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EVOLUTION OF PHASE MICROSTRUCTURE
DURING IRRADIATION*

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Invited Paper for the Proceedings of the Workshop on The Relation between Mechanical Properties and Microstructure under Fusion Irradiation Conditions, June 27 to July 2, 1985, Ebeltoft, Denmark.

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Abstract

The phase microstructure of alloys is frequently severely altered during irradiation. Sluggish precipitation reactions including precipitation coarsening are accelerated by irradiation-enhanced diffusion. Radiation-induced segregation redistributes existing precipitate phases within the microstructure, induces precipitation of nonequilibrium phases and affects the composition of phases in multicomponent alloys. The displacement process causes disordering of ordered alloys and frequently amorphization, especially in intermetallic compounds, at low temperature. Although a good qualitative understanding of the basic process involved, i.e., displacement mixing, radiation-enhanced diffusion and radiation-induced segregation exists, methods for detailed quantitative modeling of the evolution of the microstructure of alloys remain to be developed.

1. INTRODUCTION

A number of the properties of alloys are significantly affected by the presence, composition and distribution of phases within the microstructure of alloys. Such properties include thermal and electric conductivity, elastic moduli, corrosion resistance and, most important, mechanical properties such as yield and tensile strength, ductility and susceptibility to stress

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corrosion cracking. Concerns about the effects of irradiation on the properties of materials existed since the construction of the earliest fission reactors. Initially, research on the underlying causes of property changes in the microstructure of alloys concentrated on the production of defects and defect clusters, the disordering of ordered phases, and on the enhancement, by the excess concentration of point defects, of thermal processes such as diffusion-controlled phase transformations and precipitate coarsening. With the discovery of the voids swelling phenomenon by Cathorn and Fulton¹ in the late sixties, microstructural investigations of irradiated alloys intensified enormously, and it became evident that radiation-enhanced diffusion and radiation-disordering were insufficient to explain many of the observed changes in the phase microstructure, such as the appearance of non-equilibrium phases, precipitate dissolution, and the redistribution of phases in association with other microstructural features, e.g., dislocations, voids and grain boundaries. Much of the original work and a number of review articles can be found in proceedings of conferences and special publications.²⁻⁸

Here we will give a short overview of changes in the phase microstructures of alloys during irradiation. More detailed, recent reviews on various aspects can be found in references 6-8. After a discussion of the basic mechanisms involved in the microstructural evolution in Section 2, effects of irradiation on the equilibration of alloy microstructures and on the redistribution of phases within the microstructure will be described in Section 3. In Section 4, radiation-induced non-equilibrium phases will be treated; this includes the formation of amorphous phases, metastable solid solutions, radiation-induced disorder, and precipitation of non-equilibrium phases of radiation-modified phase compositions. Although at present the major emphasis in fusion-related materials research is placed on the property,

and the underlying microstructural changes, occurring during irradiation at elevated temperature, disordering, amorphization and displacement mixing phenomena will be included into the discussion. These phenomena which are especially important at lower temperature are relevant in the present context because in a fusion reactor with superconducting magnets materials will be exposed to radiation over a large temperature range. Although the superconducting magnets for a Tokamak reactor are envisioned to be well shielded from high fluxes, this may not be the case for barrier coils in mirror machines.

2. BASIC ATOMIC PROCESSES

Three distinct processes lead to changes in the phase microstructure of alloys during irradiation: displacement mixing, radiation-enhanced diffusion and radiation-induced segregation. Although more than one of these processes contributes to microstructural changes under most circumstances, a clear conceptual distinction is useful because their effects on thermodynamic systems are different.

2.1. Displacement Mixing

Displacement mixing is the consequence of the strong interactions of energetic neutrons or charged particles with atoms of the solid that cause displacements of atoms. After the initially highly localized kinetic energy has dissipated into the surrounding matrix within a rather short time ($\approx 10^{-11}$ s), a considerable number of atoms are situated on different locations from those prior to the event. This process has been called cascade, ballistic, recoil or displacement mixing. Here we will adopt the term displacement mixing with the understanding that it includes all atomic

rearrangements which occur during the cascade event including atom and defect motions induced by the transient, localized high energy density, i.e., all processes that cannot be suppressed even at an ambient temperature near absolute zero.

