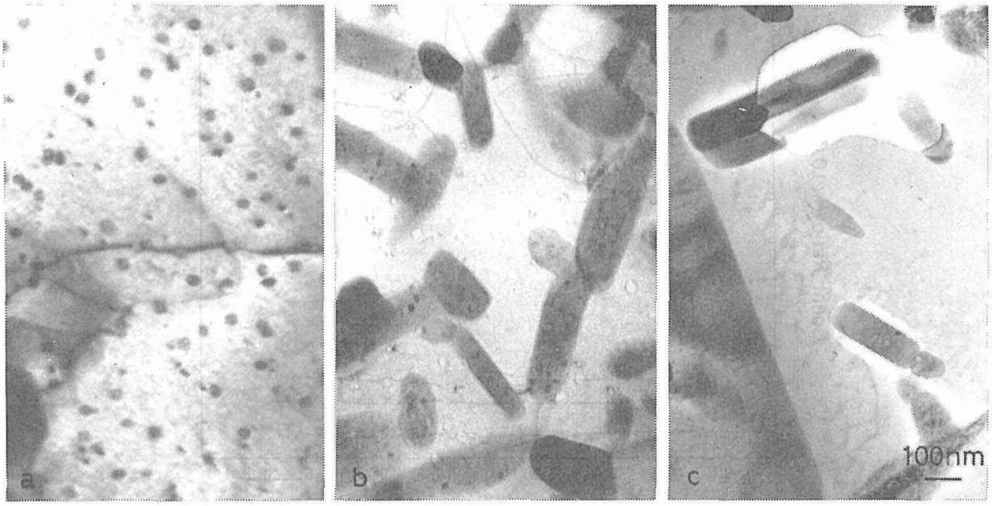


Fig10. Temperature dependence of void structures in Fe-13Cr alloy irradiated by C^+ ion to 114 dpa at (a) 750, (b) 800 and (c) 850 K.

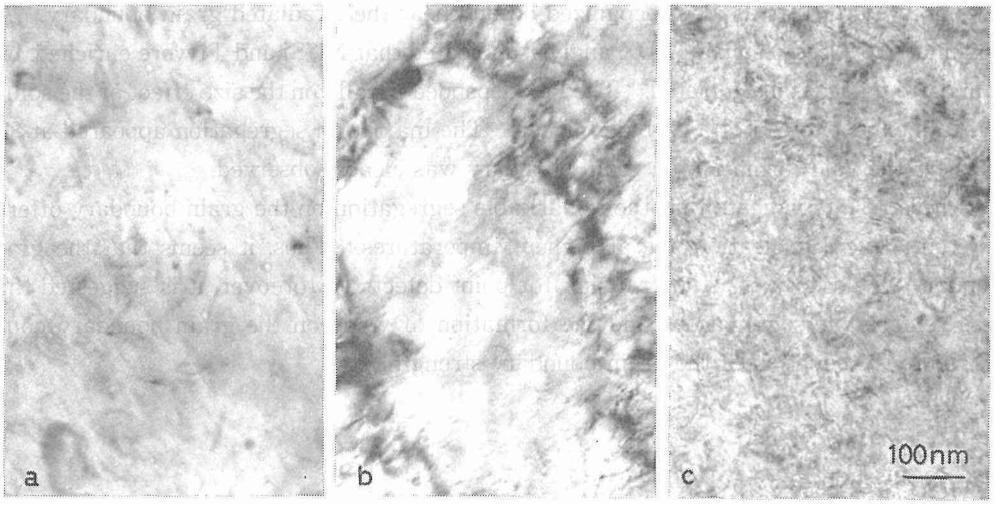


Fig11. Temperature dependence of void structures in Fe-13Cr-1Ti alloy irradiated by C^+ ion to 114 dpa at (a) 750, (b) 800 and (c) 850 K.

of Fe-Cr-Si alloy was the same as that of Fe-Cr alloy. In case of Fe-Cr-Ti alloy, voids were observed only at 750 K after 114 dpa as shown in Fig. 11, in which the mean diameter and number density were 10 nm and $2x10^{21}m^{-3}$, respectively. At higher temperatures, though the voids could not be confirmed, it was important to note that the dislocation density of Fe-Cr-Ti alloy was higher than other alloys.

