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Evolution of voids and swelling under irradiation

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Outline

- Generalisation of void nucleation theory in metals
- Variety of small vacancy cluster configurations
- Effect of mobile divacancies on void nucleation and growth
- Effect of RIS on swelling in alloys
- Segregation-induced bias
- Kirkendall forces
- Forces due to PD formation and migration energy gradients
- Voids attached to precipitates
- Swelling in Fe-Cr-Ni and V-Fe alloys

Introduction

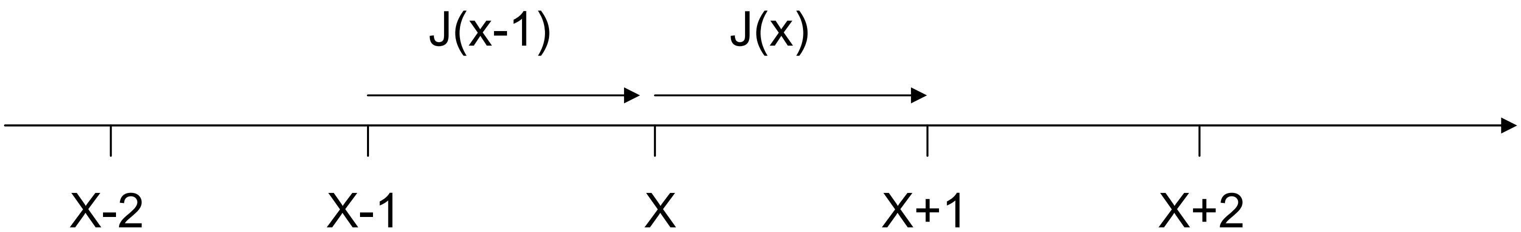
Since the discovery of void swelling by Cawthorne and Fulton in 1966 this phenomenon is of intense interest for materials performance in radiation environments at elevated temperature.

Comprehensive rewies are given by Was, 2007; Kluhe, 2001; Garner, 1994, and others .

Here we will consider only two aspects : void nucleation theory in metals and effect of RIS on swelling in alloys.

VOID NUCLEATION

The theory of steady – state void nucleation during homogeneous irradiation was developed by Katz and Wiedersich (1971) and Russell (1971)



$f'(x) = J(x-1) - J(x)$

$J(x)=\alpha_V(x)f(x) - (\beta_i(x+1)+\gamma_V(x+1))*f(x+1)$

$J(x)=J_s$ at **steady – state** $(f'(x)=0)$

$$\beta_V(x)=W^V x^{1/3} D_v C_v,$$

$$\beta_I(x)=W^V x^{1/3} D_i C_i,$$

$$\gamma_V(x)=W^V x^{1/3} D_v C_{ve} \exp\left(\frac{2\gamma\Omega}{R_c kT}\right),$$

The capillarity approximation for the void energy was used: $E(x)=S(x)\gamma$

This approximation overestimates the nucleation rates

VOID NUCLEATION

Steady-state void nucleation rate is

$$J = \frac{C_{\alpha} \cdot P(1)}{1 + \sum_{x=2}^{x_L} \prod_{j=2}^{x} \frac{Q(j)}{P(j)}}$$

where $P(x,t) = \{\beta_v + \gamma_i\}$,

$Q(x,t) = \beta_i$

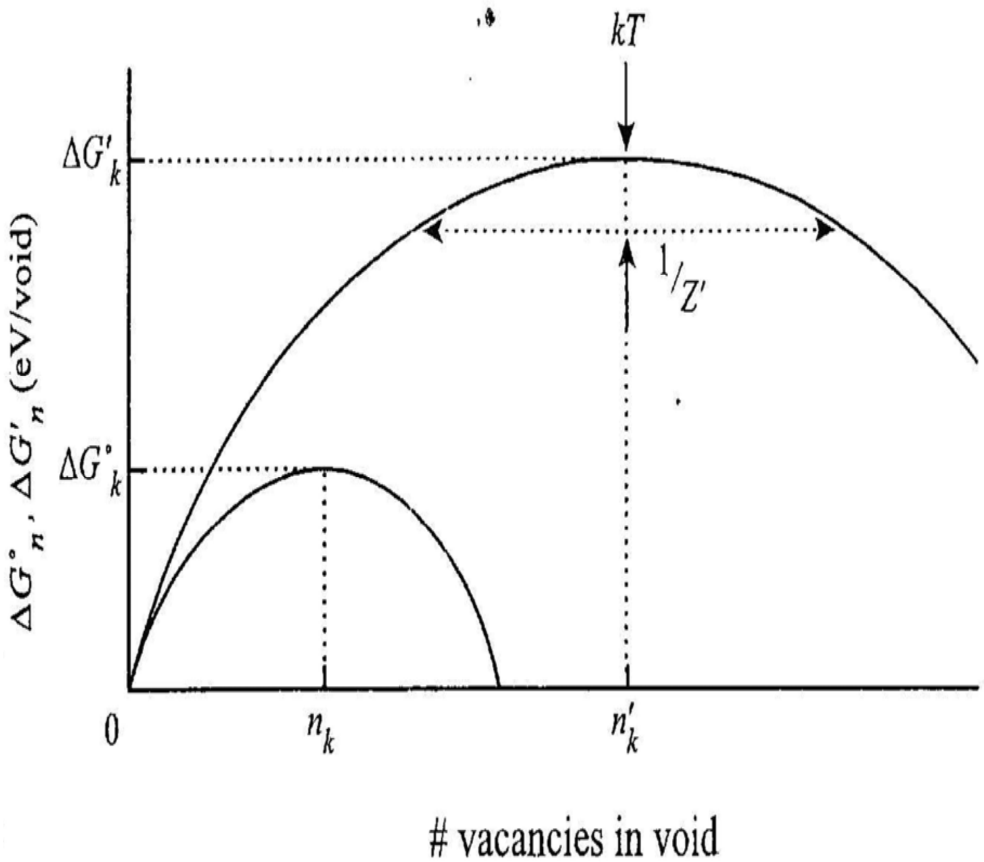
It can be approximated by

$$J(x_c) = Z_0 P(x_c) n^0(x_c)$$

$$n^0(x) = N_0 \cdot \exp\left\{-\frac{\Delta G_x^0}{kT}\right\} = N_0 \cdot \exp\left\{-\left[W(x) - xkT \ln S\right]/kT\right\}$$

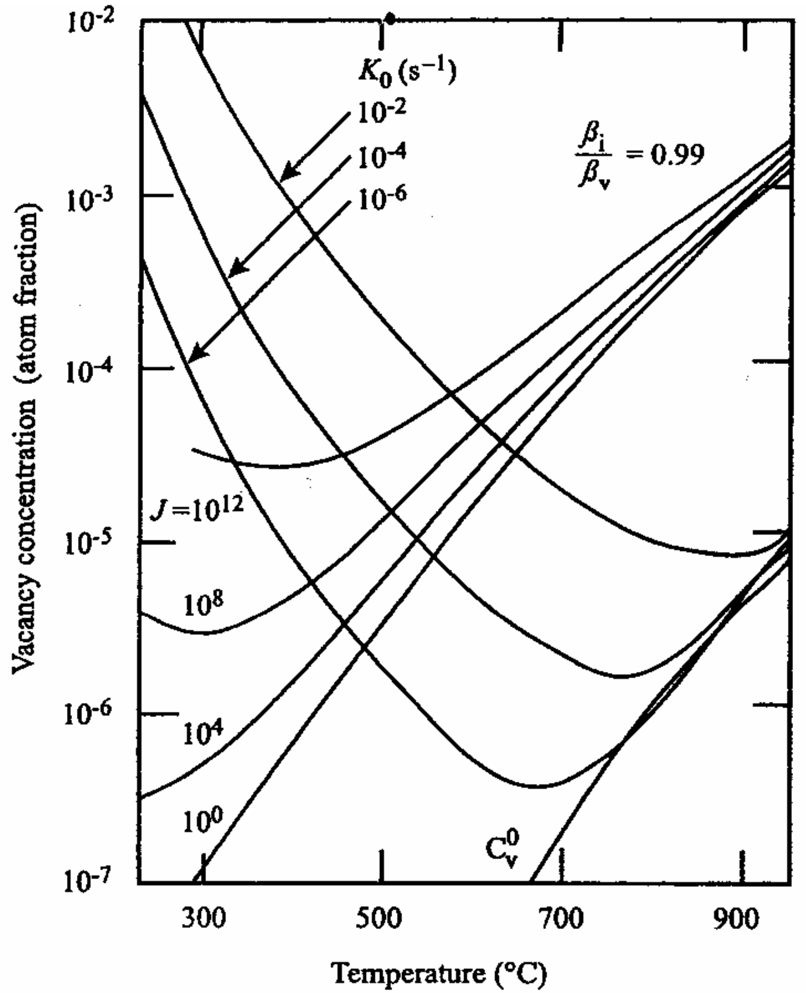
S – vacancy supersaturation, W(x) – reversible work to create x-cluster, Z - Zeldovich factor

VOID NUCLEATION



Schematic nucleation curves showing the various parameters which are important in void nucleation. ΔG^0_k is the activation barrier to nucleation if interstitials are not present, while $\Delta G'_k$ is the same quantity if interstitials are present during the nucleation process (after Mansur, 1978)

VOID NUCLEATION



Steady state vacancy concentrations for several defect production rates and a sink annihilation probability p=10^{-7} , and vacancy concentrations required for several nucleation rates J (in cm^{-3} s^{-1}) at an arrival rate radio of 0.99.

(after Katz, 1972)

VARIETY OF VACANCY CLUSTER CONFIGURATIONS

Since various configurations j are possible for a cluster of x vacancies, the two-dimensional distribution function f (x, j) should be considered together with the transitions (a) (x, j) →(x±1,j') and (b) (x, j) → (x, j')

Since (b)- processes are faster than (a) ones, one can introduce the thermodynamically equilibrium distribution function $f^0(x, j)$, which allows to average various transitions and to calculate J_S:

$$f^0(x, j) \sim K(x, j) * \exp\left(-\frac{\Delta F(x, j)}{kT} + x \ln\left(\frac{C_V}{C_{V0}}\right)\right)$$

K (x, j) accounts for the change in configurational entropy of the crystal due to (x, j) clusters and ΔF(x,j) is the change in free energy due to formation of one (x, j) cluster in the lattice, e.g.

$$\Delta F(x, j) = xE_v^f - m(x, j)E_b - \frac{3}{2}kT\sum_i\left(1 - \frac{z(i)}{z}\right)$$

Effect of mobile divacancies on void nucleation

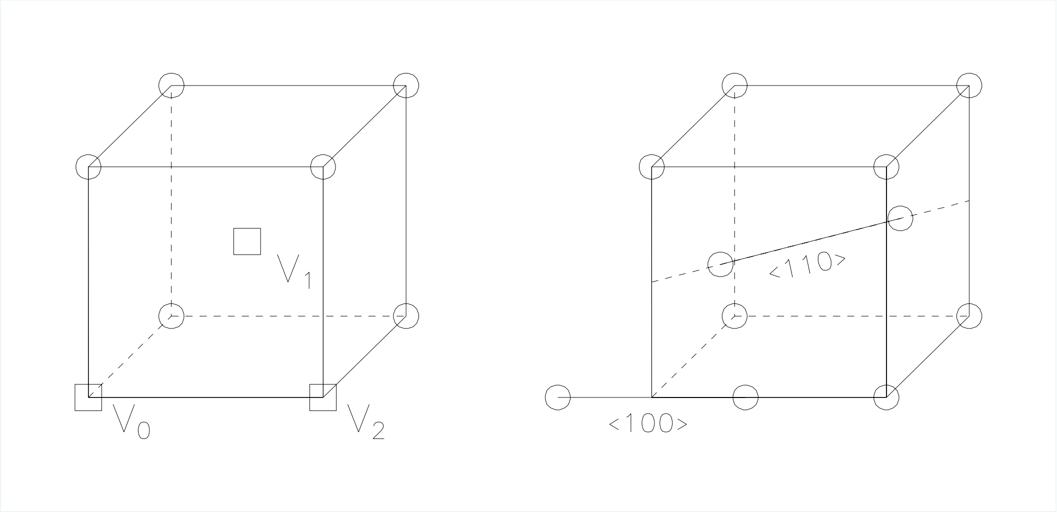
It is known that diffusivities of di-VACs and three-VACs in f.c.c. metals are higher than diffusivity of mono-VACs:

$$E_{2v}^{m} = (0.6\text{-}0.8)E_{v}^{m}$$

Therefore, in these metals diffusion fluxes of smallest vacancy clusters may essentially contribute to the void formation and growth under irradiation.