Although displacement mixing is a general radiation effects phenomenon and had been recognized as the cause of radiation-induced disordering of ordered compounds early on, it has attracted much interest only in recent years in conjunction with compositional depth profiling by methods involving sputtering, and with surface modifications by surface alloying with ion beams. Several recent papers review the state of knowledge of ion beam mixing mostly from the experimental point of view.⁹⁻¹¹ Most of the theoretical treatments of the mixing process are based on transport theory¹²⁻¹⁴ and, hence, do include only atomic relocations occurring during the "collisional" phase of the cascade development, but not induced defect and atomic motions during the "cooling" phase.¹⁵ Peak and Averback have shown that atomic rearrangements during the cooling phase are important, and may be even dominant in certain cases, in the mixing process and have developed a thermal spike model to take into account atomic motions during the cooling phase.¹⁶

Displacement mixing can be described in a rather simple way as a diffusion problem as was pointed out by Anderson¹⁷ and Matteson et al.¹⁸ Neglecting any anisotropy, the mixing process can be considered as a random walks of atoms in three dimensions. Following standard diffusion theory,¹⁹ the diffusion coefficient D can then be expressed in terms of the jump rate Γ of atoms and the mean square jump distance $\langle r^2 \rangle$ as

$$D = (1/6) \Gamma \langle r^2 \rangle. \quad (1)$$

The jump rate of atoms for mixing at low temperature should be proportional to the displacement rate \dot{n} . The proportionality factor ϵ contains contributions of atom relocations, replacement sequences, spontaneous recombinations between defects produced within the cascade and with preexisting defects, and induced defect jumps during the cooling phase of the cascade. Thus, ϵ is expected to be appreciably larger than one; molecular dynamics calculations by King and Benedek indicate a value of ~ 35 even for primary recoil energies of < 500 eV.²⁰ The mean square displacement distance, $\langle r^2 \rangle$, of atoms during a cascade event is expected to be larger, but not very considerably, than b^2 where b is the nearest neighbor distance. This obtains because most of atom displacements occur by replacement sequences along more or less close-packed directions.²⁰ Similarly, atom motions during the cooling phase are likely to occur mostly over a distance b . The diffusion coefficient resulting from displacement mixing is written conveniently as

$$D_m = (b^2/6) \dot{n} \cdot \epsilon \alpha \quad (2)$$

where α is a factor (> 1) relating the mean square displacement distance of atoms to b , $\langle r^2 \rangle = \alpha b^2$. Low temperature experiments on ion beam mixing²¹ and on disordering^{22,23} indicate values of 10^2 to 10^3 for the factor $\epsilon \alpha$. The diffusion coefficient D_m resulting from the displacement mixing process as defined here should be nearly temperature independent as shown semi-schematically on Fig. 1.

It should be noted that the highly energetic events in displacement cascades are always expected to randomize the system, e.g., to mix fairly insoluble elements at a precipitate-matrix interface. However, less energetic events occurring during and after the collisional phase, such as

induced defect motion and, perhaps, induced recombination are subject to thermodynamic forces. These "quasi-thermal" diffusion processes in cascades are likely the cause of the observation that elements with high negative heat of mixing show significantly more interdiffusion during ion beam mixing than those with positive heat of mixing.²⁴ Averback has shown recently that essentially no intermixing occurs between Cu-Mo bilayers during heavy ion bombardment at liquid helium temperature, indicating that quasithermal motion under the strong chemical driving force in this highly insoluble system can fully counteract the ballistic mixing resulting from high energy events.²⁵

Displacement mixing is the dominant atomic transport mechanism during irradiations at low temperatures where point defects are immobile at specimen ambient temperature. As the ambient temperature is increased the defects with the lower activation energy of motion, usually interstitials and small interstitial clusters become mobile. However, their contribution to atomic transport is fairly limited up to temperatures at which both vacancy and interstitial type defects are thermally mobile. This obtains from the increase of the density of the immobile defects with increasing dose which limits the diffusion distance of the mobile species severely. Spontaneous recombination and induced migration processes become more important to atomic transport than the limited thermal migration of the fast defects at doses above ≈ 0.1 dpa, when the density of thermally immobile defects approaches saturation. This is born out by mixing experiments which show little or no temperature dependence at temperatures below that required for mobility of the slow defects.²¹

2.2 Radiation-Enhanced Diffusion

Radiation-enhanced diffusion has been reviewed in detail by Sizmann²⁶ and by Rothman.²⁷ Atomic transport in alloys is predominantly caused by the motion of point defects, vacancies and interstitials. Here we will define the expression "radiation-enhanced diffusion" as diffusion of alloying elements occurring by random motions of point defects present in considerable excess of their thermal equilibrium concentrations as a consequence of the radiation. In contrast, "radiation-induced segregation" is defined as the preferential transport of alloying elements by persistent defect fluxes set up during high temperature irradiations. Although both phenomena occur almost always simultaneously in a material, a clear distinction is useful because radiation-enhanced diffusion tends to bring the system always toward a thermodynamically preferred state whereas radiation-induced segregation can drive the system away from it by, e.g., building up concentration gradients in an initially homogeneous solid solution.

