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Effect of light impurities on the early stage of swelling in austenitic stainless steel

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Abstract

The objective of this study is to analyse the early stage of swelling and clarify the role of light impurities (nitrogen) in swelling of austenitic stainless steel. Recent results show that light impurities affect the swelling of 316 Stainless Steel under HVEM irradiation up to 10 dpa. At low concentration of light impurities the radiation swelling increases then decreases through the maximum as the concentration of light impurities increases. In the present paper the theoretical model is presented for the explanation of this effect. The model is based on the two factors: the influence of absorbed impurities on the voids caused by the production of an additional gas pressure in voids for their stabilization and the affect of impurities segregated around the surface of voids by the lowering of surface tension. These two affects are taken into account in the calculations of the critical size and the growth rate of cavities. The theoretical predictions on the radiation swelling rate dependent on the impurity concentration and temperature coincided with the experimental results on 316 Stainless Steel irradiated by HVEM.

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1. Introduction

In candidate structural materials (austenitic and ferritic/martensitic alloys) for fusion reactor, the radiation swelling is one of the most important physical phenomenon which determines their radiation resistance. Although many studies [1–6] have been made on this phenomenon including the effect of gas atoms such as helium and hydrogen on swelling [3,5,6], the influence of light gas impurities like nitrogen on the physical mechanisms of swelling is not yet so clear. Earlier [7–9] the effect of surface active gases (oxygen) on cavity surface energy has been used for the explanation of void stability in alloys. Recently [10,11] the first experimental data concerning the affect of nitrogen on the radiation swelling in 316 Stainless Steel have been obtained by one of the author. The aim of this paper is to clarify the role of light gas impurities (nitrogen) in radiation swelling of 316 Stainless Steel on the basis of the theoretical model taking into account the effect of light gas impurities on two physical parameters: cavity pressurization and cavity surface energy simultaneously.

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2. Experimental results

At first we shall briefly describe the experimental data [10,11] on the influence of light impurities (nitrogen) on radiation swelling of 316 Stainless Steels. The concentrations of nitrogen and carbon atoms in specimens were changed from 0.002 up to 0.083 wt% for nitrogen and from 0.002 up to 0.015 wt% for carbon atoms. The chemical compositions are shown in Table 1. Electron irradiations were performed using HVEM with fast electrons ($E = 1$ MeV). The damage rate was 2×10^{-3} dpa/s. The irradiation temperatures were changed from 773 up to 873 K and the total dose was up to 10 dpa. The changes of microstructure in irradiated samples (the dislocation density, the cavity density, the mean cavity radius and radiation swelling) were studied using TEM by in situ observation. The number density of dislocation loops and cavities increased with the increase of

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Table 1
Chemical composition of specimens (wt%)

	C	Si	Mn	P	S	Ni	Cr	Mo	N	Fe
*N*1	0.002	0.52	1.59	0.029	0.001	15.6	14.6	2.2	0.002	Bal.
*N*2	0.004	0.54	0.79	<0.002	0.0006	12.45	15.65	2.20	0.003	Bal.
*N*3	0.013	0.48	0.98	0.033	0.0028	14.72	17.59	2.56	0.0202	Bal.
*N*4	0.015	0.50	1.06	0.041	0.0030	12.22	17.49	2.48	0.0837	Bal.
*N*5	0.009	0.50	0.95	0.028	0.0037	11.95	16.91	2.18	0.1438	Bal.

impurity content then saturated. The saturated dislocation density at irradiation dose of 2.5 dpa was 3×10^{14} m^{-2}. The mean cavity radius is insensitive for the contents of nitrogen and carbon and the irradiation temperature. The radiation swelling increases then decreases through the maximum as the concentration of impurities increases.

3. Role of light impurities in the nucleation and the growth of voids

The nucleation of voids in an austenitic steel depends on light impurities atoms (nitrogen, carbon, oxygen) contained in these materials. The kinetics of the nucleation of voids with gas atoms is characterized by the two stages. At first, there occur the agglomeration of gas atoms and vacancies to form a nucleus of gas bubble, and followed by the transition from gas bubble to void due to accumulation of vacancies. The cavities then grow by the absorption of gas atoms and point defects.