According to limited literature data, in b.c.c. metals the di-VAC diffusivity is less or comparable with the mono-VAC diffusivity.

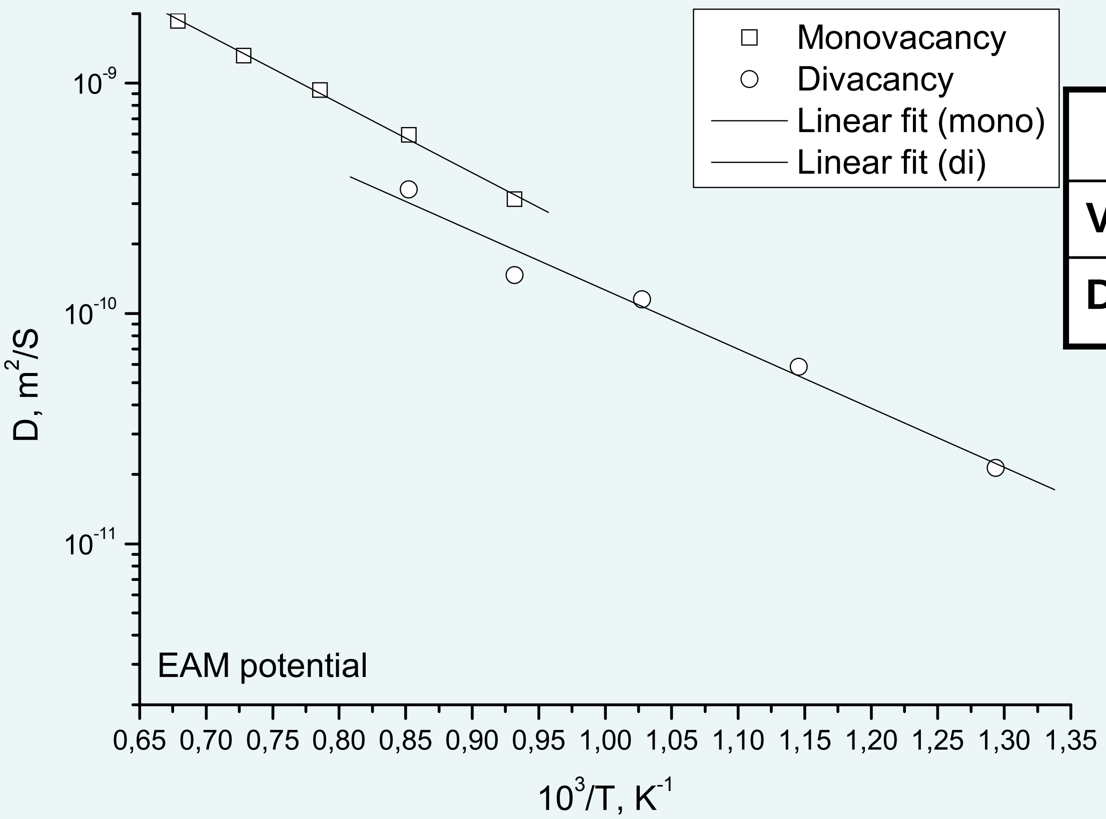
DI-VACANCIES AND INTERSTITIALS IN BCC FE



MD calculation of di-VAC binding energy (eV)

	V_0 - V_1	V_0 - V_2
Pair potential	**0.13**	**0.20**
EAM potential	**0.08**	**0.22**

Vacancy and di-vacancy diffusivities in Fe



	D_0 , m^2/s	E_m, eV
Vacancy	**2.09·10-7**	**0.6±0.02**
Di-vacancy	**4.7·10-8**	**0.51±0.05**

Production of divacancies in cascades

Point defect production rate

$$K_i = K_v + 2K_{2v} = \varepsilon\, G(1 - f_c)$$

$$K_{2v} = \varepsilon_{2v} K_i$$

G is the dose rate in the NRT– model,

ε is the cascade efficiency (0.3 for neutron irradiation from MD simulation for Fe)

ε_{2v} is the efficiency of di-VAC production in cascades (taken as 0.2)

f_c is the fraction of SIAs lost due to a correlated recombination

According to experimental estimates by Theis and Wollenberger (1980) values of f_c for Cu and Al under electron and neutron irradiation are approximately equal (f_c ~ 0.6-0.7)

Balance reactions

$$I, V, V_2 \rightarrow S_\alpha \, , \; \alpha = I, V, V_2$$

$$V + V \leftrightarrow V_2 \, ,$$

$$I + V_2 \rightarrow V,$$

$$I + V \rightarrow 0$$

$$S_\alpha = \varepsilon_\alpha L + D \, ; \qquad L = \rho_d + 2\pi r_e N_e$$

$$D = 2\pi d_c N_c$$

Relative diffusion fluxes

Since void growth rate is proportional to

$R'_c \sim (D_V C_V + 2D_{2V} C_{2V} - D_i C_i - D_V C_{VE}(R_c))$,

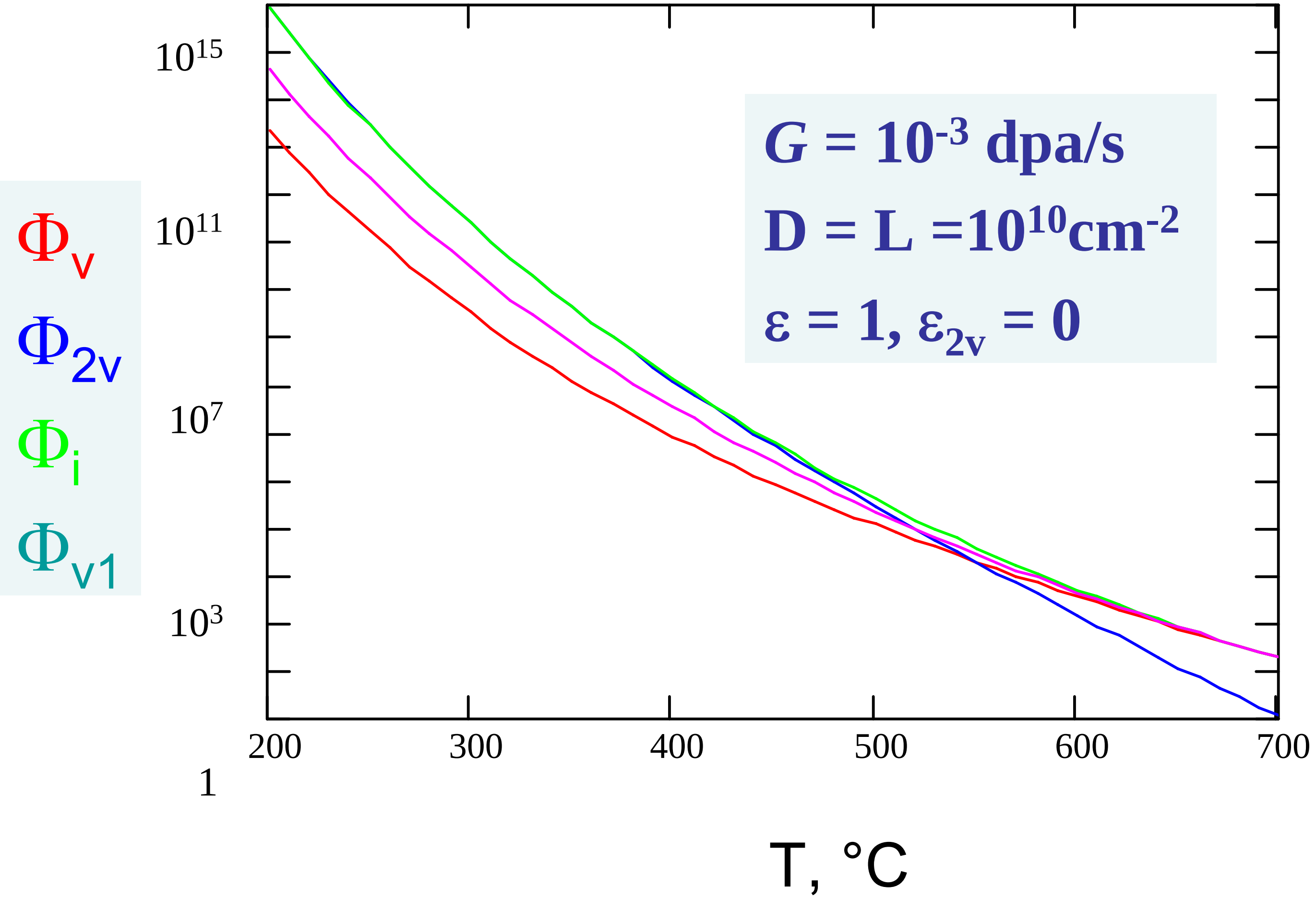
then relative "point defect fluxes" are of interest:

$$\Phi_v = \frac{D_v C_v}{D_v C_{v0}} \qquad \Phi_{2v} = \frac{2D_{2v} C_{2v}}{D_v C_{v0}} \qquad \Phi_i = \frac{D_i C_i}{D_v C_{v0}}$$