Figure 12 shows the temperature dependence of void swelling of these alloys compared with the results of pure iron. In the case of pure iron, swelling showed maximum value at

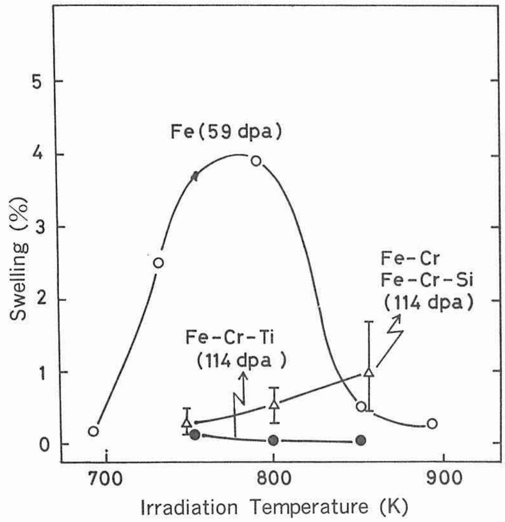


Fig12. Temperature dependence of void swelling in ion-irradiated pure iron and Fe-13Cr base alloys.

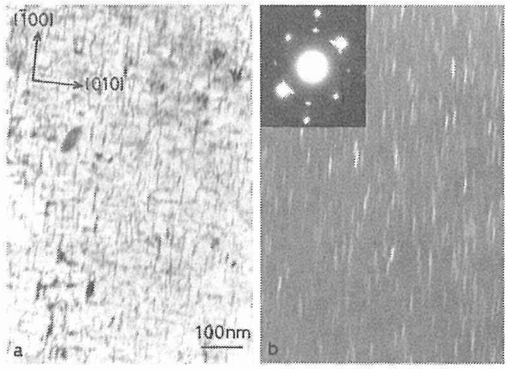


Fig13. Precipitate structure in Fe-13Cr-1Ti alloy irradjated by C^+ ion to 114 dpa at 850 K. (a) bright and (b) dark field images.

800 K and reached about 10% at 118 dpa. On the contrary, void swelling of Fe-Cr and Fe-Cr-Si alloy reduced to less than 1% even at high temperatures and the effect of Si addition on the swelling was not obvious. In case of Fe-Cr-Ti alloy, the swelling could be confirmed to be less than 0.1% at 750-800 K and was almost zero at higher temperatures. It is clear that titanium addition led to strong void suppression even at higher dose.

Fine plate-like particles precipitated in the matrix of Fe-Cr-Ti alloy irradiated to 114 dpa, and were about 40 nm in size and about 10^{20} m^{-3} in number density as shown in Fig. 13. The precipitates grew with the increasing temperature, and was identified as MC type titanium-carbide. From the trace analysis, the precipitates showed {100} habit plane.

Dislocation loops were preferential damage structures in Fe-10Cr alloy during electron-irradiation at 563-783 K. Fig. 14 shows the temperature dependence of Fe-10Cr alloy irradiated to 0.25 dpa. At lower temperatures of 563 and 617 K, dot-like loops were observed with high number density and it appears that they assemble and grow in a<100> and<110>direction. From the loop analysis of the specimen irradiated at 670 K, most loops have the nature of b=a<100>. At higher temperatures the loops grew rapidly in a <100>direction. However in irradiation up to 5 dpa, further increase of loop number density, and voids was not observed.