The growth rate of a cavity with radius R can be expressed as

$$\frac{dR}{dt} = \frac{1}{R}[Z_v^c D_v C_v - Z_i^c D_i C_i - Z_v^c D_v \overline{C}_v^e], \tag{1}$$

where D_v and D_i are the vacancy and interstitial diffusion coefficients, C_v and C_i are the concentrations of vacancies and interstitials, Z_α^c is the capture efficiency of void for point defect type α (for vacancies $\alpha = v$ and for interstitials $\alpha = i$). Here $\overline{C}_v^e$ is the equilibrium vacancy concentration at a void surface, $\overline{C}_v^e = C_{v0} \exp\left\{\left(\frac{2\gamma}{R} - P\right)\frac{\Omega}{kT}\right\}$, where C_{v0} is the thermal equilibrium vacancy concentration, γ the surface tension, P the gas pressure, Ω the atomic volume and T the absolute temperature.

The arrival rate of gas atoms to a cavity is given by the following equation

$$\frac{dn_g}{dt} = 4\pi R D_g Z_g^c (C_g - \overline{C}_g^e), \tag{2}$$

where D_g and C_g are the diffusion coefficient and concentration of interstitial impurity atoms; $\overline{C}_g^e$ is the equilibrium concentration of light impurities at a cavity surface ($\overline{C}_g^e = \frac{\delta \omega_g P}{kT}$, $\delta = \exp(-E_g^f/kT)$; E_g^f is the energy solution of impurity); Z_g^c is the capture efficiency of void for impurity.

The conservation equations for the point defects C_v and C_i, gas impurities C_g and gas-point defect complexes $C_{\alpha g}$ are generally expressed by

$$\frac{dC_v}{dt} = G + G_v^e + \beta_{vg} C_{vg} - \alpha_{vg} C_v C_g - D_v C_v (k_{vc}^2 + k_{vd}^2) - \alpha_{vi} C_v C_i, \tag{3}$$

$$\frac{dC_i}{dt} = G + \beta_{ig} C_{ig} - \alpha_{ig} C_i C_g - D_i C_i (k_{ic}^2 + k_{id}^2) - \alpha_{vi} C_v C_i, \tag{4}$$

where G is the generation rate of point defects under irradiation, G_v^e the total thermal production rate of vacancies due to the evaporation of vacancies from voids and dislocations,

$$G_v^e = k_{vc}^2 D_v \overline{C}_v^e + k_{vd}^2 D_v C_{v0},$$
$$k_{\alpha c}^2 = 4\pi R N_c Z_\alpha^c, \quad k_{\alpha d}^2 = \rho_d Z_\alpha^d,$$

where $k_{\alpha c}^2$ is the sink strength of voids for vacancies ($\alpha = v$) and interstitials ($\alpha = i$); N_c the cavity density; ρ_d the dislocation density; Z_α^d the capture efficiency of dislocation for point defect type α. In the Eqs. (3) and (4) α_{vi} and $\alpha_{\alpha g}$ are the recombination constant for point defects and the reaction coefficients of gas atom and point defect type α, respectively; $\beta_{\alpha g}$ is the spontaneous decay coefficient for impurity–point defect complex ($\beta_{\alpha g} = \frac{D_g}{a^2}\exp(-E_{\alpha g}^b/kT)$, where D_g is the diffusion coefficient for interstitial impurity, $E_{\alpha g}^b$ the binding energy of impurity–point defect complex, and a the lattice spacing.

