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Alloys under irradiation

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Abstract

During the last two decades, some effort has been devoted to establishing a phenomenology for alloys under irradiation. Theoretically, the effects of the defect supersaturation, sustained defect fluxes and ballistic mixing on solid solubility under irradiation can now be formulated in a unified manner, at least for the most simple cases: coherent phase transformations and nearest-neighbor ballistic jumps. Even under such restrictive conditions, several intriguing features documented experimentally can be rationalized, sometimes in a quantitative manner and simple qualitative rules for alloy stability as a function of irradiation conditions can be formulated. A quasi-thermodynamic formalism can be proposed for alloys under irradiation. However, this point of view has limits illustrated by recent computer simulations. © 1997 Elsevier Science B.V.

1. Introduction

The following is an extended abstract of Ref. [1], where all the works quoted here are referenced.

In the mid seventies, the Saclay group proposed that it could be fruitful to consider an alloy under irradiation as an open dissipative system, the stability of which and the kinetic paths it follows should be handled by appropriate tools, distinct from classical thermodynamics. Indeed, thermal equilibrium is characterized by the absence of fluxes (micro reversibility) and by a single source of noise, i.e., the thermal vibrations. On the contrary, irradiation produces persistent point-defect fluxes, toward defect sinks or recombination centres and introduces a new noise term, i.e., the ballistic mixing (in cascades or along replacement chains).

The former idea has since been contorted by several sets of systematic experiments and by developing a theoretical framework able to incorporate the atomistic details of irradiation effects (e.g., cascade mixing, the dynamics of point defects release from cascades, etc.). Parallel efforts (sometimes coordinated, sometimes not) have been developed at Kalpakkam (India), Kurchatov (Moscow) and HMI (Berlin). New groups now joined this point of view (e.g., Matsumura at this conference).

2. Experimental facts

The following is now well established:

– Under irradiation, alloys may develop quasi steady states (e.g., the degree of long-range order in FeAl reaches a steady value under 1 MeV HVEM irradiation).

– The steady state depends on irradiation conditions and the change of steady state on varying the latter may be smooth or abrupt, e.g., in the above experiments the steady degree of long range order decreases smoothly as the irradiation temperature is decreased; however on reaching 320 K, the latter decreases abruptly, as it would on crossing the transition temperature of a first order reaction. The transition is reversible, with hysteresis: reordering only occurs above 370 K. Another well documented example is Ni_4Mo which achieves one out of three structures (random solid solution, short-range ordered alloy or long-range ordered phase) depending on the irradiation temperature.

– The irradiation 'conditions' are defined by the irradiation temperature, the irradiation flux and details of the cascade structure (number of replacements per displacement, dense versus dilute cascade); the temperature effect has been discussed above; the flux effect is established,

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e.g., for irradiation induced precipitation in NiSi and AlZn; the cascade structure effect is established for irradiation induced precipitation in NiSi and for the type of phase to be stabilized in Ni_4Mo.

– The kinetic path for reaching the dynamical equilibrium state depends also on the irradiation conditions. This has been established by the Berlin group for γ' precipitate dissolution in a PE16 alloy: for a given irradiation flux, the precipitates first disorder and then dissolve in the lower temperature range, while they dissolve in the ordered state at higher temperature.

The references to the above works are to be found in Ref. [1].

3. Theoretical tools: Modelling techniques

Four classes of models have been developed, each of which has it's own advantages and limitations. The connection between all four classes is established either in a strict or in a more intuitive manner. All the models approximate the same underlying idea: under irradiation, the a priori possible atomistic configurations of the alloy are explored by two mechanisms acting in parallel, the thermally activated migration of point-defects on the one hand and ballistic mixing on the other hand.

The most refined description defines the occupation state of each lattice site at every time, by an operator $n_i^\alpha(t)$ which takes the value 1 at time t if site i is occupied by species α; it takes the value 0 otherwise. The change of value of the operator is deduced from the jump probability of species α out of (or towards) site i. The probability for species α to jump from site i to site j per unit time is the sum of a thermally activated and of a ballistic jump frequency:

$$\Gamma_{ij}^\alpha = n_j^v \nu \exp - \beta(E_{\text{saddle}} - E_{\text{initial}}) + \Gamma_{ij}^\alpha|_{\text{ball}},$$

where ν is an attempt frequency, E_{saddle} and E_{initial} are the energy of the configuration with α at the saddle point between sites i and j and, respectively, α on site i and the vacancy on site j, for the vacancy diffusion mechanism and $\beta = 1/k_B T$; $\Gamma_{ij}^\alpha|_{\text{ball}}$ is the ballistic contribution to $\Gamma_{ij}\alpha$. All the above parameters can be given more or less sophisticated forms: the simplest one is to take ν as a constant, to evaluate $E_{\text{saddle}} - E_{\text{initial}}$ from a broken bounds approximation, to model ballistic jumps by nearest-neighbor exchanges at a frequency proportional to the irradiation flux. $\Gamma|_{\text{ball}}$ can also be taken from cascade computer simulations.

Based on the above expression of Γ_{ij}^α, the evolution of the configuration can be modelled by the Monte-Carlo technique with the 'residence time' algorithm, in order to keep track of the physical time. We thus get a *stochastic, atomistic* modelling (Table 1): the latter incorporates the alloy thermodynamics (brought by $E_{\text{initial}} = E\{n_i\}$) and the details of the diffusion mechanism (enhanced diffusion reflected by n_j^v, Kirkendall and correlation effects brought by the configuration dependent activation barrier) and the details of the ballistic mixing. With such a model, we can study the *steady states* of the alloy as a function of irradiation conditions as well as the *kinetic path* followed when the irradiation conditions are varied (e.g., when the alloy prepared by some thermal treatment outside irradiation is suddenly exposed to irradiation). The very same model can be handled in an analytical manner, with the aid of a master equation for the probability distribution $P\{n_i^\alpha\}$ of $\{n_i^\alpha\}$. This has been achieved by Vaks et al. for the direct interstitial diffusion mechanism and a spatially-homogeneous distribution of ballistic jumps in a binary alloy. A mean-field effective free energy could be deduced, which allows the assessment of the *relative stability* of single- versus two-phase solid solutions and thus to draw a dynamical equilibrium phase diagram under irradiation.