To determine the solute concentration on the dislocation loops compared with the matrices in Fe-Cr and Fe-Cr-C alloy, EDX analysis were carried out precisely and more than 15 point on the loops and matrices were counted. Table. 3 shows the results of slightly (0.9%) enriched Cr on<100>dislocation loops. Table. 4 also shows the results of solute segregation on voids in ferritic alloys irradiated by C^+ to 114 dpa at 800 K. In both Fe-13Cr and Fe-13Cr-1Si alloys, Cr was enriched on voids. Cr is oversized in Fe, so the segregation

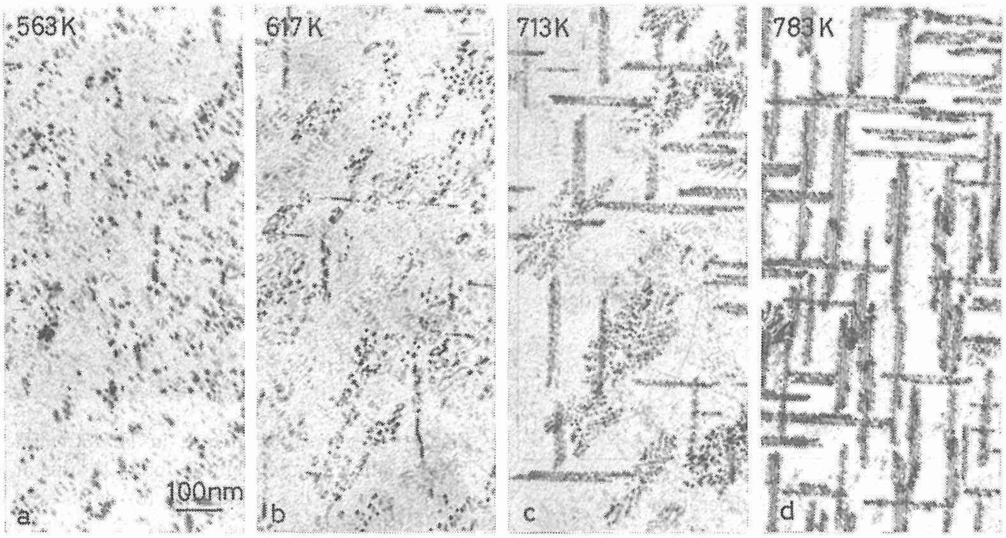


Fig14. Dislocation structure in Fe-10Cr alloy irradiated by electron to 0.25 dpa at (a) 563, (b) 617, (c) 713 and (d) 783 K.

Table 3. EDX analysis on loops and matrices.

Fe-10Cr	(Cr/Fe+Cr)
Loop Matrix	12.78 (0.9% enrich) 12.67
Fe-10Cr-C	(Cr/Fe+Cr)
Loop Matrix	13.13 (2.6% enrich) 12.80

Table 4. EDX analysis on voids and matrices in the ion-irradiated samples.

Fe-13Cr	(Cr/Fe+Cr)
Void Matrix	15.2 (2.6% enrich) 12.6
Fe-13Cr-1Si	(Cr/Fe+Cr+Si)
Void Matrix	16.6 (2.7% enrich) 13.9

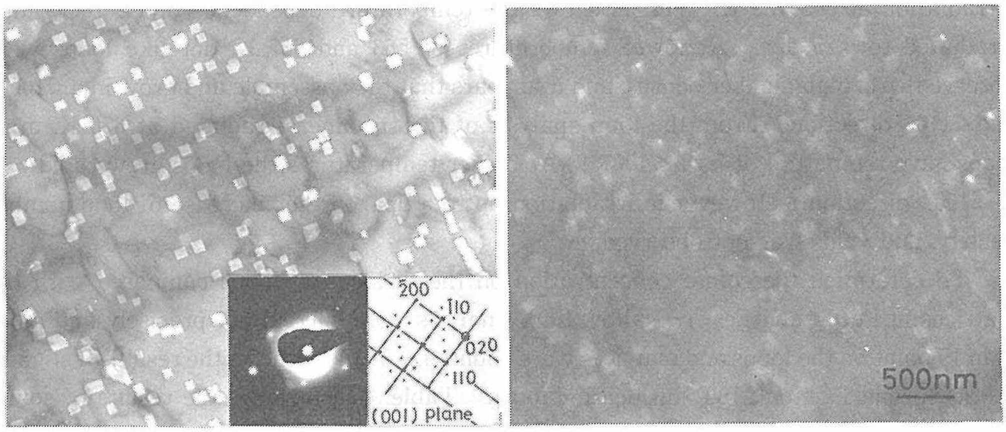


Fig15. Bright and dark field images in Fe C^{+} irradiated to 59 dpa at 798 K. Fe_3C was formed on voids.