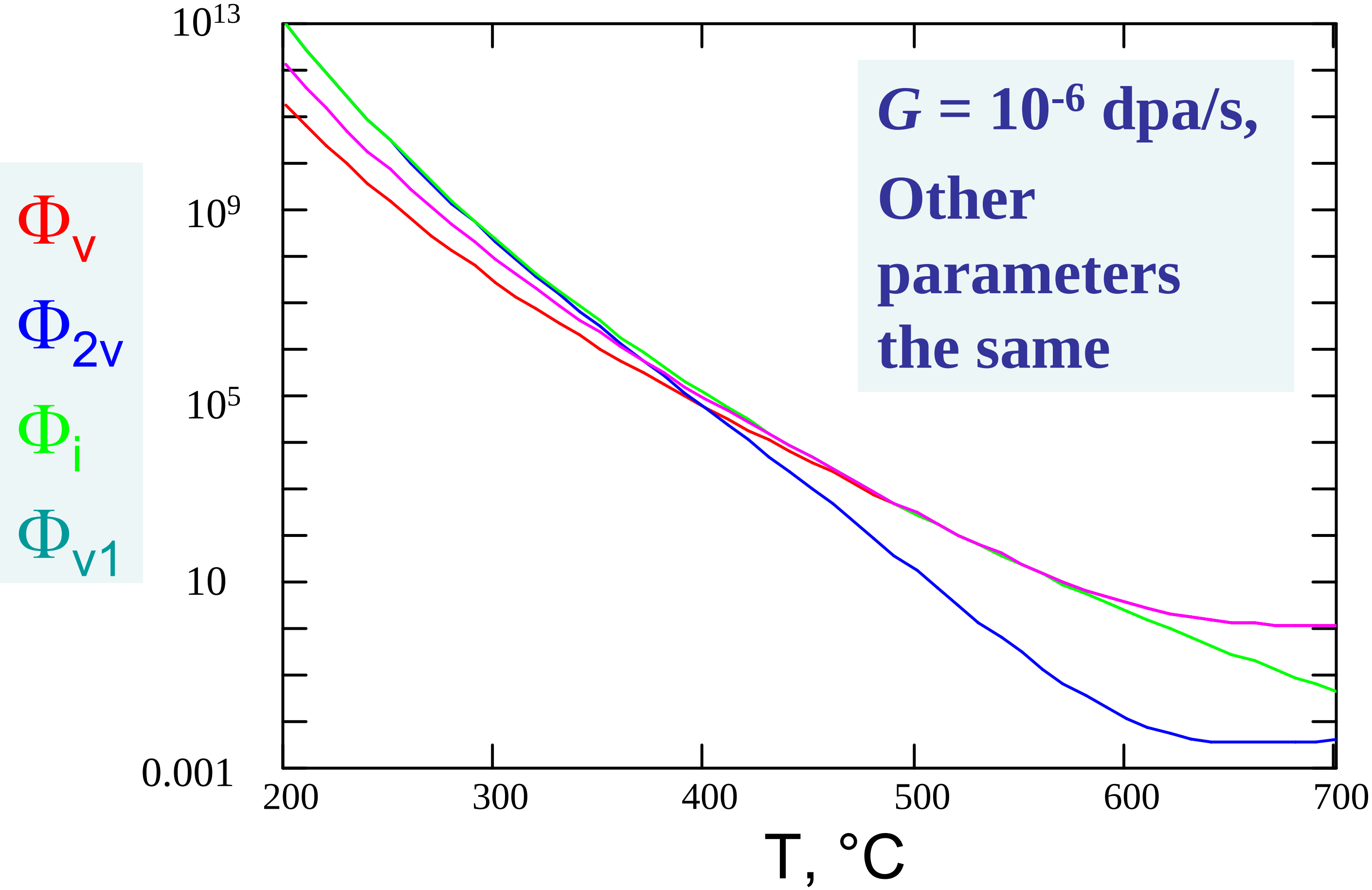
If di-VACs are immobile and $\varepsilon=1$

$$\Phi_{v1} = \frac{D_v C_{v1}}{D_v C_{v0}}$$

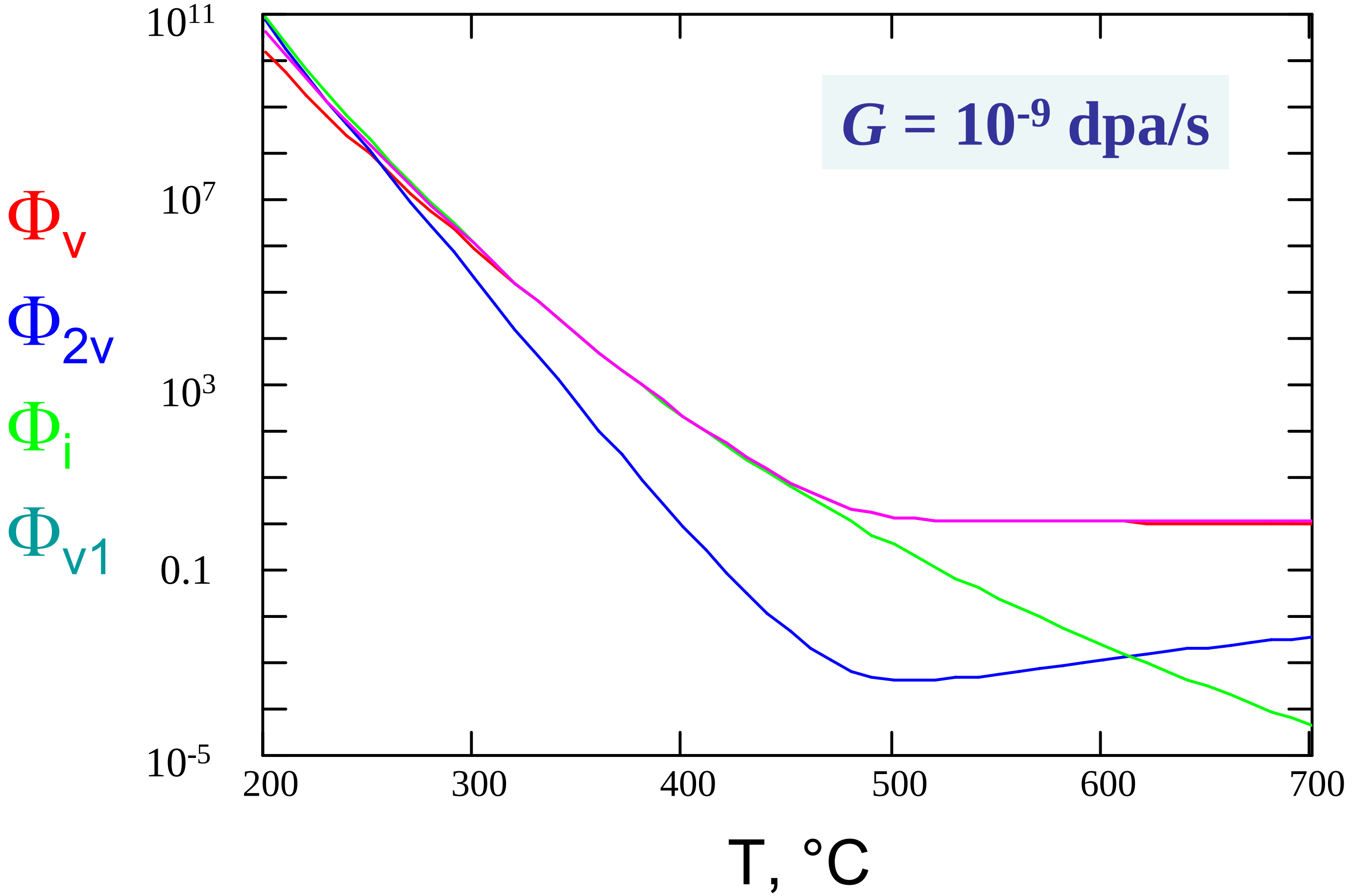
Relative diffusion fluxes in Ni



Relative diffusion fluxes in Ni



Relative diffusion fluxes in Ni



Nucleation rate

If a mobility of V_2 is accounted for, then for x>2

$J(x) = \alpha_{2V}(x-1)f(x-1) + (\alpha_{2V}(x)+\alpha_V(x))f(x) - (\beta_i(x+1)+\gamma_V(x+1))f(x+1)$, or

$$J(x) = P_1(x-1)f(x-1) + [P_1(x) + P(x)]f(x) - Q(x+1)f(x+1)$$

Here the transitions should be averaged with $f^0(x, j)$, e. g.

$$\alpha(x) = \sum_j \sum_{j'} f^0(x, j')\, \alpha_{j'j}(x) / \sum_{j'} f^0(x, j')$$

$$J(x) = J_S \text{ at } f'(x) = 0$$

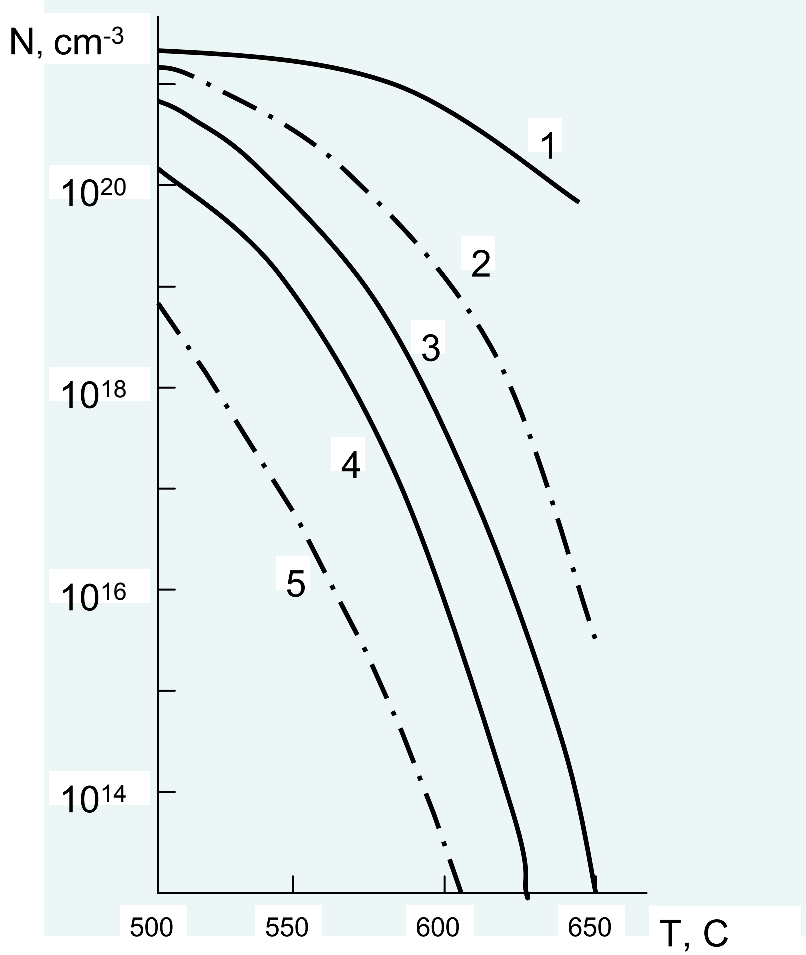
Nucleation rate

$$J = \frac{1}{\sum_{x=2}^{\infty} \frac{1}{\xi_1(x)} [1 + \sum_{j=2}^{x-1} \prod_{i=j}^{x-1} (-\frac{\xi_2(i)}{\xi_1(i)})]}$$

$$\xi_1(x) = P_1(x-1)n(x-1) + [P_1(x) + P(x)]n(x), \xi_2(x) = P_1(x)n(x)$$

Expressions for J are derived also with additional account of small vacancy clusters formation in cascades

