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Displacement rate effects in void formation

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ABSTRACT

Displacement rate changes are reflected in a variety of explicit and implicit ways in the parameters governing the void formation rate. The nodal line-critical point formalism of Poincaré is used to analyze these changes and provide guidance for experimental studies.

1. Introduction

Radiation experiments on alloys are conducted over a wide range of atomic displacement rates. These range from ca. 10^{-9} dpa/s (displacements per atom per second) in light water reactor pressure vessel steels through ca. 10^{-6} dpa/s rates characteristic of fast reactor cladding and ducts and some proposed fusion first walls through ca. 10^{-3} dpa/s rates in heavy ion irradiation to ca. 10^{-1} dpa/s rates sometimes achieved in the high voltage electron microscope. These irradiations produce a variety of point, linear, area, and volume defects.

Helium is known to play an important role in the evolution of radiated microstructures: it may be introduced by (n,α) transmutation reactions or by ion injection. In the former case the helium production rate depends on the neutron spectrum and the (n,α) cross sections of the various atoms in the irradiated material.

Irradiation is known to alter phase formation in a myriad of systems and by a multiplicity of mechanisms, most of which depend on the displacement rate. Void swelling is of particular interest [1–4]. This paper will restrict itself to displacement rate effects in void formation.

A void is an aggregate of vacancies and (usually) helium atoms that may grow freely under the ambient irradiation conditions. Vacancy: helium aggregates too small to undergo free growth are referred to as void embryos or simply as embryos. Voids are distinct from bubbles, in which the internal gas pressure is high enough to balance the surface energy.

2. The irradiated state

In the case of MeV energy neutrons or heavy ions, the energetic particle produces a primary knock on atom (PKA) that loses energy by producing secondary knock on atoms. The mean free path between collisions decreases as the particle energy decreases and displacement events become closer and closer together. Ultimately the energetic atoms come to rest in hot, disordered regions known as displacement cascades, or spikes. Early investigators [3,4] based void nucleation theories on the cascades decaying into a uniform sea of individual vacancies and self-interstitials.

Later studies give a much more complex picture of the irradiated state. Wei et al. [5] studied field ion microscope tips that had been irradiated with heavy ions. Irradiation was at a temperature so low that even self-interstitials were immobile. The cascades produced ca. hundreds of vacancies. Many of these vacancies were nearest neighbors to one or more other vacancies so that early clustering was to be expected.

Various workers [6–9] have made molecular dynamic studies of displacement cascade formation and evolution. Calder and Bacon [6] modeled cascade formation in Fe due to an incident 2 keV Fe atom and found a maximum damage level of about 500 atoms at 0.34 ps. However, very rapid point defect recombination occurred so that only 28 displacements survived at 9.8 ps. A crucial result of these molecular dynamics studies was that approximately a quarter of the surviving self-interstitials formed stable clusters of up to dozens of defects. These clustered self-interstitials never become part of the defect sea and produce a ‘production bias’ in favor of vacancies as enunciated by Woo and Singh [10].

Wirth [11] and others [12,13] used computer simulation to study cascade evolution. Wirth studied Fe at 563 K, after the initial point defect recombination had taken place. He found that within about a microsecond heavy vacancy clustering had occurred. Clusters containing up to a dozen vacancies formed. But, unlike interstitial clusters most of the vacancy clusters decayed to mono-vacancies within about one microsecond.

Electron irradiation produces only isolated Frenkel pairs rather than cascades. The remarks on cascade behavior and production bias are irrelevant to such irradiations.