Thermal diffusion in metals occurs predominantly by the exchange between atoms and vacancies. In this case, the diffusion coefficient can be written from eq. (1) as

$$D^v = (b^2/6) Z_v P_v \nu_v \quad (3)$$

by realizing that $\langle r^2 \rangle = b^2$ and the jump frequency, Γ , of an atom equals the product of the probability, $Z_v P_v$, that one of the Z_v nearest neighbor sites is occupied by a vacancy with the probability P_v , and the exchange frequency, ν_v , of an atom with a neighboring vacancy. Neglecting effects of binding energies between vacancies and specific alloying elements, P_v equals the atomic fraction of vacancies, C_v . Under thermal equilibrium condition, C_v is

proportional to a Boltzmann factor containing the enthalpy of formation of vacancies. The corresponding diffusion coefficient, eq. (3), is shown by the dashed line in Fig. 1. During irradiation, C_v is increased above that at thermal equilibrium by an amount determined by the balance between the rate of formation of vacancies by displacements and losses due to recombination with interstitials and to vacancy sinks.

Diffusion is also enhanced by the presence of mobile excess interstitial defects during irradiation. Motions of interstitials move atoms in similar ways as vacancies, and the diffusion coefficient of atoms moved by interstitials, D^i , can be written in an analogous fashion as D^v in eq. (3). Neglecting potential differences in coordination numbers and jump distances for interstitials and vacancies and contributions from mobile clusters, the radiation-enhanced diffusion coefficient due to the thermal motion of defects is then given by

$$D_{\text{rad}} = D^v = D^i = (b^2/6)Z [C_v v_v + C_i v_i] \quad (4)$$

The defect concentrations in eq. (4) can be estimated from rate theory.^{28,29}

As an example, Fig. 1 shows semi-schematically the diffusion coefficient in a nickel based alloy as a function of the inverse temperature during irradiation at a displacement rate of 10^{-6} dpa/s as the solid line. The contributions from displacement mixing, eq. (2), dash-dotted line, radiation-enhanced diffusion, eq. (4), dotted line, and from thermal diffusion, eq. (4) with thermal defect concentrations, dashed line, are indicated. It is apparent that radiation-enhanced diffusion is dominant in the intermediate temperature regime where vacancy mobility is high but thermal diffusion is low because of the low thermal vacancy concentration. At low temperature, the

contribution to diffusion by thermal motion falls below that by athermal displacement mixing primarily because the high steady state concentration of the slow defects severely limits the number of thermal jumps a defect makes between its creation and annihilation. In the case of low sink density, the defect concentration is limited in the radiation-enhanced regime by the thermal recombination between vacancies and interstitials and it can be easily shown²⁸ that the radiation-enhanced diffusion coefficient, D_{rad} , is proportional to $v_v^{1/2}$. Therefore, the slope of the line in the Arrhenius plot corresponds to one-half of the activation energy for motion for vacancies (the slower moving species). At high sink density, e.g., $p = 10^{-3}$, the lifetime of excess defects is reduced and, therefore, the diffusion coefficient is diminished relative to that for the recombination limited case. When sink annihilation is dominant, D_{rad} becomes temperature independent reflecting the fact that the average number of jumps a defect makes is then determined by the sink density independent of temperature.

2.3 Radiation-induced Segregation

The phenomenon of radiation-induced segregation has been reviewed recently by several authors.³⁰⁻³² Early model descriptions for dilute solid solutions were based on tightly bound solute-defect complexes.³³ A generalized formalism for treating radiation-induced segregation in multi-component alloys has been developed by Chen.³⁴

Excess point defects produced by irradiation migrate thermally over significant distances at elevated temperatures before being eliminated by recombination or by annihilation at sinks such as grain boundaries and dislocations. The spatial separation between defect production and annihilation leads to persistent defect fluxes, e.g., between grain interior and grain

boundaries. Motion of defects requires motion of atoms, i.e., a vacancy exchanges with an atom, or interstitialcy motion forces a substitutional atom into an interstice while returning another atom to a substitutional site. In alloys, defects migrate frequently preferentially via atoms of some of the alloying elements. This, in turn, couples fluxes of alloying elements to defect fluxes. The combination of persistent defect fluxes and preferential coupling of some of the alloy components to defect fluxes leads to a non-uniform distribution of the elements within the microstructure of an initially uniform alloy phase. This phenomenon of radiation-induced segregation is rather common.^{7,32} In contrast to radiation-enhanced diffusion, which accelerates the approach to a thermodynamic equilibrium distribution of elements, radiation-induced segregation leads to concentration gradients and, frequently, to non-equilibrium precipitates.

A simple description of the phenomenon can be formulated as follows.³¹ A flux of atoms equal in magnitude and direction is associated with the interstitial flux, $\underline{J}_a^i = \underline{J}_i$. Similarly, a flux of atoms induced by the vacancy flux is equal in magnitude but opposite in direction to that of the vacancies, $\underline{J}_a^v = -\underline{J}_v$. Each of the atom fluxes can be subdivided into fluxes of the alloying elements identified by subscripts k

$$\underline{J}_a^i = \sum \underline{J}_k^i = \sum \alpha_k^i \underline{J}_i = \underline{J}_i \sum \alpha_k^i$$

and

(5)

$$\underline{J}_a^v = \sum \underline{J}_k^v = \sum \alpha_k^v \underline{J}_v = \underline{J}_v \sum \alpha_k^v$$