Nucleation rates in Ni



$N = J_S t$; $Gt = 13$dpa

$G = 7x\ 10^{-2}$ dpa/s

$D = 10^8\ cm^{-2}$, $L = 10^9\ cm^{-2}$

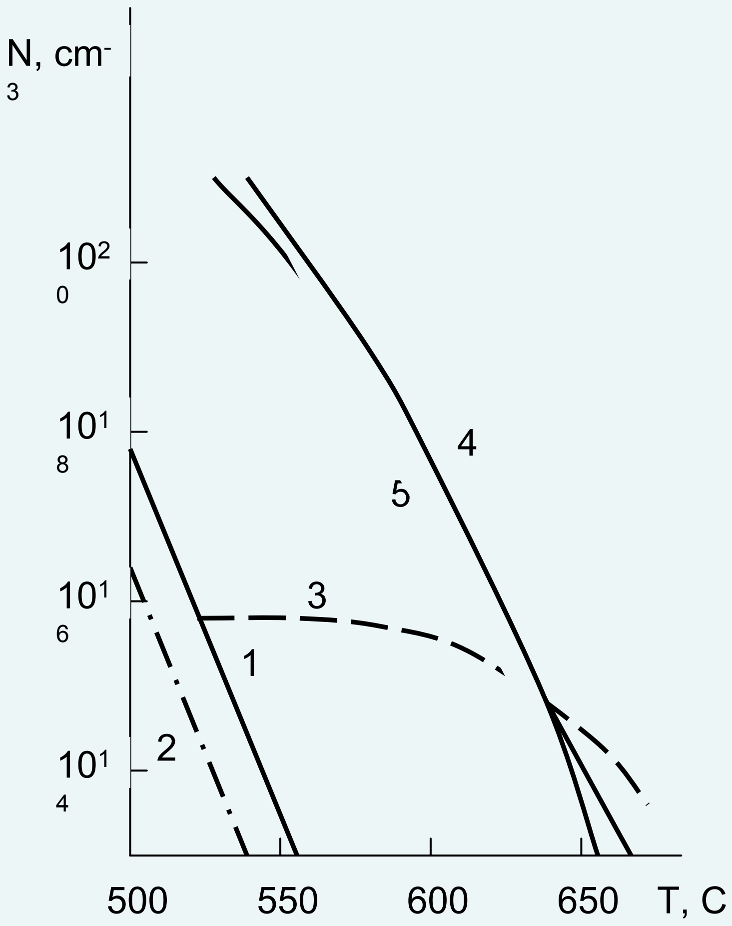
$\varepsilon_i = 1.\ 01$

1, 2 – “capillarity” approximation

3, 4, 5 – “broken bonds”

2, 5 – di-VACs are immobile

Void nucleation rates in Ni



$N = J_S t$; $Gt = 13$dpa

$G = 7x\ 10^{-2}$ dpa/s

1, 2 – D = L = 10^{12} cm^{-2},

2 – di-VACs are immobile

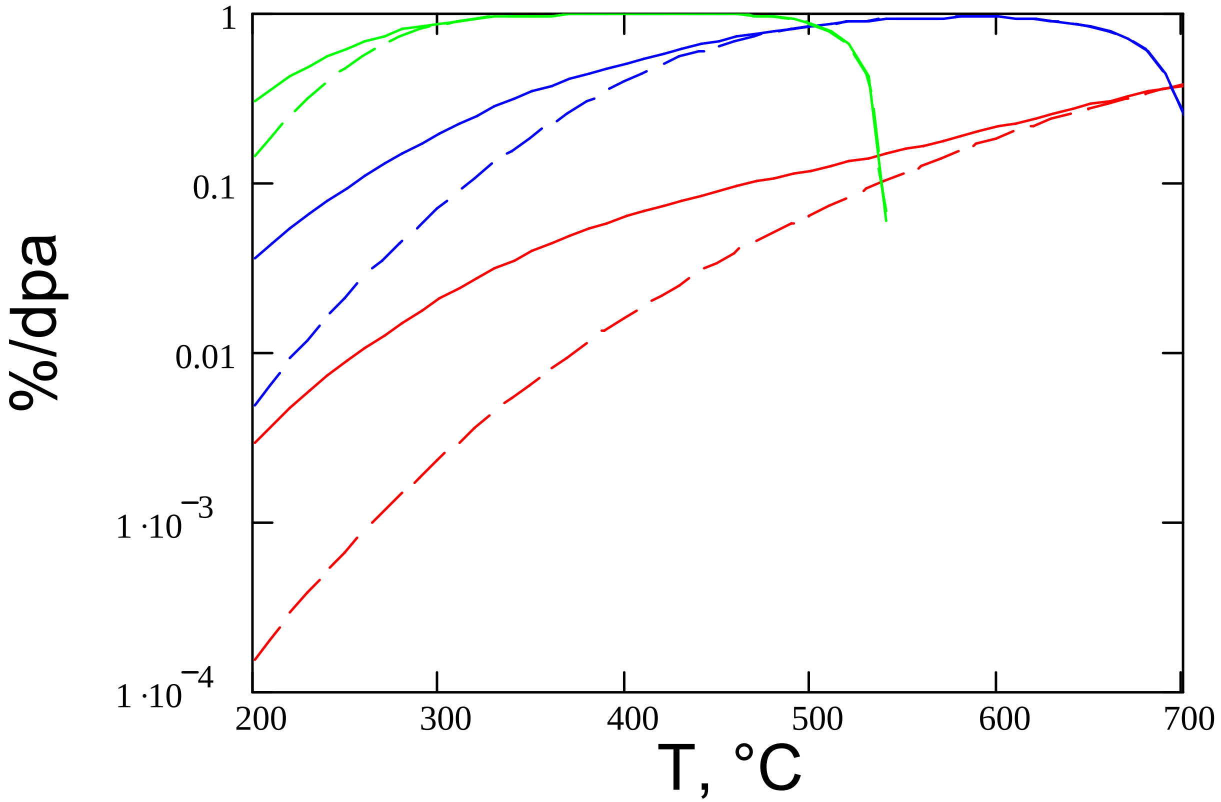
3 – data by Spraque (1974)

4,5 – D = 10^8 cm^{-2},

L = 10^9 cm^{-2},

(4 - $\varepsilon_i = 1.05$, 5 - $\varepsilon^L_{2V} = 0.9$)