3. Point defect concentrations

Wiedersich [14] and Brailsford and Bullough [15] derived equations for the steady-state concentrations of radiation-induced

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Nomenclature

A	energetic parameter in nucleus formation
C_i, C_v, C_x	concentrations of self-interstitials vacancies, and helium interstitials
C_{ve}	equilibrium vacancy concentration
C_T	concentration of trapped helium
D_v, D_x	diffusivities of vacancies, and helium interstitials
J_s^*	steady-state nucleation rate
K_i, K_v	rates of self-interstitial and vacancy production
kT	Boltzmann factor
K_x^c	rate of helium detrapping from voids
K_x^T	rate of helium detrapping from vacancies
n	number of vacancies in a void
n^*	number of vacancies in critical nucleus
$\dot{n}$, $\dot{x}$	velocities of a point in n, x space
$\hat{n}$, $\hat{x}$	coordinates of stable node in Poincaré analysis
S_e	radiation modified vacancy supersaturation
S_v	vacancy supersaturation
X	number of helium atoms in a void
Z	Zeldovich factor
Z_i, Z_v, Z_x	dislocation sink strength constants for self-interstitials, vacancies, and helium interstitials
α_v, α_x	emission rates of vacancies and helium atoms from embryos
β^*	impingement rate of vacancies on the critical nucleus
$\beta_i^0, \beta_v^0, \beta_x^0$	impingement rates of self-interstitials, vacancies, and helium on a mono-vacancy
γ	void: matrix surface energy
δ	width of activation barrier kT below its maximum
ΔG^*	activation barrier for void nucleation
$\rho(x)$	number density of embryos or voids containing x gas atoms
ρ_c	total number density of embryos and voids
ρ_d	dislocation number density
Ψ	constant governing nodal lines
Ω	atomic volume of solid

vacancies and self-interstitials. The general equations are of necessity complex. Simplification is possible for fast reactor irradiation conditions with displacement rates of ca. 10^{-6} dpa/s and temperatures between about 0.4 and 0.5 T_m, where T_m is the absolute melting point. Under these conditions dislocations are the main point defect sinks and thermal creation of vacancies is unimportant. Defect arrival rates at a single vacancy are then:

$$\beta_i^0 = K_i/a^2 Z_i \rho_d \tag{1}$$

$$\beta_v^0 = K_v/a^2 Z_v \rho_d \tag{2}$$

where i, v refer to interstitials and vacancies, respectively.

K_i, K_v = production rates of isolated self-interstitials and vacancies per lattice atom per second.
ρ_d = dislocation density in length per unit volume.
Z_i, Z_v = dislocation sink strength constants.

The arrival rate of mobile vacancies is about a quarter greater than that of mobile interstitials due to the production bias discussed earlier. The Table gives a list of symbols used in this paper.

The vast majority of dissolved helium is immobilized in traps, which include dislocations, mono-vacancies, void embryos, and voids. Detrapping puts the helium in an interstitial site where it may diffuse rapidly until captured by another trap. Simple conservation shows that the impingement rate of mobile helium on a mono-vacancy is:

$$\beta_x^0 = K_x^T C_T/a^2 Z_x \rho_d \tag{3}$$

- K_x^T = rate of detrapping from the dominant trap.
- C_T = concentration of trapped helium, which is very close to the total concentration.
- Z_x = dislocation sink strength constant for helium.

Calculations [16] have shown that a helium atom trapped in a mono-vacancy site reacts spontaneously with a self-interstitial to produce a helium interstitial and a lattice atom. Thus, $K_x^T = \beta_i^0$ and:

$$\beta_x^0 = \beta_i^0 C_T/(a^2 Z_x \rho_d). \tag{4}$$

Dislocations climb rapidly under irradiation so that any trapped helium is quickly left behind in vacancy traps. There is thus no need to consider the detrapping rate of helium lying on dislocation lines.

If the helium is trapped primarily by voids and embryos:

$$\beta_x^0 = K_x^c C_T/(4\pi a^2 r_c \rho_c) \tag{5}$$

where r_c is the mean radius of the void embryo distribution and ρ_c is the total number density of voids and embryos.

K_x^c = detrapping rate from these volume defects.