where α_k^i and α_k^v are coupling constants between element k and the interstitial

and the vacancy fluxes, respectively, with the property $\sum \alpha_k^i = 1$ and $\sum \alpha_k^v = -1$. Note that the α_k^v 's are negative unless the element migrates as tightly bound pairs with the vacancies. A net flux of the element k is induced unless $\underline{J}_k^v = -\underline{J}_k^i$, i.e., unless the vacancy induced flux of the component is exactly balanced by the interstitial-induced flux. At steady state with respect to defects, the flux of vacancies to sinks equals that of interstitials, because both defects are created in equal numbers and recombination eliminates defects in equal numbers. This assures that the net rate of atoms arriving at sinks approaches quickly zero, neglecting for the moment effects of bias factors. In this approximation, local compositional changes will continue to occur unless the coupling constants of each element to vacancies and interstitials are equal in magnitude and opposite in sign, $\alpha_k^v = -\alpha_k^i$. As concentration gradients of the alloying elements are built up in the vicinity of sinks, fluxes of alloying elements driven by these induced concentration gradients counteract the defect driven fluxes, ultimately leading to a steady state composition distribution within the microstructure which frequently includes radiation-induced or compositionally modified phases.³⁵

The preferential precipitation of interstitials on dislocations and of vacancies on voids leads to swelling of alloys under irradiation. Therefore, an imbalance between the interstitial and the vacancy fluxes to particular types of sinks does exist during irradiation even when a quasi-steady state with regard to defect fluxes has been established. The imbalance will perturb segregation to different types of sinks to some degree. Although some observations of preferential association of precipitates with dislocation loops rather than with other defect sinks³⁶ could be interpreted as a consequence of the imbalance of the defect fluxes, the phenomenon does not appear to be prevalent. No systematic investigation of the effects of the

imbalances of interstitial and vacancy fluxes on segregation to different type of defect sinks has been reported.

Radiation-induced segregation is most prevalent at intermediate temperatures where sink annihilation of defects is important. At lower temperatures, the high density of defects and defect clusters suppresses long range migration of defects and, hence, segregation over significant distances. At high temperatures, high thermal diffusivities prevent the build-up of significant local concentration differences.

3. EVOLUTION OF THERMALLY STABLE MICROSTRUCTURES DURING IRRADIATION

Radiation-enhanced or thermal diffusion has to be a dominant kinetic process if an alloy is to approach and/or maintain a state close to thermodynamic equilibrium despite the randomizing effects of energetic displacement events, or the dehomogenizing consequences of radiation-induced segregation. Thus, the temperature regime of interest here is above that of dominant displacement mixing, see Fig. 1, where the slow moving defects are sufficiently mobile to assure many thermally activated jumps between the creation and annihilation of a defect. Here we will discuss the effects of radiation-enhanced diffusion on ordering reactions, phase decomposition and particle coarsening before we address phase redistribution by radiation-induced segregation under near equilibrium conditions.

3.1. Radiation-enhanced Equilibration

Effects of irradiation on ordering reactions of alloys have been recognized more than thirty years ago.³⁷ Enhancements of long range order has since been observed in many alloys during irradiation at temperatures at which vacancies are mobile, provided the state of order, S , was significantly lower

than that in thermodynamic equilibrium.³⁸⁻⁴⁰ For example Kirk and Blewitt found that the order parameter of Cu_3Au specimens increased from $S = 0.84$ to 0.95 during irradiation with thermal neutrons to a dose of 6×10^{-5} dpa at 135°C .²² Ardell and Janghorban concluded that the ordered phase Pd_8W , which forms in Pd rich Pd-W alloys during proton irradiations at temperatures between 300 and 600°C , is the result of a vastly accelerated ordering reaction of an equilibrium phase that has not been observed after thermal aging.³⁹

The displacement process always counteracts the enhanced ordering process during irradiation. Zee and Wilkes⁴¹ and Banerjee and Urban⁴² have developed detailed models to describe the kinetics of the order-disorder transformation. One important result of these models is that the steady state order under irradiation is close to the thermodynamic equilibrium at high temperatures; the degree of steady state order drops to zero at lower temperatures over a rather narrow temperature range; and the transition temperature between the ordered and the disordered steady state shifts by small amounts towards higher temperature with increased displacement rate.⁴² Experimental results on Ni_4Mo agree well with model calculations. The model predictions are also in agreement with other experimental observations, e.g., intermetallic compound phases remain highly ordered during irradiation at temperatures where vacancies are mobile.