The rate equations for the concentration of impurities (C_g) and a complex impurity–point defect type $\alpha(C_{\alpha g})$ are given by

$$\frac{dC_g}{dt} = \beta_{vg} C_{vg} - \alpha_{vg} C_v C_g + \beta_{ig} C_{ig} - \alpha_{ig} C_i C_g - 4\pi R N_c D_g Z_g^c (C_g - \overline{C}_g^e) - \rho_d D_g Z_g^d (C_g - C_{g0}), \tag{5}$$

$$\frac{dC_{\alpha g}}{dt} = \alpha_{\alpha g} C_\alpha C_g - \beta_{\alpha g} C_{\alpha g}. \tag{6}$$

For a given number of gas atoms the equation $\dot{R} \equiv dR/dt = 0$ has in general two roots, R_c^b and R_c^0. In the range of $R < R_c^b$ the cavities grow ($\dot{R} > 0$), $R_c^b < R < R_c^0$ cavities evaporate ($\dot{R} < 0$) and $R > R_c^0$ the cavities have a positive growth rate. In these cases the bimodal distribution of voids is formed. When the number of gas atoms in the void increases, R_c^b

approaches to R_c^0. At a critical value of gas number n_g^* the radii R_c^b and R_c^0 are equal to R_c^* which is the minimum critical radius. At $n_g > n_g^*$ cavities will grow without critical barrier.

These critical values for van der Waals gas are given by Mansur et al. [3]

$$R_c^* = \frac{2\gamma}{f}\left(\frac{1+\delta}{2+\delta}\right), \tag{7}$$

where

$$f = \frac{kT}{\Omega}\ln\left(\frac{Z_v^c D_v C_v - Z_i^c D_i C_i}{Z_v^c D_v C_{v0}}\right),$$

$$\delta = \left(1 + \frac{3B_{ef} f}{kT}\right)^{1/2},$$

and B_{ef} is van der Waals exclusion coefficient.

Very important parameters in the calculations of radiation swelling are the coefficients of capture efficiency of the void (Z_α^c) and the dislocation (Z_α^d) for the point defect of type α. These coefficients were calculated in papers [12–15]. The calculations for cavities [12–14], however, show that $Z_\alpha^c = 1 + \Delta Z_\alpha^c$, ($\Delta Z_\alpha^c \ll 1$).

The calculations for straight dislocation [15] in FCC materials (Stainless Steel 316) taking into account the anisotropic diffusion for point defects show that the capture efficiency of dislocation Z_α^d is expressed by $Z_\alpha^d = 2\pi/\ln\frac{R_d}{R_\alpha^s}$, where R_d is a measure of dislocation spacing ($R_d = (\pi\rho_d)^{-1/2}$), R_α^s is the dislocation capture radius for point defect type α, and typical capture radius for interstitials in 316 Stainless Steel $R_\alpha^s \approx 10a$. Using the experimental data [11] for dislocation density $\rho_d = 3 \times 10^{10}$ cm^{-2}, we have the estimation of $Z_\alpha^d \approx 3$.

At low dose where the dislocations are dominant sink for point defects and using the quasi-stationary equations for point defects (3) and (4) we can see, that at low generation rate in neutron irradiation with $G \approx 10^{-6}$–10^{-7} dpa/s and intermediate temperatures $\left(\frac{GB}{Z_v^d D_s \rho_d} \ll 1\right)$, the critical radius is approximated by

$$R_c^* = \frac{2\gamma\Omega Z_v^d D_s \rho_d}{GBkT}\left(\frac{1+\delta}{2+\delta}\right), \quad B = \frac{Z_i^d Z_v^c - Z_v^d Z_i^c}{Z_v^d Z_v^c}. \tag{8}$$

We can see, that $R_c^* \propto 1/B$.

In the case of electron irradiation the generation rate G is very large ($G = 2 \times 10^{-3}$ dpa/s), so that we have $GB/Z_v^c D_s \rho_d \gg 1$, and in this case the critical radius is approximated by

$$R_c^* = \frac{2\gamma\Omega}{kT\,\ln(GB/Z_v^d D_s \rho_d)}\left(\frac{1+\delta}{2+\delta}\right). \tag{9}$$

The calculations using the typical material constants in Table 2 and the experimental results for 316 Stainless Steel under electron irradiation show, that at the concentration of gas atoms $C_S = 0.0215$ wt% the minimum critical number of gas atoms n_g^* is estimated as 8270 and the minimum critical radius $R_c^* = 8.54$ nm.