phenomena cannot explained by the size misfit theory of solute. In contrast, it has been clarified that C segregates on void surfaces and forms Fe_3 C in Fe irradiated by C^+ ion as shown in Fig. 15. These anomalous segregation phenomena of Cr would be related to the minor impurity segregation such as C.

It is possible that chromium and interstitial solutes enhance the mutual recombination through the process of point defect trapping[9]. Reduction of swelling in the C^+ ion-irradiated Fe-Cr alloys may be partially due to the trapping mechanism, however, it must be pointed out that the strong suppression in Fe-Cr-Ti is related to the precipitation. It has been reported that precipitates such as MC appear to have a strong effect on the movement of dislocations.

As indicated in the results of electron irradiation at lower temperatures, the effect of high dislocation loop density can be considered for other factors on swelling suppression. Especially, in Fe- Cr-Ti alloy irradiated even at higher temperatures, dislocations of high density were observed with MC phase formation. Moreover, titanium addition will intensify the stability of the dislocation at high doses through the fine precipitation on it. It can be assumed that the dislocation density becomes higher, since the<100>dislocation does not cross slip easily, and as a result the swelling will be suppressed. Therefore, it is suggested that the stability of<100>type dislocation structure may be an important factor on swelling resistance in the ferritic steels.

(2) Effect of Minor Elements in Fe

(a) Fe-Ti Alloys

In the case of Fe-0.1at% Ti alloy[10], the void formation was prominently suppressed and the formation temperature shifted to the higher side about 50 degrees. The effect of void suppression was more remarkable in Fe-0.2at% Ti. It is not obvious because void formation has been suppressed by an addition of a small amount of Ti in Fe. However, in Ti -Fe alloys during prolonged irradiation, the secondary defect clusters of vacancy type

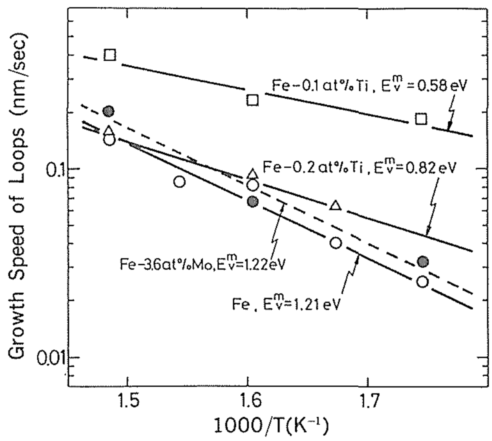


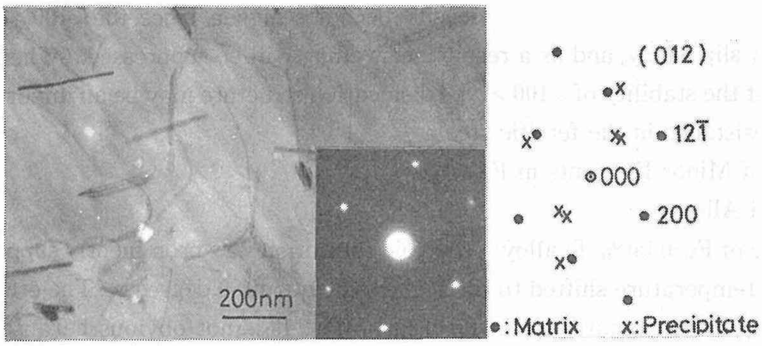
Fig16. *Relation betweeen growth speed of loops and inverse of irradiation temperature.*

which were not void appeared near the tangled dislocations of growing interstitial loops. The clusters instead of voids showed new evidence for void suppression due to the scaveng-ing effect for interstitial impurities in Fe such as C or N. It was confirmed by the measurement of the migration energy of Fe and Ti-Fe alloys as shown in Fig. 16.