Voids and embryos constitute what might be called deep traps in that detrapping is much more difficult than from vacancies. A helium atom will be detrapped by radiation resolution only if struck hard enough to drive it back into the lattice. The required energy will be in the tens of eV range, similar to that for atomic displacements in the lattice. We may then roughly equate the detrapping rate K_x^T to the atomic displacement rate. This rate may be orders of magnitude lower than the detrapping rate from lattice sites.

Some algebra shows that voids and embryos are the dominant helium sinks when:

$$K_x^c/\beta_i^0 < 4\pi r_c/Z_x \rho_d. \tag{6}$$

Void trapping of helium thus becomes dominant at number densities far below the ca. $10^{22}/\mathrm{m}^3$ found after typical irradiation experiments.

4. Void nucleation

The steady-state rate of homogeneous void nucleation form a sea of vacancies and self-interstitials was derived by (3) and (4) as:

$$J_s^* = Z\beta^* N \exp(-\Delta G^*/kT). \tag{7}$$

The asterisk indicates quantities evaluated at the critical nucleus size. ΔG^* = height of the activation barrier to nucleation, and kT = Boltzmann factor. The frequency factor, $\beta^* = \beta_v^0 n^{*1/3}$. N = number of atoms/unit volume. The Zeldovich factor Z is a dimensionless quantity typically about 0.1.

Until fairly recently the ratio β_i/β_v was thought to be within 1% of unity. The result of interstitial involvement was a huge increase in the critical nucleus size, which resulted in orders of magnitude increase in critical nucleus size and the nucleation rate.

Existence of the production bias gives a β_i/β_v of about 3/4 and a much-reduced effect of self-interstitials on void nucleation. The nucleation rate is reduced by only a factor of ten or so over the no-interstitial case, which is fairly minor in terms of nucleation theory. We may then approximate the activation energy for nucleation by the value in the absence of self-interstitials.

Mobile helium atoms will be captured by the void embryos which will then be stabilized by the resulting internal gas pressure. The internal pressure will reduce the rate of vacancy emission and facilitate void formation. Helium atoms may also be lost from the embryos. Analyzing these effects of helium capture and loss on the rate equations for void formation has proven to be a very thorny problem [17–29].

5. Poincaré analysis

A successful analysis [26] utilized the nodal line-critical point formalism developed by Poincaré [30] for celestial mechanics. Void nucleation was represented by movement off a point in a two dimensional phase space of embryo size n (in number of vacancies) and contained helium atoms, x.

Relatively few combinations of n and x define embryos of importance in void formation. The Poincaré analysis has a large advantage over brute force numerical evaluation of the master equation in identifying these embryos. Calculation of the void formation rate is then usually a fairly simple matter.

Fig. 1 shows the various processes giving rise to embryo movement in size (n) and helium content (x) space. The velocity $\dot{n}$ equals the capture rate of vacancies minus the capture rate of self-interstitials and the loss rate of vacancies. The velocity $\dot{x}$ is the capture rate of mobile helium minus the loss rate. Helium atoms may be lost by radiation resolution or by thermal emission.

$$\dot{n} = \beta_v^o n^{1/3} - \alpha_v - \beta_i^o n^{1/3} \tag{8}$$

$$\dot{x} = \beta_x^0 n^{1/3} - \alpha_x - xK_x^c. \tag{9}$$

The defect emission rates α_v and α_x are obtained by the principle of detailed balancing.

The locus of the points for which $\dot{n}$ or $\dot{x}$ is zero is known as a nodal line. An intersection of the two nodal lines is known as a critical point. An embryo at a critical point is immobilized, neither gaining nor losing helium atoms nor vacancies. The $\dot{n}$ nodal line may only be crossed by embryos moving in the x direction and the $\dot{x}$ nodal line by embryos moving in the n direction.