Swelling rate in Ni



dpa/s

G=10^{-3}

G=10^{-6}

G=10^{-9}

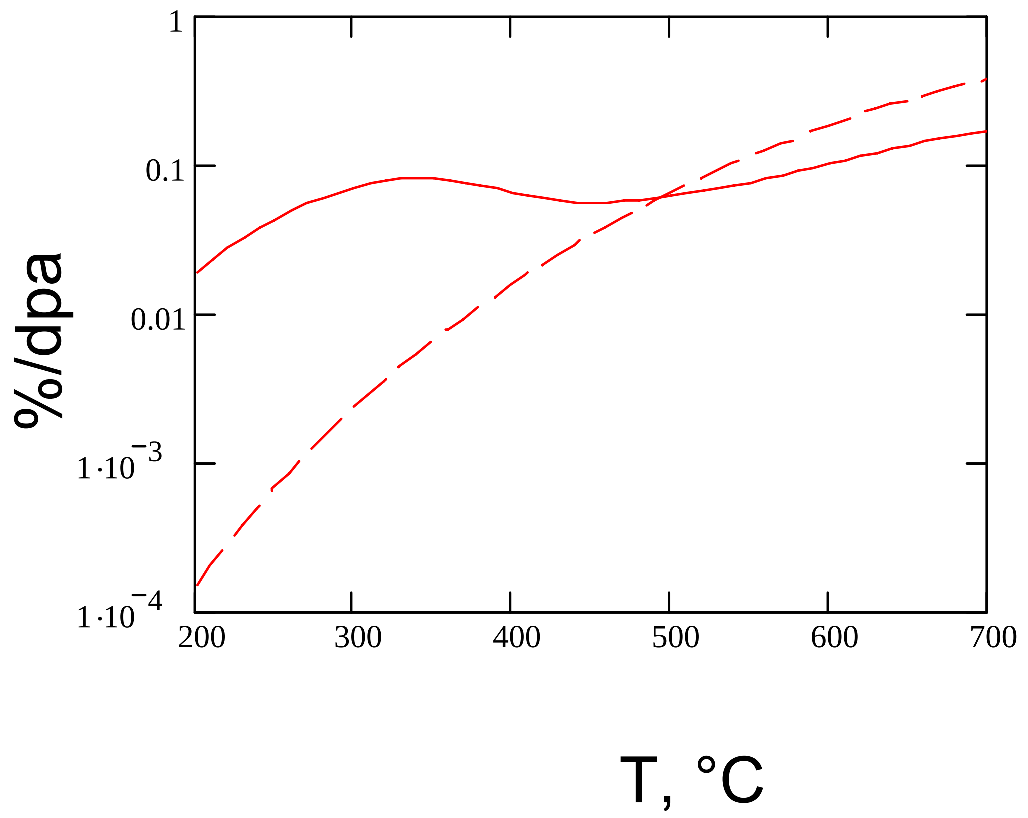
ε_i = 1.04

D = L = 10^{10}cm^{-2}

ε = 1

Solid line – V_2 are mobile; dashed line - V_2 are immobile

Swelling rate in Ni



$G = 10^{-3}$ dpa/s

$\varepsilon = 0.3$

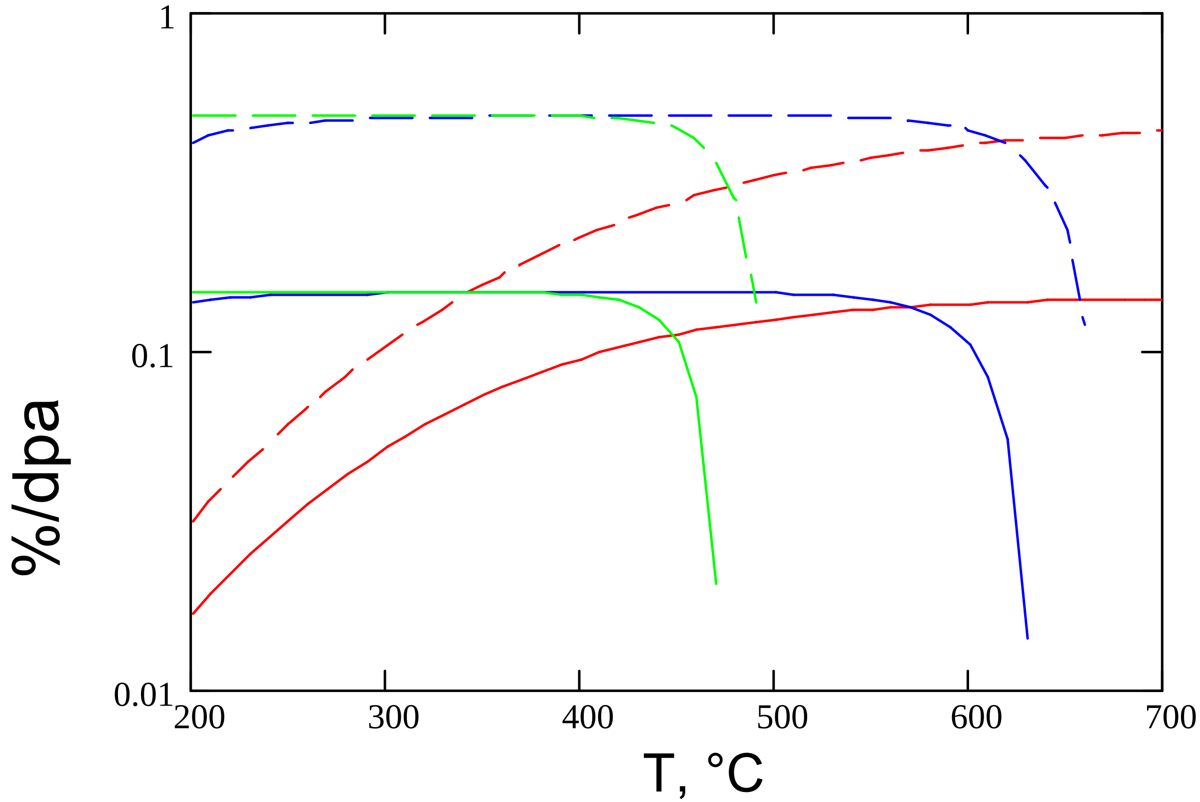
$\varepsilon_{2v} = 0.2$

$\varepsilon_i = 1.04$

$D = L = 10^{10} cm^{-2}$

Solid line: V_2 are mobile; dashed line: V_2 are immobile, electron irradiation

SWELLING RATE IN Fe



dpa/s

$G = 10^{-3}$

$G = 10^{-6}$

$G = 10^{-9}$

$\varepsilon = 0.3$

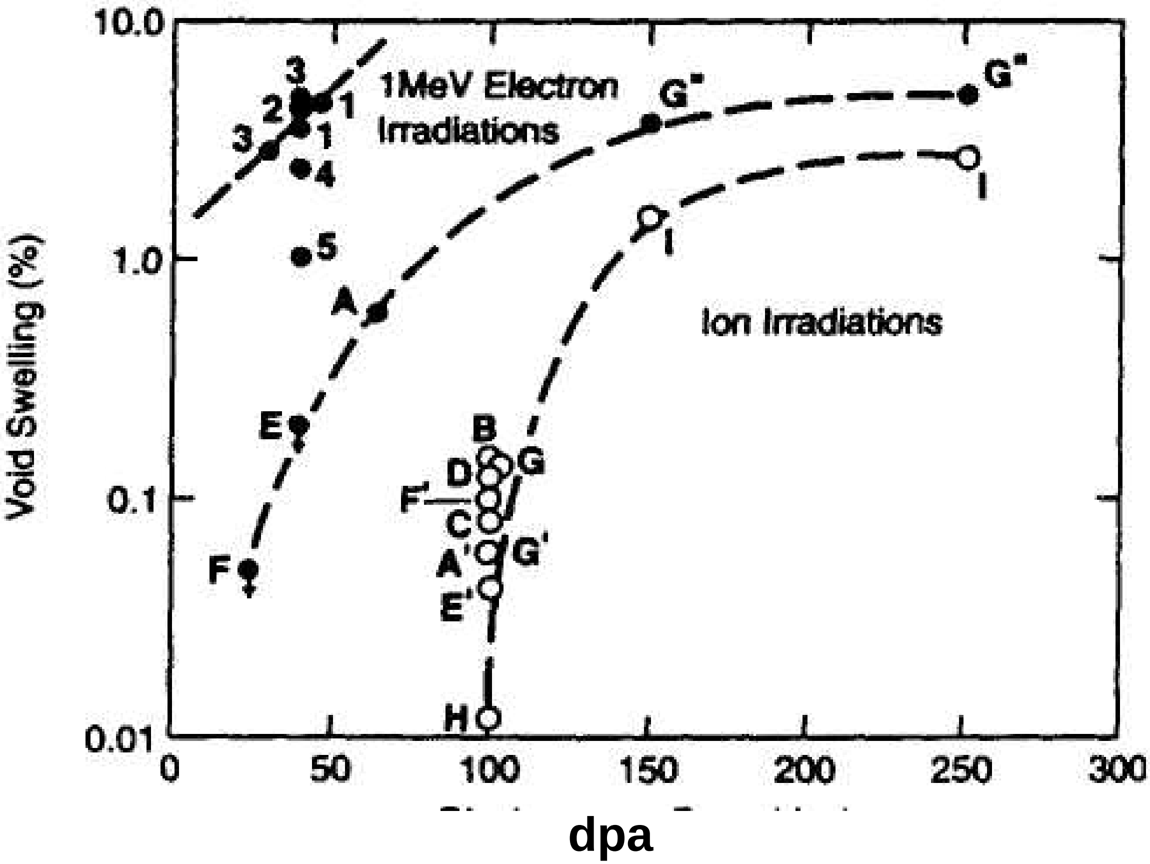
$\varepsilon_{2v} = 0.2$

$\varepsilon_i = 1.04$

Solid line – neutron or ion irradiation;   dashed line – electron irradiation

Damage accumulation in Fe is more effective under electron in comparison with neutron or ion irradiation

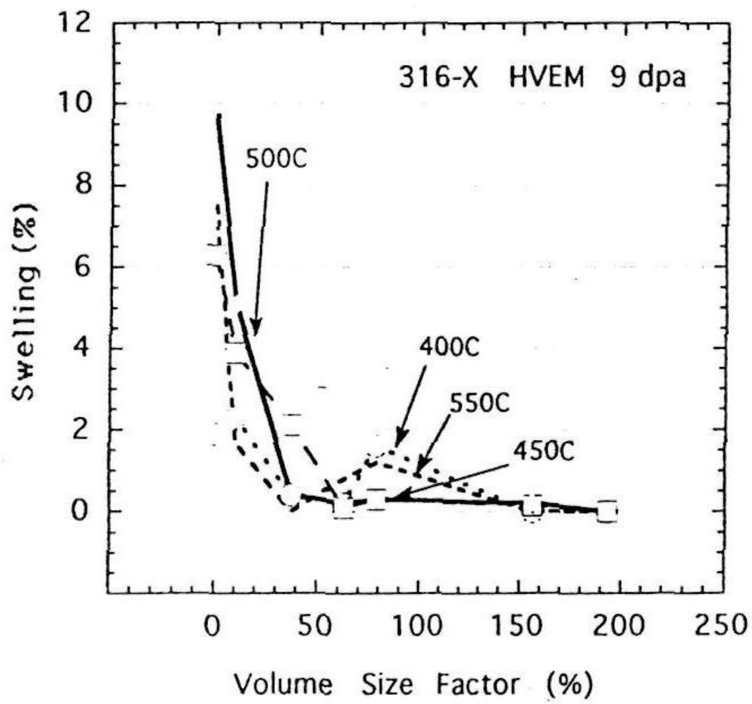
VOID SWELLING IN F/M STEELS IRRADIATED WITH ELECTRONS AND IONS

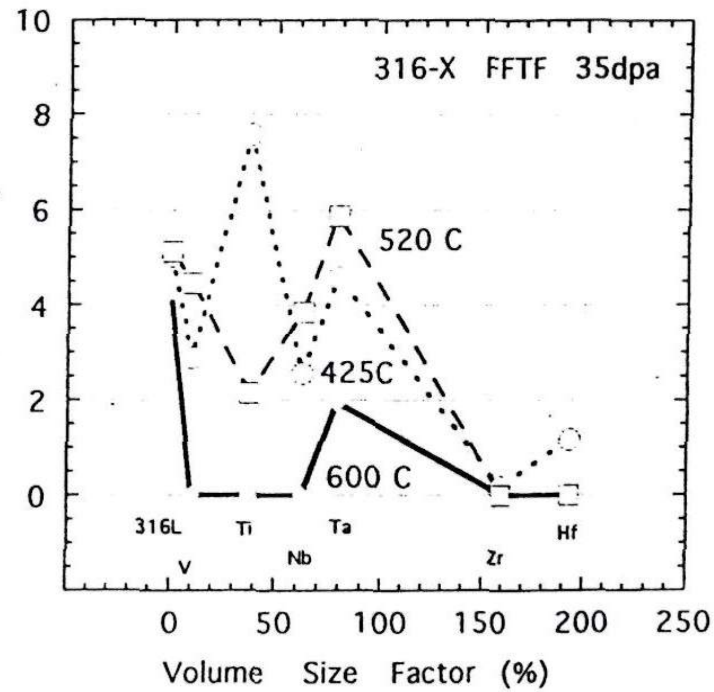


Experimental data from the book by Klue and Harries, 2001

Electrons are more effective in swelling than ions or neutrons in f/m steels

Effect of oversized alloying elements





Relationship observed between void swelling and volume size factor for electron and neutron irradiation (after Ohnuki, 1995)

Most effective elements: Zr, Hf

Swelling suppression is related to enhanced PD recombination due to large vacancy-element binding energy:

$$R_{eff} \approx R \cdot \left(1 + C_p \cdot \exp\left(\frac{E_v^b}{kT} \right) \right)$$

Effect of He

Helium has an extremely low solubility in the metal lattice and thus initially precipitates as bubbles, often in association with other microstructural features, including dislocations, grain boundaries, and precipitate interfaces.

Without stabilization by He pressure, small vacancy clusters rapidly dissolve owing to the Gibbs-Thompson effect.

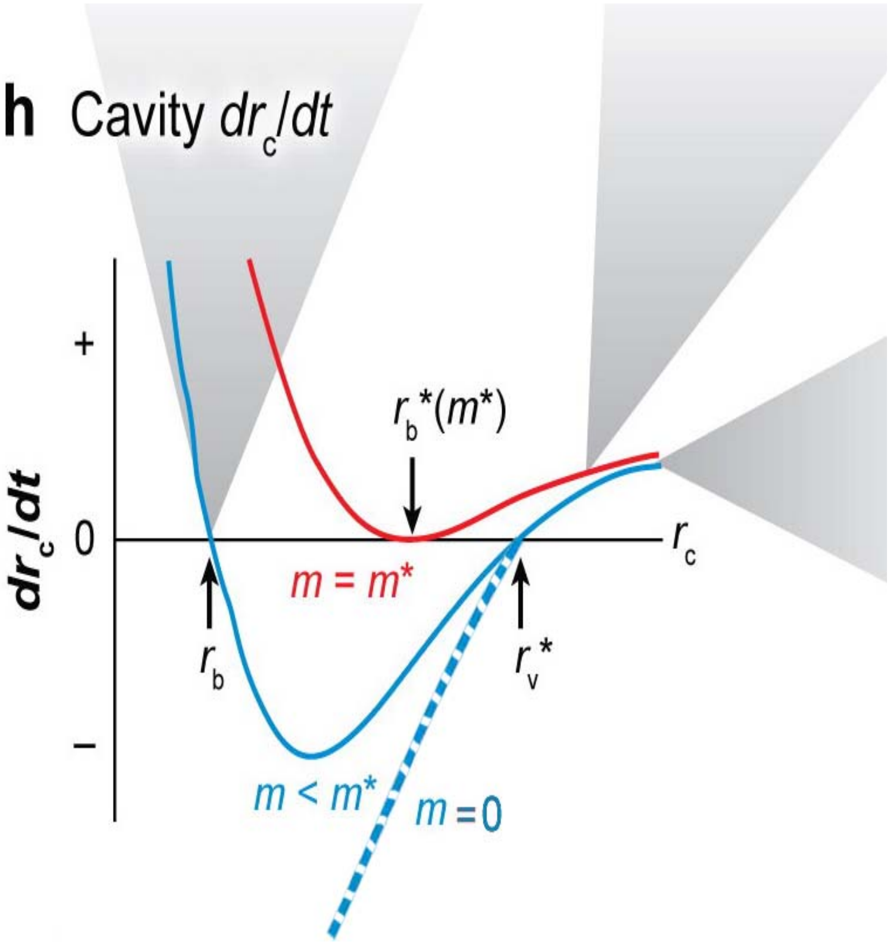
The growth rate of a cavity containing *m* He atoms is

$$dr_c/dt=\{D_vC_v - D_iC_i - D_{sd}\ exp\ [(2\gamma/r_c - 3ZmkT/\{4\pi r_c\})/\Omega/kT]\}/r_c$$

Here *Z* is a compressibility factor, *γ* is the surface energy, and *Ω* is the vacancy volume.