On the other hand, the light impurities (oxygen, nitrogen, carbon) can be absorbed on the cavity surface and effect on the surface tension of materials. The physical basis for this effect lies in the reduction in surface tension of materials. The physical basis for this effect lies in the reduction in surface tension due to segregation of impurity atoms near the cavity surface. This model derived for a pure metal [7] and follow was proposed for the explanation of void stability in nickel and alloys caused by the absorption of oxygen on void surfaces [8,9].

In this case the surface tension is given by the following relation

$$\gamma = \gamma_0 + \frac{R_S T \theta^{sat}}{A}\ln\left(1 - \frac{\theta}{\theta^{sat}}\right), \tag{10}$$

where γ_0 is the surface tension of the pure metal, R_S the gas constant, A the molar area per surface metal atom, θ the degree of nitrogen coverage at the surface, θ^{sat} is the saturated value of θ. The value of θ is determined by the following equation

$$\frac{\theta}{\theta^{sat}} = \frac{C_N \exp(-\Delta E/RT)}{1 + C_N \exp(-\Delta E/RT)}, \tag{11}$$

where ΔE is the activation energy for surface segregation and absorption at the metal surface (note, that in Eq. (11) C_N denotes usual atomic concentration of impurities).

The numerical estimations using the following values, $\Delta E = 1.9$ eV, $C_{N1} = 0.002$ wt% and $C_{N2} = 0.0837$ wt%, show that the surface tension can be decreased by $\gamma(C_{N1})/\gamma(C_{N2}) \approx 1.5$. According to Eq. (9) the critical radius R_c^* decreases by the same way when the nitrogen concentration increases.

The typical dependence of cavity growth rate on cavity radius at $T = 823$ K is illustrated in the Fig. 1.

4. Radiation swelling

On the steady stage of swelling at high temperatures we can neglect the recombination process between point defects and gas atom–point defect complex formation.

Table 2
Material constants of typical 316 Stainless Steel ($D_\alpha = D_{\alpha 0}\exp(-E_\alpha^m/kT)$, $C_{v0} = \exp(-E_v^f/kT)$)

D_{v0} (cm^2/s)	E_v^m (eV)	E_v^f (eV)	D_{i0} (cm^2/s)	E_i^m (eV)	D_{g0} (cm^2/s)	E_g^m (eV)	E_g^f (eV)	E_{gv}^b (eV)	E_{gi}^b (eV)	γ_0 (erg/cm^2)	Ω (cm^3)
0.6	1.3	1.3	0.001	0.15	0.055	1.18	1.5	1.5	0.5	2000	8×10^{-24}

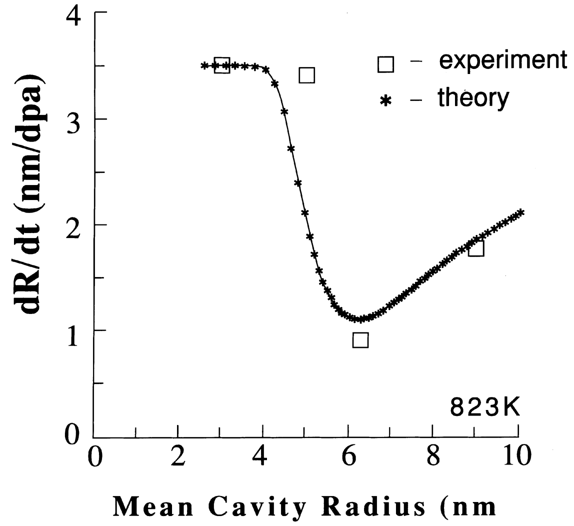

Fig. 1. The dependence of cavity growth rate on cavity radius at $T = 823$ K.

In this case the main sinks for point defects are cavities and dislocations, then using the quasi-stationary Eqs. (3) and (4) for nearly equilibrium cavities ($P \approx 2\gamma/R$) and in the range of doses ($\Phi \geqslant 2$ dpa), the swelling rate can be written as

$$\frac{\mathrm{d}S}{\mathrm{d}t} = 4\pi N_c R^2, \quad \frac{\mathrm{d}R}{\mathrm{d}t} = \frac{A}{(1+Q_v)} + \frac{GBQ_i}{(1+Q_v)(1+Q_i)}, \tag{12}$$

where $Q_\alpha = \frac{Z_\alpha^d \rho_d}{4\pi N_c R Z_\alpha^c}$, $A = \frac{Z_v^d \rho_d D_s \Omega}{kT}\left(P - \frac{2\gamma}{R}\right)$.