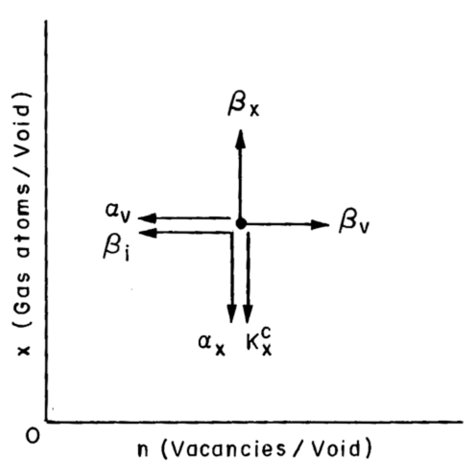

Fig. 1. Atomic processes involved in void nucleation showing mechanisms for vacancy and gas atoms capture and loss. Symbols are defined in the table.

The nodal lines may take one of two configurations, depending on the parameter Ψ where

$$\Psi = (9\beta_x^0 \ln S_e)/(A^2 K_x^c). \tag{10}$$

The effective supersaturation is:

$$S_e = (C_v/C_{ve})(1 - \beta_i^0/\beta_v^0) \tag{11}$$

where C_v/C_{ve} is the ratio of the actual and equilibrium vacancy concentrations.

The energetic parameter A is

$$A = (36\pi\Omega^2)^{1/3}\gamma/kT \tag{12}$$

where Ω = atomic volume of solid and γ = void: matrix surface energy. The key variables in Ψ are the effective supersaturation and the ratio of helium capture and detrapping rates.

At low vacancy supersaturations and helium arrival rates Ψ <1 and the nodal lines will intersect twice, as shown in Fig. 2, which indicates the directions of embryo movement in the (n,x) phase space. Embryos above the $\dot{x}$ nodal line are losing helium more rapidly than they are gaining it. The reverse is true for embryos below this nodal line. Embryos outside the $\dot{n}$ nodal loop are growing in size while those underneath are shrinking.

The critical point at larger n is known as a saddle, but is of no physical significance. The critical point at $\hat{n}, \hat{x}$ is known as a stable node. It attracts embryos from the regions around it as shown by the arrows in Fig. 2. The theory thus predicts that irradiation conditions giving nodal line intersection may lead to large concentrations of embryos that are trapped at the stable node.

Fig. 3, also at Ψ <1 shows possible heterogeneous nucleation paths at constant helium concentrations. Size fluctuations may

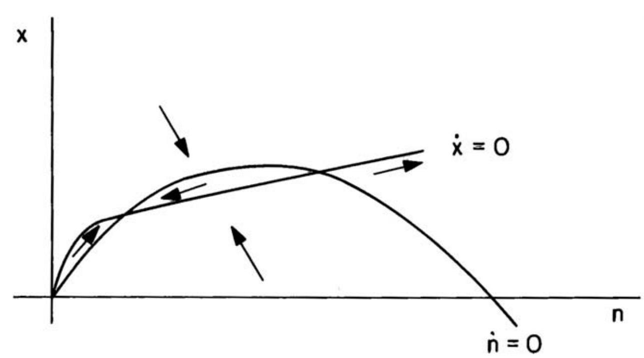

Fig. 2. Schematic diagram of nodal lines for Ψ < 1. Nearby clusters are attracted to the stable node at $\hat{n}, \hat{x}$.

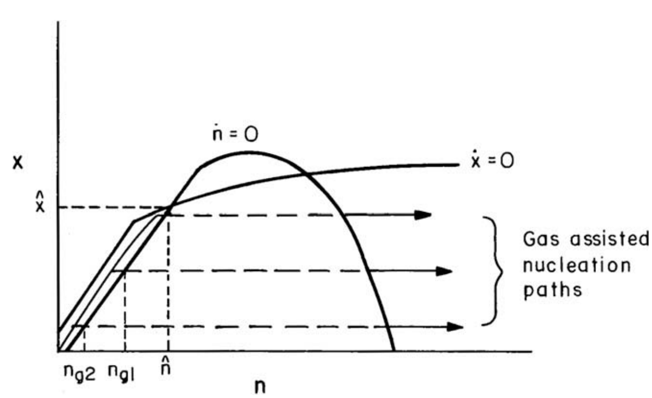

Fig. 3. Nodal line configuration with Ψ < 1. Clusters up to the size $\hat{n}$ and $\hat{x}$ may serve as heterogeneous nucleation sites (after Ref. [29]).

carry the embryos from the left side of the nodal loop to the right, where they become voids. Heterogeneous nucleation may occur on developing embryos as well as those trapped at the node.