This equation has two real roots: the smaller is the stable bubble radius, $r_c = r_b$, whereas the larger is the critical unstable void radius, $r_c = r_v^*$ (see below).

Effect of He



At $r_c > r_v^*$, cavities grow unstably as voids.

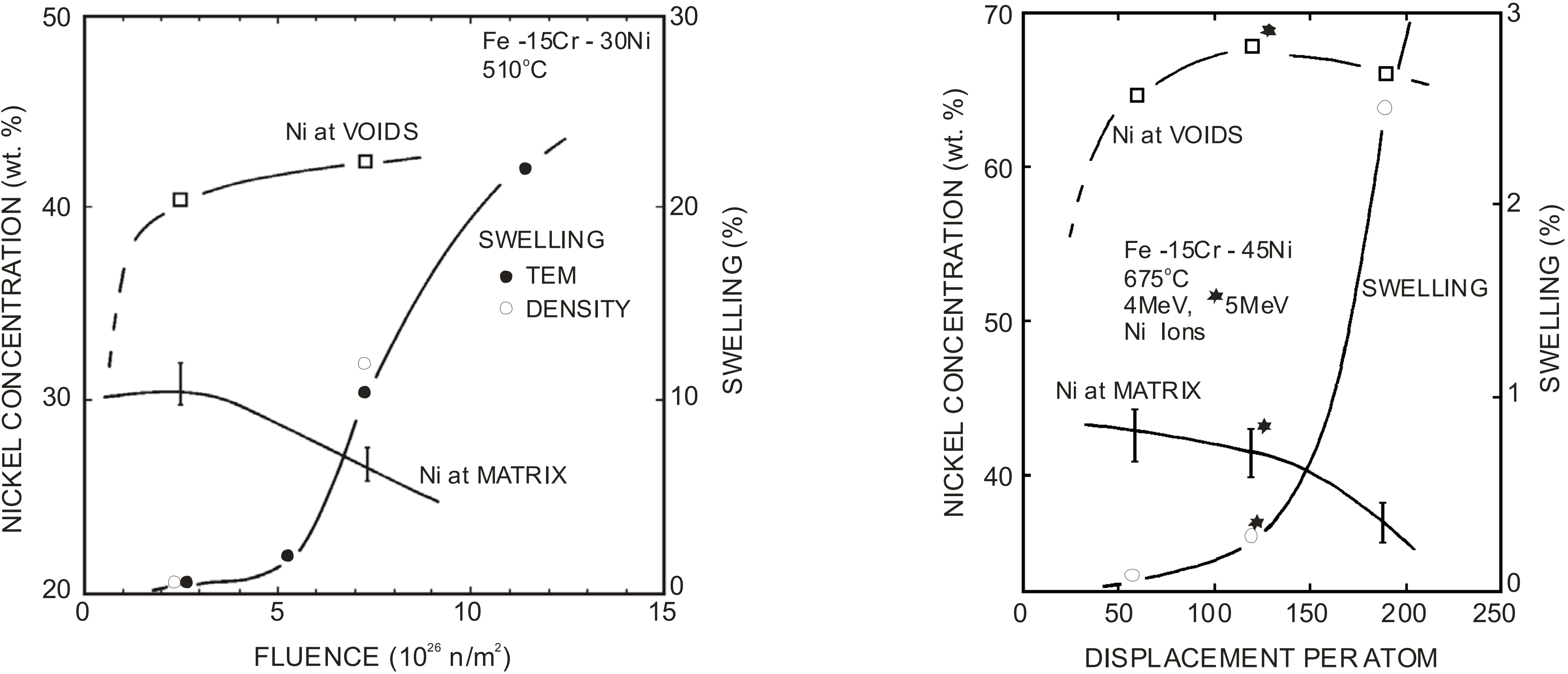
Small bubbles first grow stably (r_b increases), with the incremental addition of He atoms, whereas r_v^* decreases.

Thus, there is a critical bubble He content, m^*, at $r_b = r_b^* = r_v^*$, when the bubbles directly transform to unstably growing voids.

The critical m^* is controlled by (DvCv – DiCi – Dsd) and the various interface energies and stress fields at the bubble site

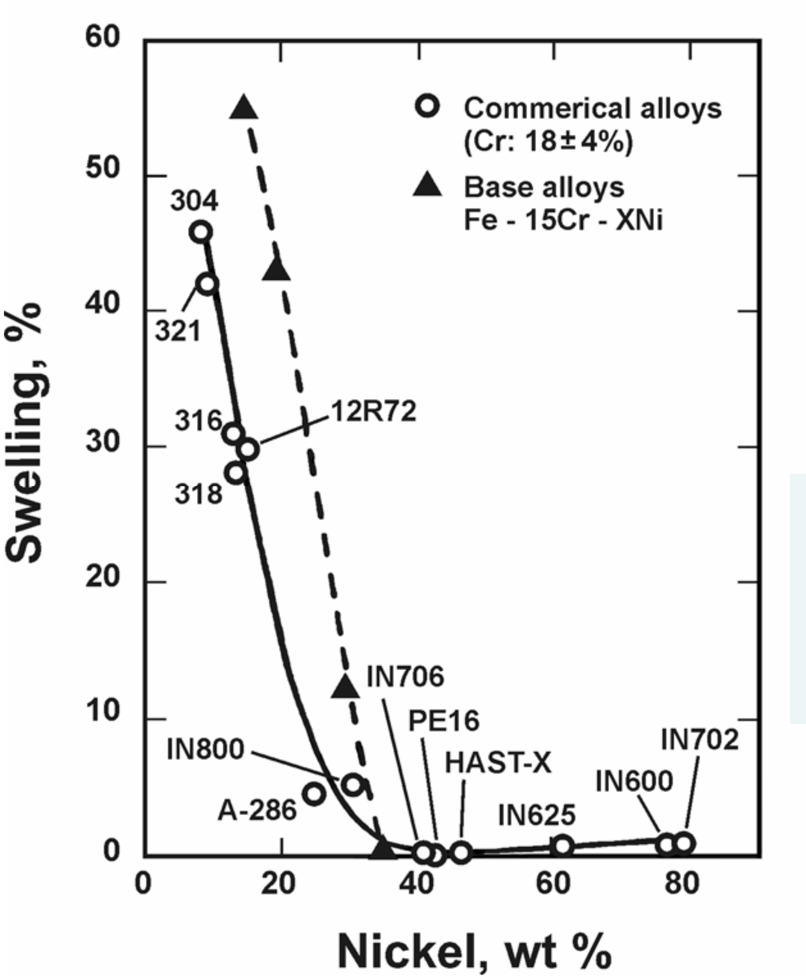
(from Odette, 2008)

Swelling in alloys



The dose dependence of swelling and nickel concentration at void surfaces and in the matrix of neutron irradiated Fe-15Cr-30Ni and Fe-15Cr-45Ni irradiated with 4 or 5 MeV Ni ions (Muroga et al., 1992)