Generally, the existence and the composition of equilibrium phases in alloys depends on temperature. Thus, mass transport by diffusion is usually required to reestablish the phase equilibrium after a temperature change. Moreover, frequently a barrier to nucleation exists as a consequence of the interfacial and strain energy associated with the formation of a new precipitate within the parent phase. The reequilibration of the composition of phases, the nucleation of a new phase and the coarsening of precipitates

are expected to be accelerated by radiation-enhanced diffusion. In the absence of radiation-induced segregation and other complicating factors, all three processes should proceed during irradiation at a rate that is higher by a factor $D_{\text{rad}}/D_{\text{th}}$ than that without irradiation, where D_{rad} is the radiation-enhanced, see eq. (4), and D_{th} is the thermal diffusion coefficient. This is rather obvious for reequilibration and coarsening, but can also be shown for nucleation.⁸ All are processes driven by thermodynamic driving forces but rate-limited by diffusion. Hence, we can expect strong enhancement of these processes over the intermediate temperature regime, see Fig. 1, where D_{rad} is the dominant contribution to the diffusion coefficient. At low temperature, the randomization due to high energy collisions frequently drives the system counter to the thermodynamic forces in the absence of sufficient thermal defect motion, and the microstructure will generally move away from the thermodynamically more stable state during irradiation at temperatures at which displacement mixing is dominant.

Quantitative information on radiation-enhanced nucleation rates is not available. However, greatly enhanced precipitation has been observed in many systems during irradiation. For example, Coleman et al.⁴³ observed β -Nb precipitates in a Zr-2.5 wt.% Nb alloy after neutron irradiation to ≈ 0.7 dpa at 570, 670 and 770 K whereas long-term thermal annealing at the same temperatures did not produce β -Nb precipitates. However, precipitates nucleated during irradiation grow during thermal anneals at 770 K.

In many cases it is difficult to distinguish whether simple enhancement of diffusion or a combination of enhanced diffusion and radiation-induced segregation is responsible for accelerated nucleation during irradiation. The latter is likely to be the case in dilute Cu-Be alloys: Greatly enhanced precipitation was found during electron irradiation in a supersaturated

Cu-0.91 wt.% Be alloy, but profuse homogeneous nucleation of precipitates in an undersaturated Cu-0.18 wt.% Be alloy occurred as well.⁴⁴

Thermal equilibration of phases in austenitic steels is generally very slow below about 600°C. A considerable amount of work on the phase microstructure of these steels after thermal aging and after irradiation has been done in recent years. For example, Lee and coworkers have identified a considerable number of precipitate phases in irradiated 316 and Ti-modified 316 steel.³⁵ They distinguish three types of phases: (a) radiation-induced phases, γ' and G, which are thermally unstable at the alloy compositions; (b) radiation-enhanced phases, e.g., η and MC, which precipitate appreciably faster and at significantly lower temperatures during irradiation than without; and (c) radiation enhanced and compositionally modified phases, such as a Laves phase that contains significantly more Ni and less Mo when precipitated during irradiation than during thermal aging. Although radiation-enhanced diffusion plays a role in the precipitation kinetics of all three types of phases, radiation-induced segregation is a vital process in the type (a) and (c) phases whereas the kinetics of precipitation of type (b) phases should be majorly affected by radiation-enhanced diffusion only. Lee et al. found that the type (b) phases form to much lower temperatures during neutron irradiations than during thermal aging despite the fact that the times for thermal aging were significantly longer than those during irradiations.³⁵ Thus, nucleation and/or growth rates of, e.g., the η and MC phases are greatly increased by radiation-enhanced diffusion.

Brager and Garner have observed a radiation-enhanced decomposition in austenitic alloys after neutron irradiation.⁴⁵ For example, a Fe-35.5% Ni-7.5% Cr alloy showed after neutron irradiation at 593°C oscillations in Ni concentration from 25 to 53% about the nominal level of 35.5%. The decomposi-

tion occurs in a spinoidal-like fashion with a period of ~200nm. The decomposition is believed to be thermodynamically favored and vastly accelerated by irradiation. It accounts for the observed increase in density during irradiation.⁴⁵

Ostwald ripening or precipitate coarsening during aging of precipitation hardened alloys is a well-known phenomenon. The coarsening is driven by the precipitate-matrix interfacial energy and its kinetics is limited by the diffusion of the precipitating element from smaller to larger particles, thus, radiation-enhanced diffusion should greatly enhance the coarsening kinetics. This has been shown to be the case, e.g., for Ni-Ni₃Al and Ni-Ni₃Si two-phase alloys by Potter and coworkers.^{46,47} The results are in good qualitative agreement with theory, however, phase redistribution driven by radiation-induced segregation occurs in either of these alloys limiting quantitative comparison of theory and experiment at higher doses.⁴⁶

It should be pointed out that particle coarsening kinetics may also be affected by radiation-induced segregation if the precipitates act as defect recombination centers or as sinks. The coarsening kinetics will be accelerated beyond that by radiation-enhanced diffusion if the precipitating element is moving in the same direction as the defect flux. Urban and Martin have developed a theory of coarsening that includes the effects of radiation-induced segregation.⁴⁸