The resulting rate equation is similar to Eq. (6) for homogeneous nucleation. The activation energy is reduced by the free energy of the embryo. The number of nucleation sites is the number density of embryos.

If Ψ >1, as shown in Fig. 4 the nodal lines do not intersect and a third mechanism of void formation comes into play. Void embryos may develop by the steady accretion of vacancies and helium atoms to move between the two nodal lines. When the embryo reaches the top of the $\dot{n}$ nodal line it becomes a void and may grow spontaneously by capture of vacancies and helium in any proportion. No activation barrier is involved. The process is referred to as spontaneous void formation.

However, even with Ψ>1 helium-containing embryos are attractive heterogeneous nucleation sites. The internal helium pressure reduces the critical nucleus size and the activation barrier for nucleation as shown in Fig. 5. These embryos must gain enough vacancies to reach the right of the $\dot{n}$ nodal loop. From this point on they may grow spontaneously. Void formation will then involve a competition between the rate of embryos climbing the barrier to reach the maximum and those undergoing fluctuations in n to reach critical nucleus size.

Fig. 2 and Eqs. (10) and (12) are based on helium being an ideal gas. Such behavior is makes for simple expressions suitable for discussion. In fact the helium tends to be at very high pressure so that a more realistic gas law is needed.

Parker and Russell [27–29] calculated nodal lines and void formation parameters values based on the van der Waals gas equation. The effect was to elevate the $\dot{x}$ nodal line and depress the $\dot{n}$ nodal line and increase the value of Ψ. The overall effect was to predict easier nucleation rates than obtained on the basis of an ideal gas. Fig. 3 is calculated from the van der Waals gas model. The change in nodal lines from Fig. 2 is clear.

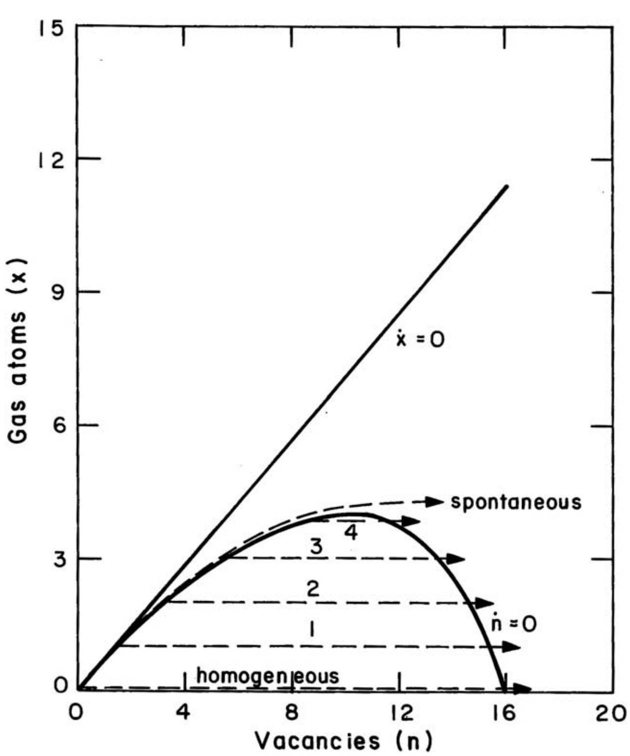

Fig. 4. Calculated void nucleation paths corresponding to simultaneous heavy ion and α-particle irradiation of Type 304 stainless steel (after Ref. [29]).