A coarser description neglects the short time fluctuations of the value of n_i^α. This is done by studying the time evolution of the 'concentration' $C_i^\alpha(t)$ on each lattice site. This concentration can be defined strictly from the above model: $C_i^\alpha(t)$ is the first moment of the distribution of the values of the operator $n_i^\alpha(t)$: $C_i^\alpha(t) = \langle n_i^\alpha(t) \rangle$. The kinetic equation for $C_i^\alpha(t)$ has been established in the mean-field approximation ('kinetic Bragg–Williams' approximation) and in the pair approximation. Higher order approximations are under development. We thus get a fully nonlinear lattice rate model: the rate equations are *deterministic*, but are written at the *atomistic* level (noise has been erased by replacing the probability distribution by its first moment) (Table 1). Such equations (integrated numerically) are used extensively to study steady states, their local stability as

Table 1
The four classes of models depending on time and space scales

Space scale	Time scale	
	short ($\approx \Gamma^{-1}$), stochastic	large ($\gg \Gamma^{-1}$), deterministic
Atomistic	$\{n_i^\alpha(t)\} = \{\}_0^1$ Monte-Carlo $P\{n_i^\alpha(t)\}$ master equation	$C_i^\alpha(t) = \langle n_i^\alpha(t) \rangle$ fully nonlinear lattice rate model
Mesoscale	$P(C(\vec{r}, t))$ master equation for macro-variables (Kubo)	$S(t)$ homogeneous state rate equation $C(\vec{r}, t)$, $S(\vec{r}, t)$ linearized rate equations

well as kinetic paths [1]. This type of model has the limitations of the mean-field approximation: in the absence of irradiation, the equilibrium phase diagram is slightly distorted for the BCC or FCC lattice with unmixing tendency, and very artificial for the FCC structure with ordering tendency. Some of the details of the diffusion mechanism are lost.

A still coarser description consists of writing evolution equations for concentration fields $C(\vec{r}, t)$ and long-range order parameter fields $S(\vec{r}, t)$ based on the classical theory of diffusion:

$$\frac{\mathrm{d}C^{\alpha}(\vec{r}, t)}{\mathrm{d}t} = -\operatorname{div} J^{\alpha}(\vec{r}, t) + \text{production rate} - \text{annihilation rate}$$

with the flux

$$J^{\alpha}(\vec{r}, t) = -\sum_{\beta} L_{\alpha\beta} \overrightarrow{\operatorname{grad}} \frac{\delta \mathcal{F}}{\delta C_{\beta}} - D^{\alpha}_{\mathrm{ball}} \overrightarrow{\operatorname{grad}} C_{\alpha},$$

where the $L_{\alpha\beta}$ are the elements of Onsager matrix and $\mathcal{F}$ the free energy functional. This expression of the flux can be established by linearizing the lattice rate theory close to equilibrium: the diffusion coefficients are found to be composition dependent. Occasionally this dependence is omitted for the sake of simplicity (Matsumura, this conference). Such models correspond to a *mesoscale deterministic* description (Table 1). In their simplest version, they yield useful rule of thumb, such as that of the 'effective temperature': an alloy under irradiation at temperature T achieves the equilibrium configuration it would have at a temperature $T' = (1 + \Delta)T$ with $\Delta = D_{\mathrm{ball}}/D_{\mathrm{thermal}}$. This rule can be established theoretically in a few special cases, but often yields a good qualitative guide to rationalize experimental observations.

Finally, some stochasticity can be reintroduced at this scale, using a 'master equation for macro variables' as introduced by Kubo et al. Here the macro-variable is, for example, the degree of long-range order in the alloy supposed to be uniform, or the concentration field. We get a *meso-scale stochastic* description (Table 1). Such a technique turned out to be very efficient in explaining the effect of cascade size on the extension of the stability fields of the three possible structures of Ni_4Mo (random solid solution, 'SRO' or 'LRO'): the experimental study was done after the theory, independently in Berlin and Argonne, and confirmed (semiquantitatively) the theoretical prediction.

4. Assessment of the theory and modelling tools

Thus far, the main successes of the above models include:

– Prediction of the occurrence of a first-order order–disorder transition in FeAl type alloy under irradiation (the transition is second-order in the absence of irradiation). The experimental verification was done several years later.

– Explanation of the hierarchy of phases in Ni_4Mo under electron irradiation, as a function of temperature and prediction of the effect of cascade size on the latter hierarchy.

– Demonstration of the dissolution path of an ordered precipitate which depends on irradiation conditions (dissolution with or without prior disordering): the experiments were done independently.

– Reproduction of all the published kinetics of irradiation-induced surface segregation in CuNi solutions (three temperatures and two largely distinct compositions) using a single set of parameters.

Several questions are still pending:

– For certain models of ballistic mixing in the FCC structure, the atomistic stochastic model exhibits a saturation of coarsening (as shown by Haider). The higher the dose rate, the finer the steady length scale. Is such a behaviour a common feature?

– The atomistic stochastic treatment does not yet incorporate self interstitials. What unique features are to be expected?

– All the above models are restricted to coherent phase transformations: it is a challenge to address incoherent cases.

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