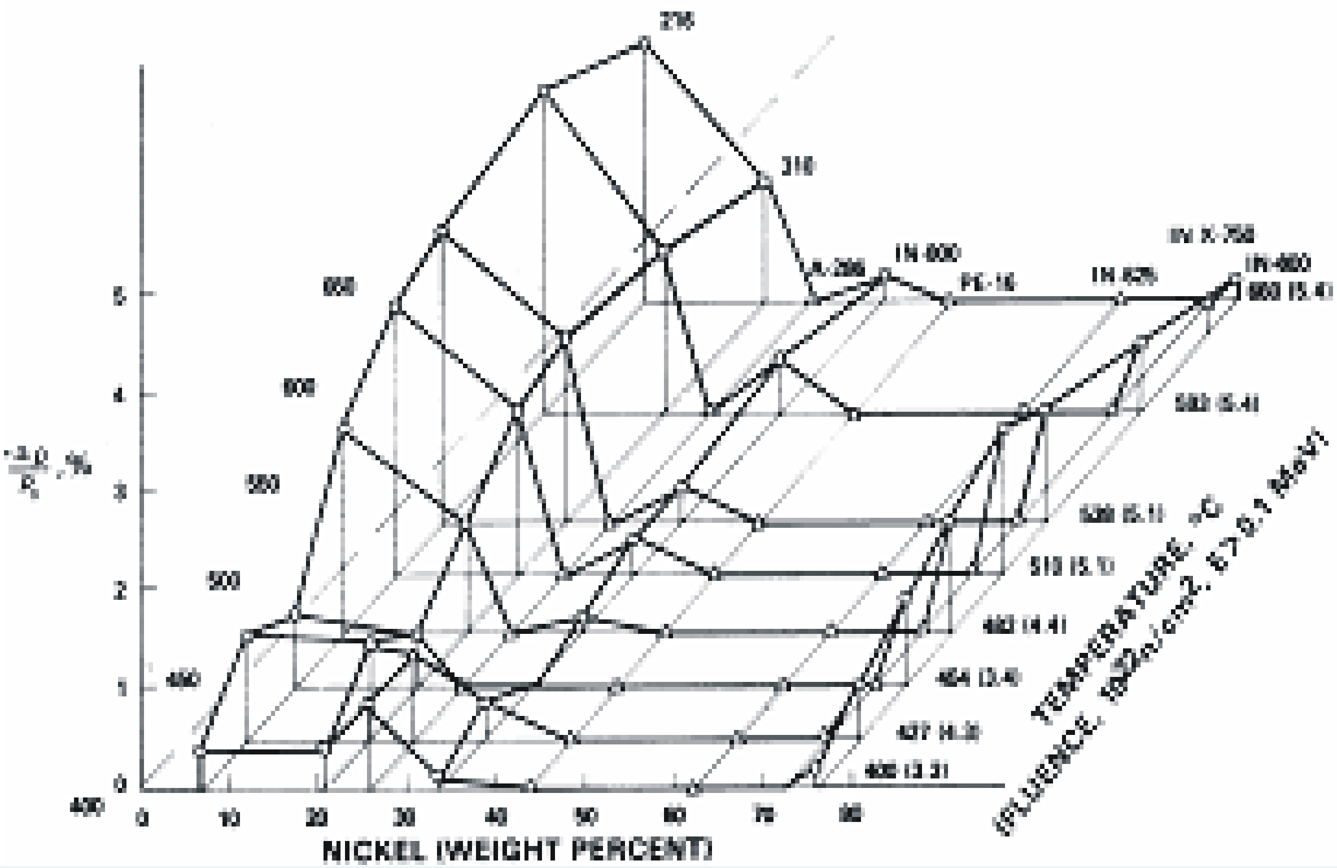
Swelling



Ion irradiation

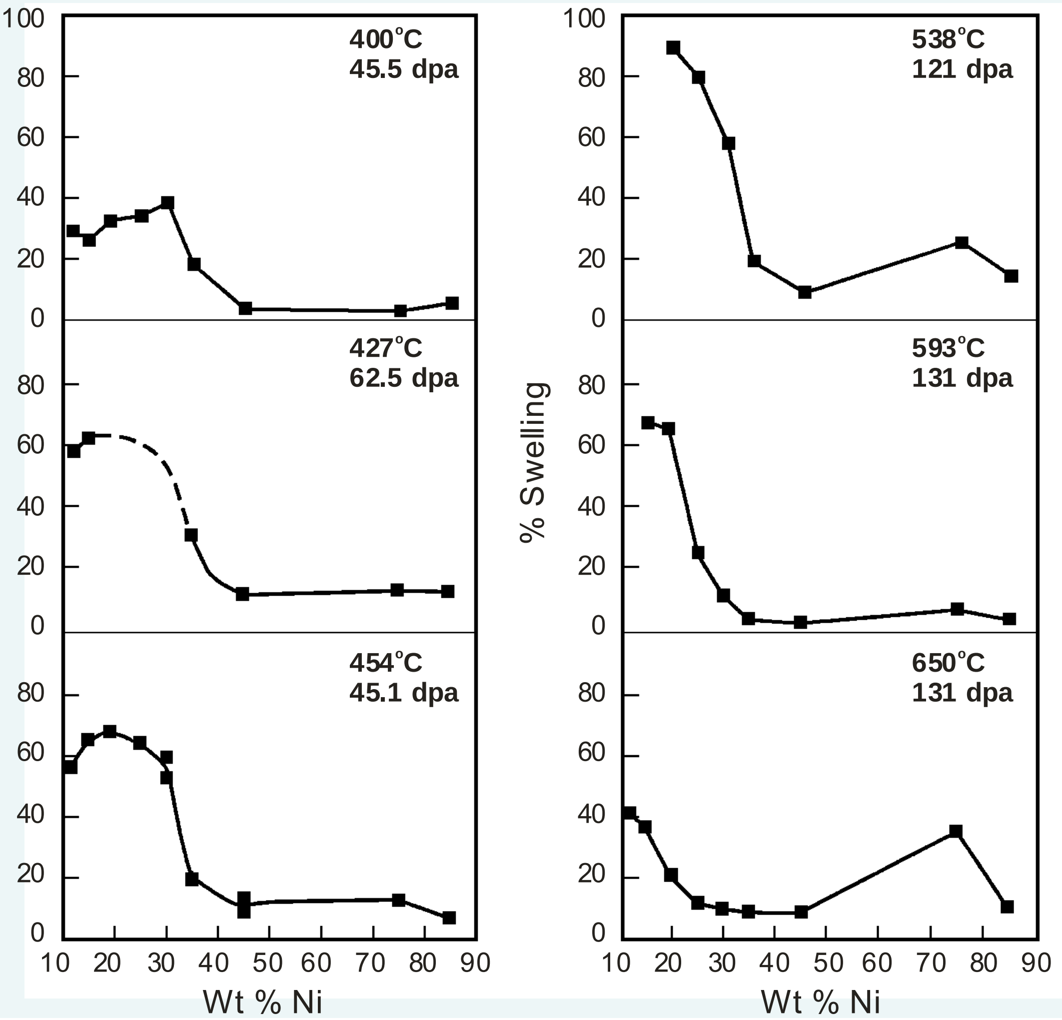
Comparison of 5MeV Ni$^+$ ion-induced swelling at 625^{0}C for commercial alloys (14–22% Cr) and Fe-15Cr-Ni ternary alloys (after Johnston et al., 1976)

Swelling



Relative swelling behavior of eight annealed austenitic alloys over a limited range of temperature (400-650^{0}C) and neutron exposures corresponding to 16 to 27 dpa (after Bates and Powell, 1981)

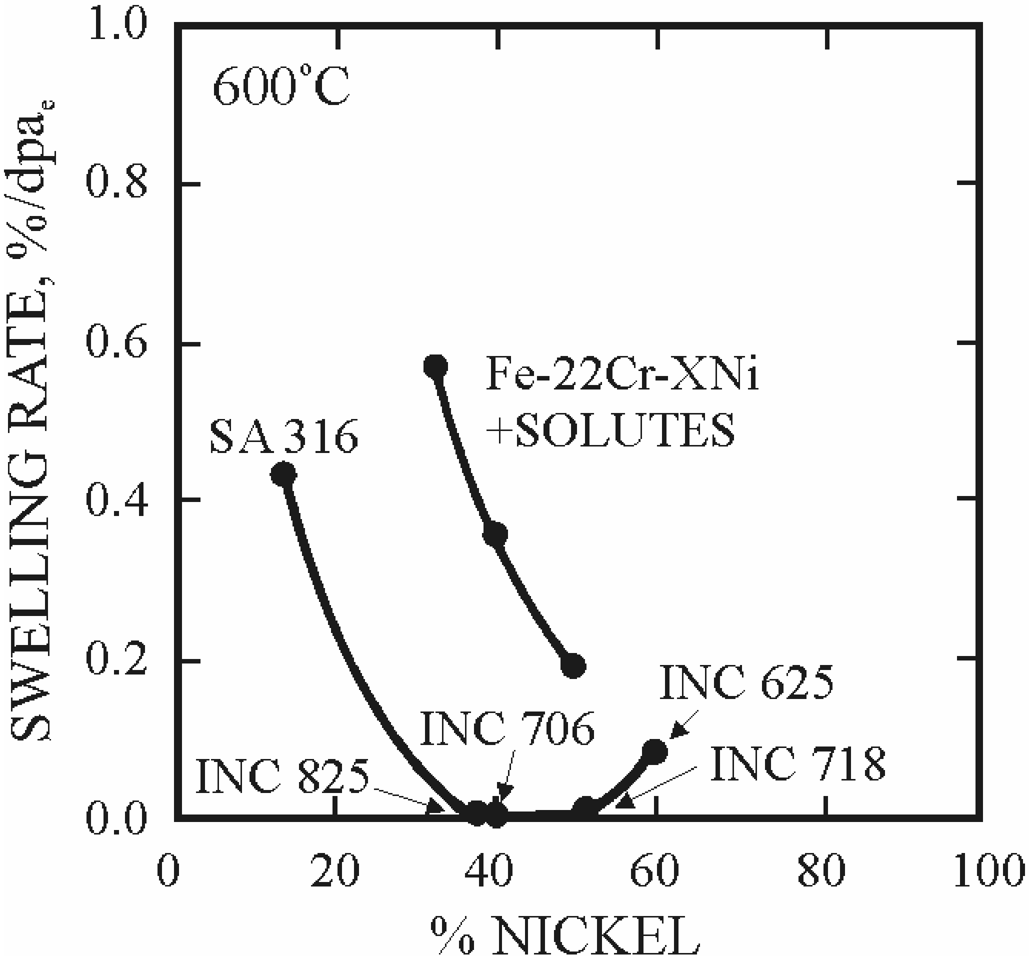
Swelling



Neutron irradiation

Swelling of Fe-15Cr-XNi alloys observed in EBR-II at six irradiation temperatures (Garner, Black, 2000)

Swelling



Electron irradiation

Effect of nickel on swelling rate of various alloys irradiated at 600^0C with 1 MeV electrons (after Levy et al.,1977)

Effect of RIS on Swelling

1. *Segregation-induced bias of PD sinks (Kirkendall effect)*
   Dependence of swelling in Fe–Cr–Ni alloys on Ni content
   Large swelling in V–Fe, V–Cr alloys

2. *Enhanced growth rate of voids attached to radiation-induced precipitates*

(G – phase, phosphides)

   in austenitic steels and in Xastelloy X

Component and point defect fluxes in alloys under irradiation

If we account the dependence of PD formation and migration energies on alloy composition then

$$J_k = -D_k \alpha_k \nabla C_k + C_k[(d_{kv}\nabla C_v - d_{ki}\nabla C_i + (d_{kv} C_v \frac{\nabla G_v^f}{kT} - d_{ki} C_i \frac{\nabla G_i^f}{kT})],$$

$$J_v = -D_v \nabla C_v - \frac{D_v C_v}{kT}\nabla G_v^f + C_v \sum_k d_{kv}\alpha_k \nabla C_k$$

$$J_i = -D_i \nabla C_i - \frac{D_i C_i}{kT}\nabla G_i^f - C_i \sum_k d_{ki}\alpha_k \nabla C_k$$

Drift forces on PD:

Kirkendall forces and

forces due to gradients of PD formation and migration energies

Segregation-induced bias

Radiation-induced segregation of components near point defect sinks results in changes of both the concentration profiles of point defects $C_n(r)$ and the sink strengths . One can write

$$C_n(r) = C_{no}(r) + f_n(r),$$
$$k_n^2 = k_{no}^2(1 + B_n),$$

where r is the distance from a sink surface, $n = v,i$ stands for vacancies and interstitials, respectively.

The segregation-induced bias (SIB) B_s of a given type of sinks to interstitials may be calculated as follows:

$$B_s = B^s{}_i - B^s{}_v = \frac{k_i^2 - k_{io}^2}{k_{io}^2} - \frac{k_v^2 - k_{vo}^2}{k_{vo}^2} =$$
$$= -\frac{< f_i >}{< C_{io} > + < f_i >} + \frac{< f_v >}{< C_{vo} > + < f_v > + C_v^s}$$

Segregation-induced bias

The total bias is the sum

$$B = B_s + B_0$$

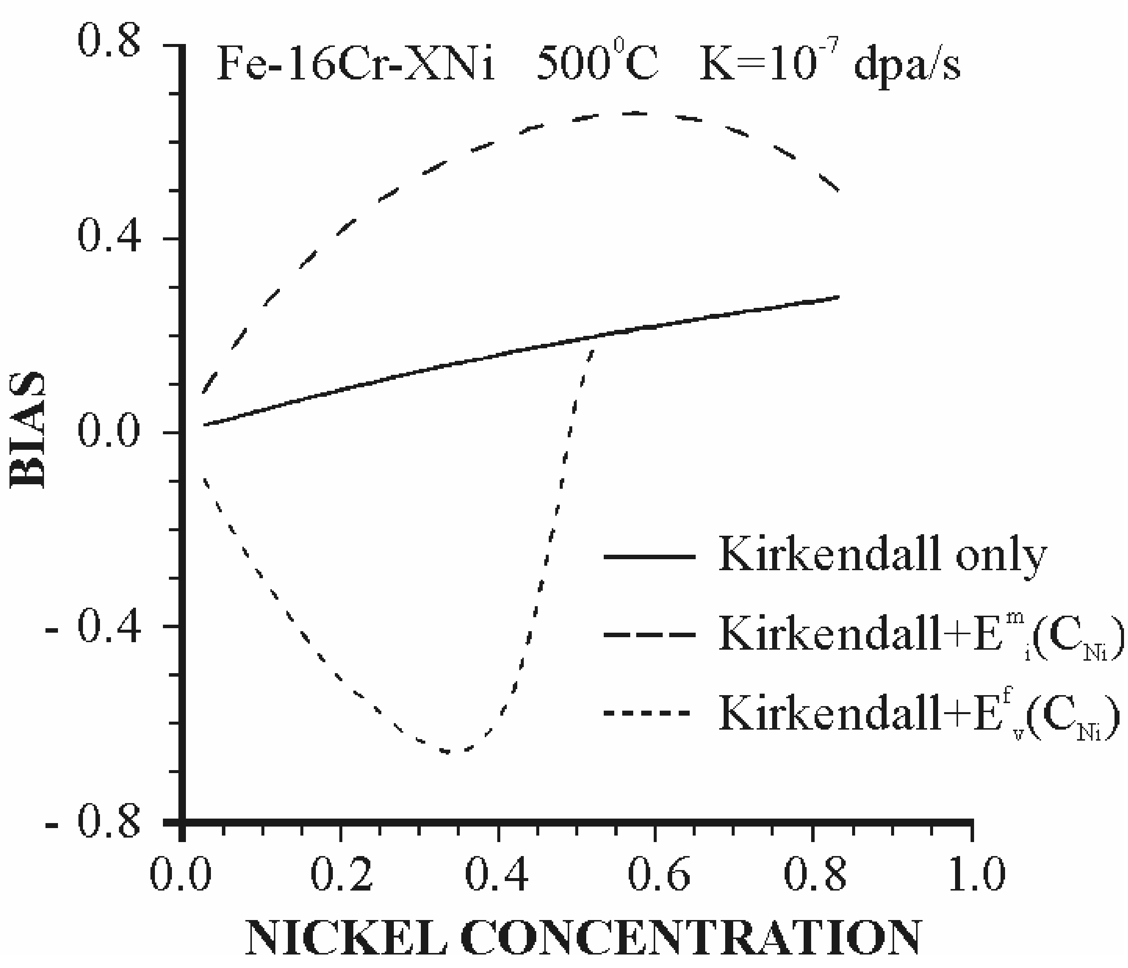
where B_0 is the bias in pure metals or nonsegregated alloys due to more strong elastic interaction of dislocation with interstitials than with vacancies