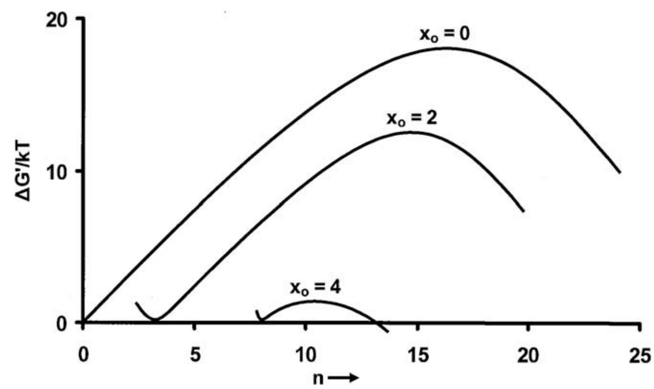

Fig. 5. Activation barriers for homogeneous nucleation and for heterogeneous nucleation on clusters of two and four helium atoms (after Ref. [29]).

However, the more realistic gas law made for very messy equations for the various parameters. These equations are not useful for illustrating the physics of void formation.

Figs. 4 and 5 give the results of calculations for type 304 stainless steel under simultaneous heavy ion and α-particle irradiation at 873 K. The van der Waals gas law was used in these calculations. Homogeneous nucleation is possible, as is nucleation on embryos of from 1 to 4 helium atoms and spontaneous void formation. Significant amounts of void formation are predicted to occur by all six paths. Homogeneous nucleation was most rapid at first, with heterogeneous nucleation plying a greater and greater role as the concentrations of small embryos developed over time. Ultimately spontaneous formation became the dominant mechanism.

The irradiation conditions were such that $\beta_v^o \gg \beta_x^o$. Accordingly heterogeneous void nucleation took place at constant helium content and simple heterogeneous nucleation theory was applicable.

6. Displacement rate effects

Irradiation displacement rate affects nucleation most strongly through C_v in the supersaturation ratio, C_v/C_{ve}. In the fixed sink regime, where defect loss at dislocations is dominant, C_v is linear in K_v. However, over time the higher rate would tend to give an increased dislocation density that would decrease the vacancy concentration. Displacement rates may be varied over several powers of ten. Dislocation number densities do not change nearly as much.

In the absence of helium ΔG^* is proportional to $[\ln(C_v/C_{ve})]^{-2}$ and any increase in C_v will result in a sharply reduced value of ΔG^* and a greatly increased homogeneous nucleation rate. Strong displacement rate effects are thus predicted.

Spontaneous void formation without an activation barrier may occur when the parameter $\Psi > 0$. Eq. (10) shows that in the ideal gas approximation Ψ is proportional to $(\ln S_e)\beta_x^o/K_x^c$. Both β_x^o and K_x^c are proportional to the displacement rate when dislocations are the primary defect sink. An increase in displacement rate is reflected in Ψ in a larger value of S_e.

The spontaneous void formation rate is governed by the time needed for an embryo to capture enough helium atoms and escape over the top of the $\dot{n}$ nodal line. The required number of helium atoms, varies as the inverse cube of $\ln S_e$, where S_e is the effective radiation altered super saturation defined earlier. The capture rate of helium β_x^o varies linearly with the displacement rate whether trapping is by dislocations or by voids. An orders of magnitude increase in displacement rate should give a corresponding increase in β_x^o. An increase in displacement rate thus favors spontaneous nucleation in several ways.

Heterogeneous nucleation may occur on vacancy-helium embryos. As usual, the primary effect of displacement rate should be in the value of ΔG^*. Fig. 5 illustrates the effect of helium content on ΔG^* for heterogeneous nucleation. The value of ΔG^* depends strongly on both vacancy supersaturation and helium content. An increased displacement rate will give a significantly reduced value for ΔG^*.

Mobile defect concentrations tend to depend strongly on the dislocation density. The overall effect of irradiation on the network dislocation density is a complex phenomenon [31] beyond the scope of this paper.

7. Conclusions

- Displacement rate affects void nucleation in several interrelated ways.
- Nucleation with an activation barrier is predicted to increase strongly with displacement rate.
- Spontaneous void formation is predicted to increase much less with displacement rate.