3.2 Radiation-induced Phase Redistribution

Radiation-induced segregation leads frequently to a spatial redistribution of precipitates in multiphase alloys with regards to defect sinks within the microstructure on a scale much larger than that of interparticle spacings. Evidence for such redistributions has been frequently observed,

e.g., precipitate association with dislocations, grain boundaries, voids and free surfaces, but only few systematic studies have been reported. The most extensive studies have been carried out by Potter and coworkers on two-phase Ni-Al and Ni-Si alloys with coherent γ' precipitates (Ni_3Al or Ni_3Si).^{46,47,49-51} The alloys contained in the initial state a uniform distribution of small coherent cuboidal (Ni_3Al) or spherical (Ni_3Si) precipitates throughout the f.c.c. solid solution matrix. In these alloys, the undersized Si segregates during irradiation in the same direction as the defect fluxes whereas the oversized Al segregates in the opposite direction. Thus, the alloys become enriched in the Si solute and the Ni solvent, respectively, in the neighborhood of defect sinks during irradiation. As a consequence, the phase redistribution occurs quite differently in these two alloys.

In the Ni-12.8 at.% alloy, small γ' precipitates are observed uniformly throughout the solid solution matrix after low doses except no precipitates are found in the immediate vicinity of radiation-induced interstitial dislocation loops and other defect sinks.⁴⁶ As the dislocation loops grow with increasing dose, the precipitate-free zones enclosing the loops grow correspondingly by dissolution of the precipitates because of radiation-induced segregation of nickel into these regions. Corresponding precipitate-free zones are established at other defect sinks such as grain boundaries and preexisting dislocations. The precipitates in the sink-free regions between precipitate-free zones grow in size at a radiation-enhanced rate. At higher doses, γ' precipitates renucleate in colonies within precipitate-free zones associated with growing interstitial loops, presumably because the Al concentration increases again in regions sufficiently removed from the current dislocation loop perimeter. A consequence of the reprecipitation process is a

decrease of the average precipitate size during prolonged irradiation after the initial increase.

Radiation-induced segregation in two-phase Ni-Al alloys moves the composition in proximity of defect sinks toward the single phase, γ -solid-solution field. In contrast, segregation in the two-phase Ni-Si alloys moves the composition in the near sink regions toward the single phase Ni_3Si field. Therefore, one expects phase redistribution in two-phase Ni-Si alloys to proceed in a different manner than in Ni-Al. According to the work of Potter and coworkers, the phase microstructure in Ni-12.7 at.% alloys develops during irradiation at elevated temperature as follows.^{47,51,52} At low doses, the microstructure of the initially solution-quenched alloy contains small γ' precipitates, similar to those expected during short term thermal aging, and of small γ' -decorated interstitial loops. With increasing dose, disk-like γ' -precipitates grow in thickness and diameter with the growing dislocation loops, consuming nearly all the γ' in the matrix. At the same time, continuous Ni_3Si films grow at grain boundaries and surfaces at the expense of the precipitates in the interior of grains.

Work on phase redistribution in more complex alloys is much less comprehensive. However, the trends appear to be consistent with those observed in the simple alloys discussed above. Examples of γ' redistribution in PE16 during neutron irradiation can be found in the work Gelles⁵³ and in a series of γ -strengthened alloys in the work by Chang and Baron.⁵⁴ Redistribution of MC carbides in a cold-worked, Ti-modified type 316 steel has been reported by Rowcliffe and Lee.⁵⁵ Often the situation is fairly complex in the austenitic steels because of the simultaneous presence of several stable, metastable and radiation-induced or -modified phases.

4. RADIATION-INDUCED NONEQUILIBRIUM PHASES

Radiation can induce nonequilibrium phases in two basically different manners. (a) The crystal structure or atomic arrangement can be modified by the displacement process without necessarily being changed in composition. This occurs frequently in semiconducting but rarely in pure metallic elements. The only well documented cases in pure metals are the fcc to hcp transformation in Ni^{55a} and the crystalline to amorphous transition of Ga.⁵⁶ However, metallic alloys and intermetallic compounds are frequently amorphized or disordered by irradiation at low temperatures. Follsteadt has given a recent review of metastable phase formation in ion-irradiated metals.⁵⁷ The review article of Schulson includes also the less extensive work on disordering and amorphization during neutron irradiation.³⁸ Supersaturated solutions similar to those produced by disordering of, e.g., Ni₃Si, can also be obtained by ion implantation⁵⁸ or by displacement mixing⁵⁹ at temperatures sufficiently low to prevent phase decomposition by precipitation. In the latter cases the composition is changed; however, the displacement process is essential to produce the nonequilibrium phase. (b) The second class of radiation-induced nonequilibrium phases is caused by local, persistent changes in composition produced by radiation-induced segregation.