An analytical expression for B_s can be obtained in the simplest case of binary alloy and Kirkendall forces

$$B^s \cong \frac{C_{A0}\gamma}{a + 2\gamma/3}\left(\frac{(1-\lambda_v)(2/3+a)}{\lambda_v + C_{A0}(1-\lambda_v)} - \frac{(1-\lambda_i)(2/3-a)}{\lambda_i + C_{A0}(1-\lambda_i)}\right)$$

$$\gamma = (\lambda_i - \lambda_v)(1 - C_{A0})/(\lambda_i + \lambda_v + C_{A0}(2 - \lambda_i - \lambda_v)), \quad \lambda_n = d_{Bn}/d_{An}$$

Segregation-induced bias



Contribution of various drift forces to segregation-induced bias in Fe-15Cr-XNi alloys

Data on E_v^f, E_v^m and E_i^m dependences on Ni content in Fe-16Cr-XNi alloys obtained by Dimitrov et al. (1988) are used

Vanadium alloys

Vanadium alloys are now considered as candidate fusion reactor materials.

Matsui et al (1991) have observed exceptionally large swelling of ~100% in V-5 at. % Fe alloy after irradiation in FFTF to 34 dpa at 600^{o}C in contrast to the swelling in pure vanadium of ~1.4% in similar irradiation conditions.

Data on ion irradiation of V-(0-7) at. % Fe alloy reveal no monotonic dependence of swelling on alloy content

Vanadium alloys

Experimental data point to dependence of λ_v and λ_i on iron content

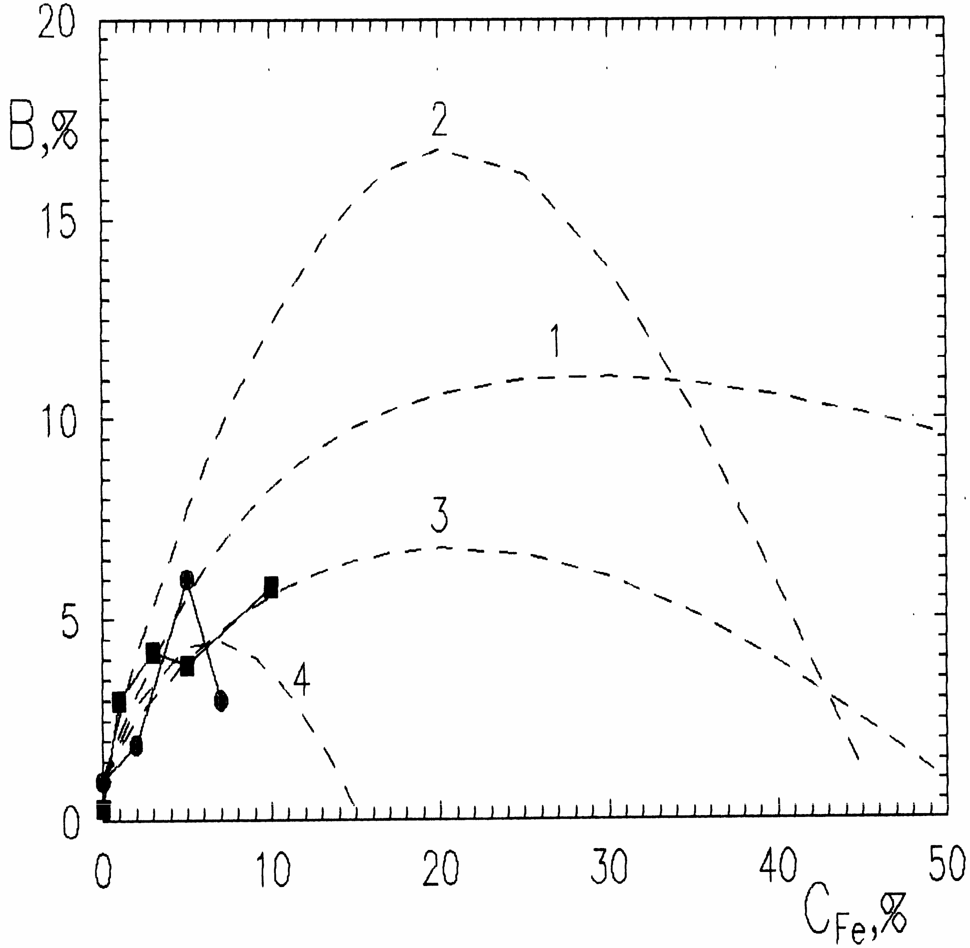
Using linear approximations:

$\lambda_v=\lambda_{v1}+C_{Fe}(\lambda_{v2}-\lambda_{v1})$, $\lambda_i=\lambda_{i1}+C_{Fe}(\lambda_{i2}-\lambda_{i1})$

one can obtain

$$\frac{C_A}{(1-C_A)^{\nu_1}}\cdot(1+\beta_1 C_A)^{\nu_2}\exp(\beta_2 C_A)=\mathrm{const}\cdot C_{vo}^{\theta},$$

Vanadium alloys



Experimental (circles-ion irradiation, squares-from Matsui et al) and predicted dependencies of SIB on iron concentration in V-Fe

alloys

1 - λv1=λv2=0.22, λi1=λi2=0.1;

2 - λv1=0.22, λv2=2.85, λi1=λi2=0.1;

3 - λv1=0.22, λv2=2.85, λi1= 0.1, λi2=0.8;

4 - λv1=λv2=0.22, λi1=λi2=0.1, parabolic dependence of point defect activation energies on iron content.

Voids attached to precipitates

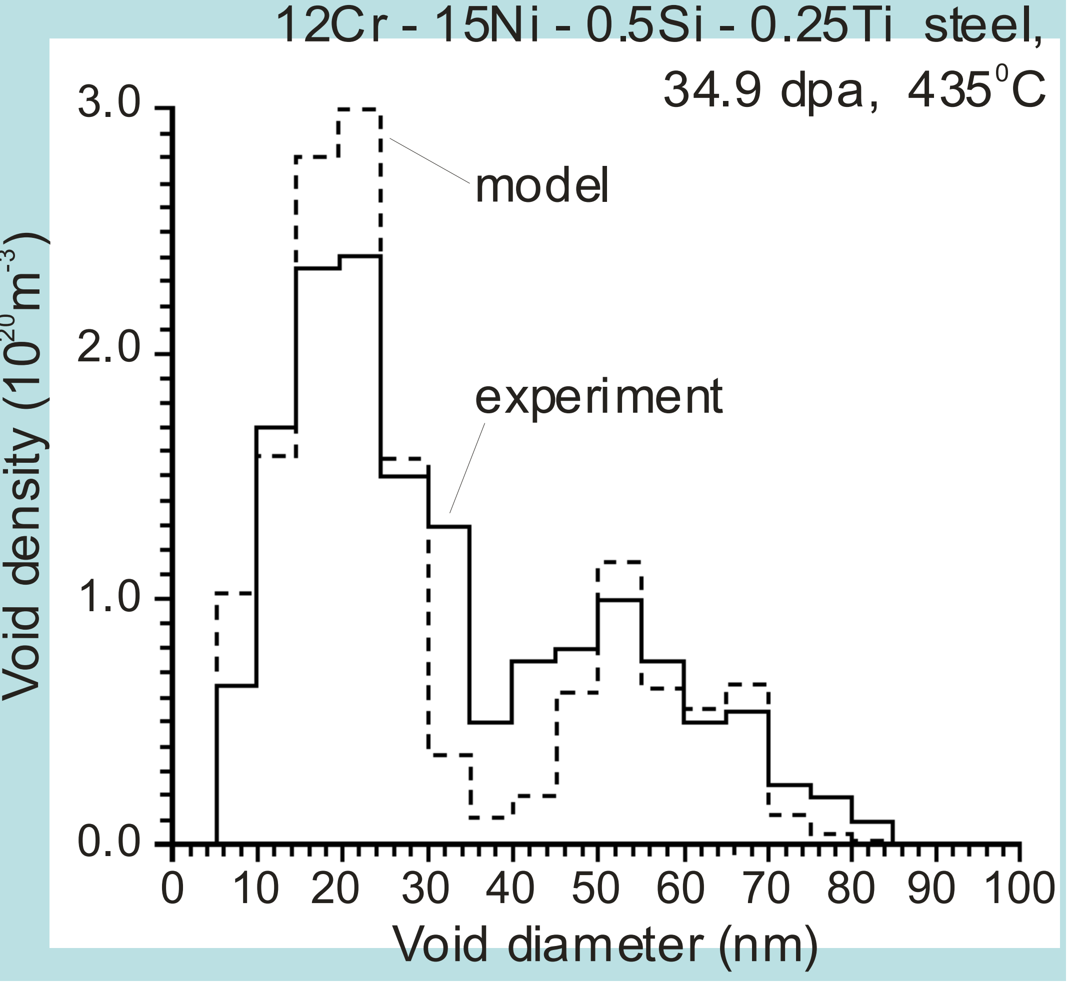
In irradiated complex alloys an association of the largest voids with secondary phase precipitates (e.g. G, η, Laves and phosphides in austenitic steels) is often observed

Two models for an explanation of enhanced growth of voids on precipitates

1.Collector mechanism (Mansur): the entire interface of a cavity-precipitate pair collects point defects

2.Difference in SIB of isolated and adjacent to precipitates voids
Usually, component profiles near voids associated with precipitates are reduced and differ from those near isolated voids

Voids attached to precipitates



Measured (Boothby, Williams, 1988) and calculated void size histograms including isolated voids and voids attached to G-phase precipitates in 12Cr-15Ni (Si, Ti) steel neutron-irradiated to 34.9 dpa

Voids attached to precipitates reveal enhanced growth due to difference in SIB

CONCLUSIONS. Pure metals

- Estimates made point to a significant income of mobile di-vacancies in void nucleation and swelling in fcc metals
- Further calculation of binding energies and diffusivities for various configurations of small vacancy and interstitial clusters are to be performed in order to specify mechanisms of void nucleation in metals during electron irradiation
- For ion and neutron irradiation additional data is needed on vacancy cluster formation directly in cascades

CONCLUSIONS . Alloys

- The appearance of segregation-induced bias (SIB) of sinks to interstitials or vacancies is an important consequence of RIS
- Values of SIB can be of the order or more than the known bias of edge dislocation to interstitials in pure metals
- SIB can be responsible for a strong dependence of swelling on alloy composition
- The difference in SIB may result in an accelerated growth of voids adjacent to precipitates as compared to the growth of isolated voids