(b) Fe-Ni Alloy

In the case of Fe-1 at% Ni alloy, electron-irradiation up to 10 dpa produced fine void formtion at 570-770 K, and the swelling was less than 0.3%. At the same time, plate-like precipitates nucleated on the dislocation loops, even though, Ni concentration of the alloy was within the solid solution limit. Also, voids tended to form on the edge of the precip-itates. From EDX analysis and electron diffraction, the precipitates were enriched in Ni and identified as gamma phase, as shown in Fig. 17.

The precipitates dissolved by post-irradiation annealing, therefore they were radiation -induced phase. This result indicates that Ni can segregate to dislocation loops and form the induced phase, because it is an undersized solute in this alloy.



Fe-Ni	K_{Ni}/K_{Fe}
matrix	0.0057
precipitate	0.028

$(K_{Ni}/K_{Fe})_P/(K_{Ni}/K_{Fe})_M=4.9$

hkl	d γ-Fe	measured d
111	2.07 A	2.12 A
200	1.79	1.80
220	1.27	1.33
311	1.08	1.09

Fig17. Results of EDX and diffraction pattern of radiation-induced precipitates in Fe-Ni alloy irradiated at 723 K.

(c) Fe-Mn Alloy

In the case of Fe-1 at% Mn alloy[10], voids were confirmed in a temperature range of between 650-720 K. The maximum swelling temperature was about 700 K, which was about 100 degree higher than that of pure Fe, and it was noted that the amount of swelling was slightly changed. As shown in Fig. 18, Mn tended to deplete from grain boundary during irradiation. This result can be explained by the fact that Mn is an oversized solute and interacts with a vacancy (Fig. 16). Therefore, Mn addition can not be expected to bring about an effective improvement of void swelling.

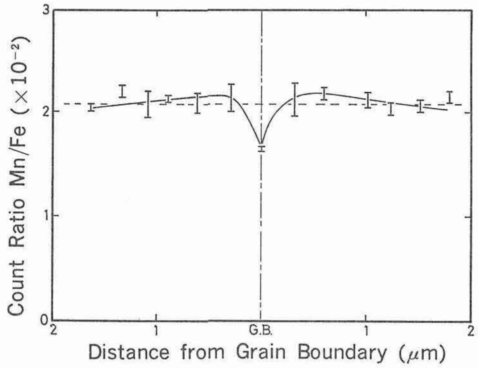
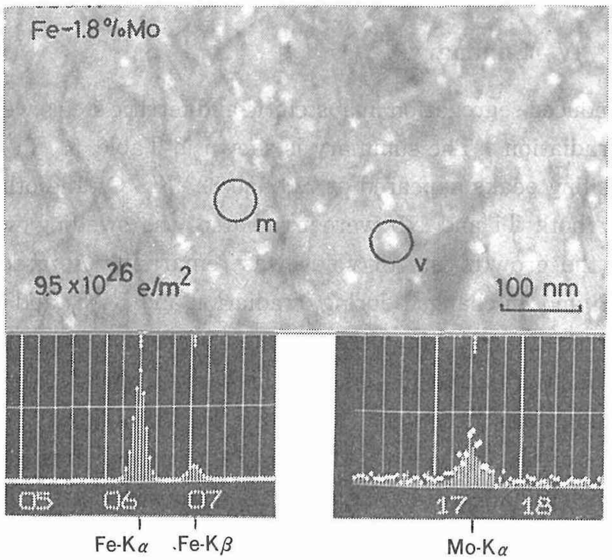


Fig18. Segregation profile near grain boundary in Fe-Mn alloy irradiated to 3 dpa at 673 K.