4.1 Displacement-induced Phases

A significant number of metal-metal and metal-metalloid alloys can be rendered amorphous during irradiation at sufficiently low temperatures. Brimhall and coworkers have studied a large number of intermetallic compounds ion-irradiated at room temperature.^{60,61} They found that the intermetallic compounds NiTi, NiTi₂, NiAl₃, FeTi, Fe₂Ti, Re₃Ta and MoNi became amorphous at doses < 1 dpa. Other compounds, Ni₃Ti, NiAl, Ni₃Al, FeAl and FeV, remained

crystalline after doses of 10 dpa and higher. Note, that in the binary systems Ni-Ti and Ni-Al some phases can be rendered amorphous whereas others remain crystalline. In fact, Potter et al. have shown that high-dose implantation of Al into Ni can produce and maintain a two phase structure of partially ordered NiAl and an amorphous phase over a wide composition range.⁶²

At present no general theory exists to predict which alloys can be expected to become amorphous during low temperature irradiation. However, a number of empirical rules have been suggested and were discussed by Follsteadt.⁵⁷ These include the "structural difference rule" which suggests that an amorphous phase should form at some compositions of binary systems whose end members have different crystal structures; metal-metal and metal-semiconductor systems with large negative heats of compound formation tend to form amorphous phases; and metalloid-metal alloys with an atomic radius ratio larger than 0.59 are prone to amorphization at sufficiently high metalloid concentrations.

Whereas at temperatures with sufficient defect mobility ordering reactions are accelerated by irradiation as discussed in Section 3.1, disordering by displacement processes becomes dominant at lower temperatures in many alloys. The formation of disordered crystalline phases from ordered compounds has been theoretically discussed, e.g., by Zee and Wilkes⁴¹ and by Banerjee and Urban.⁴²

Experimental results are in good agreement with theory in simple cases. For example, the longer-range order in Ni₄Mo is maintained essentially at the equilibrium order parameter above about 520 K during irradiation at 5×10^{-3} dpa/s.^{40,42} Below that temperature, the steady state long-range order decreases rapidly with decreasing irradiation temperature becoming essentially

zero below 450 K. The decrease in order at low temperature proceeds exponential with dose.

Whereas in many cases the radiation-induced phase assumes the simple crystal structure upon which the ordered structure is based, e.g., fcc for the $L1_2$ structure of Ni_3Si and Ni_3Al ,⁶³ this may not be the case with more complex structures. The complex σ -phase of FeV transforms during irradiation to the rather simple, partially ordered B_1 (CsCl) structure.⁶⁰ Also, in the Ni_4Mo system a short range order state is stabilized during irradiation under certain conditions.⁴⁰

4.2 Radiation-induced Precipitation

Radiation-induced segregation frequently leads to the formation of precipitates in solid solution alloys because of local changes in composition. This has been observed in many alloys. The subject has been reviewed, e.g., by Martin et al.,⁶⁴ Ardell and Janghorban,³⁹ Russell⁷ and Wiedersich.⁸

The phenomenon has been studied most extensively in dilute Ni-Si alloys and we will describe briefly the main characteristics of the phenomenon in these alloys.⁸ Radiation-induced precipitation in Ni-Si solid solutions has been found after electron, ion and neutron irradiation. It occurs over a wide dose rate range from $<10^{-8}$ to $>10^{-3}$ dpa/s and after rather low incubation doses ($<10^{-3}$ dpa for low dose rates). Radiation-induced precipitation occurs in these alloys profusely on all types of defect sinks, e.g., dislocation loops, grain boundaries and surfaces. Homogeneous precipitation of coherent γ' particles has been observed in Ni alloys with 6-8 at.% Si after proton irradiations in "mid-range" as a consequence of the significant net influx of Si from the peak damage region.³⁹ This precipitation is caused by an increase in

the local Si concentration above the solubility limit because of spatially non-uniform defect production in contrast to radiation-induced homogeneous precipitation resulting from enhanced recombination at solute clusters to be discussed below.

Radiation-induced precipitation occurs generally only over part of the temperature range where the thermal migration of excess defects dominate the diffusion coefficient, see Fig. 1. In Ni-Si alloys it has been observed from $\approx 250^\circ$ to $\approx 650^\circ\text{C}$.³⁹ The upper limit is determined by the increasingly faster back diffusion which reduces the defect-flux-induced excess solute concentration to below the solubility limit. Toward lower temperature, increased defect recombination, higher radiation-induced sink densities and the increased importance of displacement mixing reduce the range over which significant persistent defect fluxes are maintained and, therefore, limit the local changes in concentrations which result from segregation. The upper temperature limit for radiation-induced precipitation increases with increasing dose rate as one expects from the simple concept that higher radiation-induced solute fluxes to sinks can prevent resolution of precipitates by back diffusion to higher temperatures. Similarly, one would expect the lower temperature limit to move higher with increasing dose rate because of a higher fraction of defects is lost by recombination, and because the radiation-induced sink density is likely to be higher for higher dose rates.