References

[1] C. Cawthorne, E.J. Fulton, Nature 216 (1966) 575.
[2] J.W. Corbett, L.C. Ianniello (Eds.), Radiation-Induced Voids in Metals, USAEC Symposium Series 26, Conference-710601, 1972.
[3] K.C. Russell, Acta Metall. 19 (1971) 753.
[4] J.L. Katz, H. Wiedersich, J. Chem. Phys. 55 (1971) 1414.
[5] C.-Y. Wei, M.I. Current, D.N. Seidman, Phil. Mag. A 44 (1981) 459.
[6] A.F. Calder, D.J. Bacon, J. Nucl. Mater. 207 (1993) 25.
[7] R.E. Stoller, J. Nucl. Mater. 276 (2004) 22.
[8] T.J. Diaz de la Rubia, M.W. Guinan, Mater. Sci. Forum 97&98 (1992) 23.
[9] D.J. Bacon, T.J. Diaz de la Rubia, Nucl. Mater. 216 (1994) 275.
[10] C.H. Woo, B.N. Singh, Phil. Mag. A 65 (1992) 889.
[11] B. Wirth, On the Character of Nanoscale Features in Reactor Pressure Vessel Steels Under Neutron Irradiation, PhD Thesis, University of California Santa Barbara, December, 1998.
[12] M.J. Caturla, T. Diaz de la Rubia, M. Fluss, J. Nucl. Mater. 323 (2003) 163.
[13] M.J. Caturla, N. Soneda, E. Alonso, B.D. Wirth, T. Diaz de la Rubia, J.M. Perlado, J. Nucl. Mater. 276 (2000) 13.
[14] H. Wiedersich, Radiat. Eff. 12 (1972) 111.
[15] A.D. Brailsford, R.J. Bullough, Nucl. Mater. 44 (1972) 121.
[16] W.D. Wilson, R.A. Johnson, in: P.C. Gehlen, J.R. Beeler Jr., R.I. Jafee, (Eds.), Interatomic Potentials and Simulation of Point Defects, Plenum Press, New York, 1972, p. 375.
[17] J.L. Katz, H. Wiedersich, J. Nucl. Mater. 46 (1973) 41.
[18] H. Wiedersich, J.J. Burton, J.L. Katz, J. Nucl. Mater. 51 (1974) 287.
[19] H. Wiedersich, B.O. Hall, J. Nucl. Mater. 56 (1977) 187.
[20] H. Wiedersich, J.L. Katz, Adv. Coll. Interf. Sci. 10 (1979) 33.
[21] K.C. Russell, Acta Met. 20 (1972) 899.
[22] K.C. Russell, Scr. Met. 6 (1972) 209.
[23] K.C. Russell, D.H. Hall, Defects and Defect Clusters in BCC Metals and their Alloys, in: R. Arsenault (Ed.), National Bureau of Standards, Washington, DC, 1973, p. 545.
[24] K.C. Russell, Scr. Met. 7 (1973) 755.
[25] K.C. Russell, The Physics of Irradiation Produced Voids, in: R.S. Nelson (Ed.), HMSO, London, 1975, p. 158.
[26] K.C. Russell, Acta Met. 26 (1978) 1615.
[27] C.A. Parker, K.C. Russell, Scr. Met. 15 (1981) 643.
[28] C.A. Parker, K.C. Russell, in: H.R. Brager, J.S. Perrin, American Society for Testing and Materials, Philadelphia, 1982, p. 1042.
[29] C.A. Parker, K.C. Russell, J. Nucl. Mater. 119 (1983) 82.
[30] H. Poincaré, Les Methodes de la Mecanique Celeste, vols. I–III, Gauthiers-Villars, Paris 1892–1899.
[31] T. Okita, T. Sato, N. Sekimura, T. Iwai, F.A. Garner, J. Nucl. Mater. 367–370 (2007) 930.