(d) Fe-Mo Alloy

In the case of Fe-1.8at% Mo alloy[10], many voids were formed at 570-670 K, and the maximum swelling temperature shifted to 50 degrees higher as compared to pure iron. Swelling tended to be higher than pure Fe, because of the high void number density. On the voids, Mo was clearly depleted, as shown in Fig. 19. The segregation phenomena would be caused by the weak binding with vacancies (Fig.16) and also Mo is an oversized solute in this alloy. Therefore, although Mo is an important alloying element for high temperature strength, it does not affect void swelling suppression.



Fe-Mo	K_{Mo}/K_{Fe}
matrix	0.022±0.001
void	0.020±0.001

$(K_{Mo}/K_{Fe})_V/(K_{Mo}/K_{Fe})_m=0.91$

Fig19. Concentration change of Mo on voids in Fe-Mo alloy irradiated at 623 K.

Table 5. Summamy of void formation and radiation-induced segregation in austenitic and ferritic steels.

Alloys	Irradiation	Loop Dens.	Void Dens.	Swelling	Size Factor	Segregation	Precipitaion
Ti-steel	e (11dpa)	high	low	< 7 %	Cr +	D (V, GB)	
					Ni −	E (V, GB)	
					Mo +	D (V, GB)	
					Si −	E (V, GB)	
					Ti +	E (V, GB)	
Ti-Nb steel	e (11dpa)	high	low	< 2 %			
Fe-13Cr	C^+ (114dpa)	low	low	< 1 %	Cr +	E (V, GB)	$M_{23}C_6$
Fe-13Cr-1Si	C^+ (114dpa)	low	low	< 1 %	Cr +	E (V, GB)	$M_{23}C_6$
					Si −	E (V, GB)	
Fe-13Cr-1Ti	C^+ (114dpa)	very high	low	<0.1%	Cr +	D (V, GB)	Ti
					Ti +	E (V, GB)	
Fe-C	C^+ (118dpa)	low	medium	10%	C −	E (V)	Fe_3C
Fe-10Cr	e (10dpa)	high	no detect	0	Cr +	D (GB)	
Fe-0.1Ti	e (3dpa)	high	low	0.5%	Ti +	no detect	TiC
Fe-0.2Ti	e (3dpa)	high	no detect	0	Ti +	no detect	
Fe-1Ni	e (aodpa)	medium	low	0.3%	Ni −	E (look)	γ phase
Fe-1Mn	e (3dpa)	medium	low	0.6%	Mn +	D (GB)	
Fe-1.8Mo	e (3dpa)	medium	high	0.8%	Mo +	D (V)	

D : depletion, E : enrichment, V : void, GB : grain boundary,

IV. Summary

Void formation and radiation-induced segregation in austenitic and ferritic steels were investigated by electron and ion irradiation. The summary is shown in Table. 5. In Ti -modified anstenitic steel, void swelling peaks appeared at 723 and 823 K. On the other hand, when the steels modified by both Ti and Nb were irradiated, the swelling was effectively suppressed, particulary the growth rate of voids was remarkably retarded. Compositions such as Ni, Cr, Mo, Si and Ti changed during irradiation and Ni, Si and Ti were enriched around voids, whereas Cr and Mo were depleted. These segregation phenomena were also confirmed around grain boundaries. In the case of ferritic alloys, significant resistance to void swelling was observed. In Fe-Cr, Fe-Cr-Si alloys, ion -irradiation produced the precipitates of $M_{23}C_6$. In Fe-Cr-Ti alloy, TiC precipitates were formed on {100} plane. By electron-irradiation of Fe-Cr, dislocation loops with b= ⟨100⟩ were produced with high number density. The enrichment of Cr was confirmed on dislocation loops and voids in electron and ion irradiated Fe-Cr alloys. From these results, the dislocation and precipitaion structure which are stabilized by the solute segregation are impotant factors of effective swelling resistance in ferritic alloys. In Fe-Ti alloy, electron -irradiation did not produce voids but induced loops of high number density, presumably vacancy type. This fact suggests that the scavenging effect and defect trapping cause the

void suppression. In other simple ferritic alloys, segregation phenomena were observed and explained by the size effect and solute-defect interaction.

Acknowledgment

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