In addition to radiation-induced precipitation on defect sinks, a number of solid solution alloys show homogeneous, radiation-induced precipitation, i.e., second phase particles appear in the matrix without association with discernable defect sinks. Homogeneous precipitation has been reported, e.g., for Al-Zn,⁶⁵ Cu-Be⁴⁴ and W-Re⁶⁶ alloys. Martin and coworkers have developed a

theory for homogeneous radiation-induced precipitation.⁶⁴ The basic concept is as follows. Solute clusters resulting from concentration fluctuations act as defect traps; as a consequence, defect recombination is locally enhanced and a net influx of defects to the cluster results. If solute atoms are preferentially coupled to the defect flux, the cluster grows, a precipitate results and is stabilized by irradiation, provided the precipitate interface continues to act as a recombination center or defect sink.

Radiation-induced precipitation has been reported frequently for multicomponent alloys. Because of the limited knowledge of long term thermal stability of complex alloys, e.g., austenitic stainless steels, it is often difficult to assess whether a phase observed after irradiation is in fact a radiation-induced, nonequilibrium phase or a thermally stable phase formed at an accelerated rate because of radiation-enhanced diffusion. Examples of radiation-induced phases resulting from segregation in 316 stainless steel are the γ' - and G-phase;^{35,55} in hcp titanium based alloys profuse precipitation of the bcc β phase has been reported.^{67,68}

4.3. Radiation-modified Phase Compositions

At thermal equilibrium, the compositions on both sides of the interface between the matrix and a second phase precipitate are uniquely defined. Assuming reasonably fast local equilibration across interphase boundaries during irradiation at elevated temperatures, the interphase boundaries will adjust in such a way that adjacent matrix and precipitate compositions correspond to those of the equilibrium phase diagram. Thus, excess solute carried by defect fluxes from the matrix to a precipitate interface is accommodated by the growth of the precipitate at a composition determined by the phase diagram. In binary alloys, this composition is a function of the

temperature alone and, to the degree that the composition within the precipitate can be considered as spatially uniform, the precipitates are the equilibrium phase. In multicomponent alloys, the compositions of second phase precipitates can be altered significantly by radiation-induced segregation from those present in the alloy at thermal equilibrium. For example, the concentrations of Ni and Si are significantly increased and that of Cr and Mo decreased at defect sinks by radiation-induced segregation in austenitic matrices.⁶⁹ Thus, if persistent defect fluxes to precipitate-matrix interfaces are maintained, the precipitates should become enriched in Ni and Si and depleted of Cr and Mo according to the local matrix composition. Such compositional changes of the Laves phase in 316 steel have been observed with respect to Ni, Si and Mo by Lee et al. after neutron irradiation.³⁵ However, the Cr content of the precipitates remained similar to that of the precipitates after thermal aging. This may be coincidental because the effects of changes in the concentrations of the other components on the chromium activity in the precipitates could compensate for an increased Cr concentration in the adjacent matrix.

The importance of defect sinks associated with second phase precipitates on compositional changes resulting from radiation-induced segregation has been demonstrated by Zaluzec in a Ni-6 at.% Al-6 at.% Si alloy.⁷⁰ In the thermally aged alloy the $\text{Ni}_3(\text{Si}, \text{Al})$ precipitates contain nearly equal concentrations of Si and Al. After irradiation, the precipitates associated with dislocation loops or grain boundaries have a Si/Al ratio of ~2.5 whereas the coherent precipitates in the matrix show only a small or no increase in the Si/Al ratio.

Composition changes of preexisting precipitates by radiation-induced segregation also may trigger phase changes of the precipitates producing

"radiation-induced phases," or the resulting changes of the matrix composition can lead to a phase change of the matrix. For example, the partial transformation of austenitic steels to ferrite or martensite after neutron irradiation is likely a consequence of the Ni depletion of the matrix.⁷¹

It is evident that radiation-induced segregation can affect the phase structure in more complex ways in multicomponent alloys than binary, two-phase alloys, where to a good approximation the only effects are the redistribution of the precipitated phase and a change in its volume fraction arising from the nonuniform changes in matrix composition. In multicomponent alloys, the compositions of the second phases are affected in addition by differences in segregation strengths of the elements in the matrix, by competition between diverse interphase boundaries and defect sinks in maintaining defect fluxes, and by the interrelations between the chemical potentials of the components. Some of these complexities are reflected, e.g., in the simultaneous presence of the structurally similar, but compositionally different, G-phase and $M_{23}C_6$ precipitates in neutron irradiated austenitic alloys;^{35,55} or in the wide variations of compositions of extracted precipitates of the same phase which is presumably a consequence of differences in the defect-flux competition in the specific environments for individual precipitates.³⁵

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Figure Caption

1. Diffusion coefficient as a function of inverse temperature for a nickel based alloy during irradiation at a displacement rate of 10^{-6} dpa. The radiation-enhanced diffusion coefficient, D_{rad} , is calculated from rate theory for different sink annihilation probabilities, p . p^{-1} is the average number of jumps of a defect between creation and annihilation at a sink. The diffusion coefficient resulting from displacement mixing, D_{m} , is calculated from eq. (2), see section 2.1; D_{th} is the thermal diffusion coefficient.