Here Q_α is the ratio of the absorption efficiency for the point defect with type α of dislocations to that of voids.

Under electron irradiation ($G = 2 \times 10^{-3}$ dpa/s) in the temperature range of 773 K $\leqslant T \leqslant$ 873 K we can see, that $GB \gg A$. Then the swelling rate finally has the following form

$$\dot{S} \equiv \frac{\mathrm{d}S}{\mathrm{d}t} = GB\frac{Q_\alpha}{(1+Q_\alpha)^2}. \tag{13}$$

The derivation of swelling rate by concentration of nitrogen can be expressed as

$$\frac{\mathrm{d}\dot{S}}{\mathrm{d}C_N} = GB\frac{(1-Q_\alpha)}{(1+Q_\alpha)^3}\frac{\mathrm{d}Q_\alpha}{\mathrm{d}C_N}. \tag{14}$$

We can see from Eq. (14), that the extremum of Q_α coincides with that of $\dot{S}$, because in the range of $Q_\alpha > 1$, the range of the decreasing of $Q_\alpha(\mathrm{d}Q_\alpha/\mathrm{d}C_N < 0)$ coincide with that of the increasing of swelling rate $(\mathrm{d}\dot{S}/\mathrm{d}C_N > 0)$, and in the range of the increasing of $Q_\alpha(\mathrm{d}Q_\alpha/\mathrm{d}C_N > 0)$ the swelling rate decreases $(\mathrm{d}\dot{S}/\mathrm{d}C_N < 0)$, i.e. the minimum of Q_α coincides with the maximum of the swelling rate in their dependence on the concentration of nitrogen. The same tendency should be for not only for the swelling rate $\dot{S}$ but and for the swelling S.

These relations agree with the obtained experimental data. Figs. 2 and 3 show the dependencies of Q_α value and radiation swelling rate as a function of the nitrogen concentration, respectively.

Since the dislocation bias for point defect has the weak temperature dependence ($B \propto \ln^{-1} T$), the derivation of swelling rate by is temperature given as

$$\frac{\mathrm{d}\dot{S}}{\mathrm{d}T} = GB\frac{(1-Q_\alpha)}{(1+Q_\alpha)^3}\frac{\mathrm{d}Q_\alpha}{\mathrm{d}T}. \tag{15}$$

In the case of $Q_\alpha > 1$, the location of the minimum of Q_α in dependence on temperature coincides with that of the swelling rate maximum. The experimental results for 316 Stainless Steel shown in Figs. 4 and 5 illustrate this correspondence.

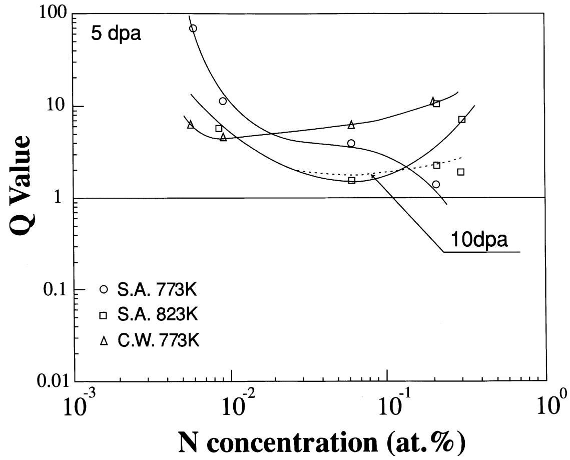

Fig. 2. Value of Q as a function of nitrogen content [11].

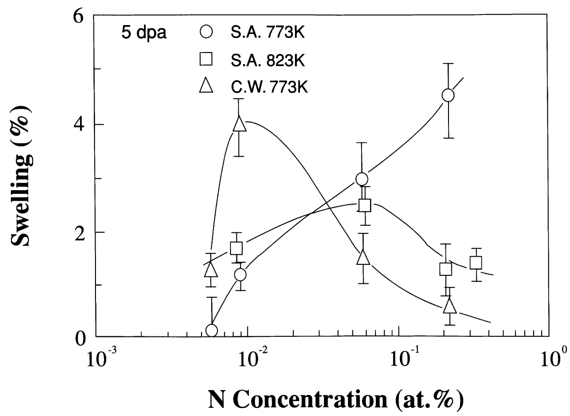

Fig. 3. The swelling rate at 5 dpa irradiation dose as a function of nitrogen content [11].

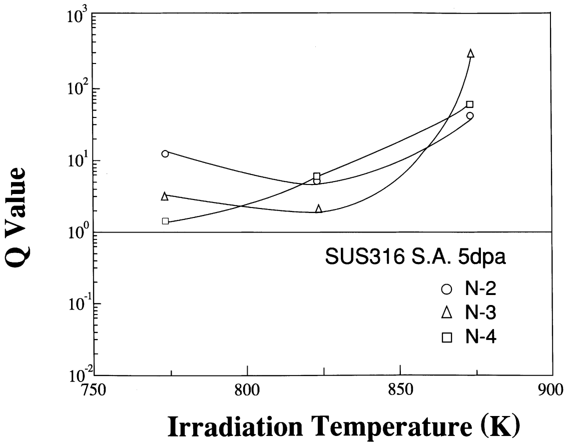

Fig. 4. Value Q as a function of irradiation temperature [11].

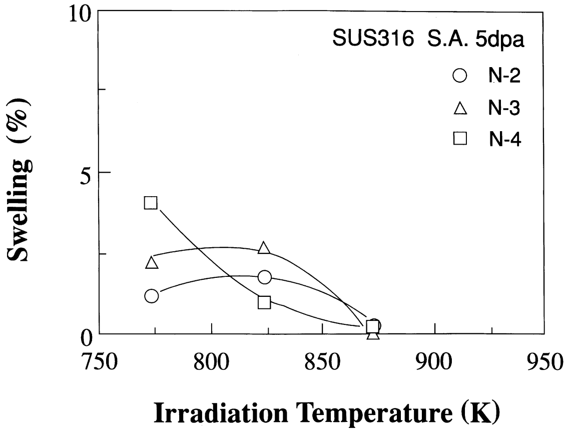

Fig. 5. The irradiation temperature dependence of swelling rate at 5 dpa irradiation dose [11].

The dependence of swelling rate as a function of Q_α is represented in Fig. 6. We can see that the swelling behavior is explained reasonably by the changes of Q_α.

5. Summary

The effects of light gas impurities and temperature on swelling behavior of 316 Stainless Steel are investigated in the temperature range of 773 K $\leqslant T \leqslant$ 873 K under electron irradiations using HVEM.

1. The impurities (nitrogen) can stabilize the cavity formation in 316 Stainless Steel through the absorption of atoms inside void and the decreasing of surface tension by segregation around void.

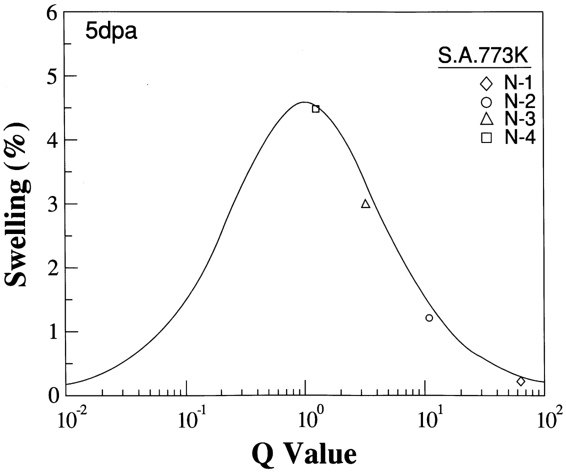

Fig. 6. The relation between Q and swelling rate at 5 dpa.

2. The swelling behavior of 316 Stainless Steel is explained by the changes of Q_α value, the ratio of the sink strength of the dislocation density to that of cavities. Close correspondence between the swelling rate and Q_α value is illustrated in their dependence on temperature and nitrogen concentrations.

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