

Radiation-induced structural changes in alloys

K KRISHAN and C V SUNDARAM

Reactor Research Centre, Kalpakkam 603 102, India

Abstract. Development of alloys for reliable performance in extreme radiation environments is vital for the viability of advanced nuclear reactor systems. Over the past decade, there has been a considerable growth in our understanding of the basic processes of radiation damage, the nature of the induced defects, their interaction and migration, and the influence of these on the mechanical behaviour of metals. This understanding has however come mainly from studies in pure metals and dilute alloys, and there are difficulties when applying these concepts to concentrated alloys, particularly of technological interest. The present article, which attempts to bridge this gap, discusses recent research developments and some of the emerging new concepts as applicable to alloy systems. Interstitialcy transport; percolation effects in defect migration; short range and long range ordering and restructuring of alloys; defects and damage behaviour of metallic glasses; synergetic processes and phase instabilities; and finally, swelling, irradiation creep and ductility behaviour of alloy systems are the topics discussed.

Keywords. Alloy systems; interstitialcy transport; percolation effects; defect migration; short range ordering; long range ordering; metallic glasses; swelling; irradiation creep; ductility.

PACS No. 61-80

1. Introduction

Growth of commercial nuclear reactors and development of advanced reactor systems have led to a demand for new alloys which can reliably be used in radiation environments. Considerable advance has been made in our understanding of radiation effects in materials over the past decade for safe and economic operation of nuclear reactors. For the pressurized heavy water reactors (PHWRs) for example, extensive investigations have been necessary to understand the in-reactor behaviour of zirconium alloys, and to improve the performance of zirconium alloy fuel tube and pressure tubes through appropriate control of texture and microstructure during tube fabrication (Sinha and Kakodkar 1983). In the case of fast breeder reactors (FBRs), radiation damage effects in structural components are orders of magnitude more severe because of the increased damage rates due to fast neutrons and embrittlement problems associated with the production of helium by (n, α) reactions. With the alloy development and evaluation efforts over the last decade (see the reviews by Rodriguez *et al* 1984; Sundaram 1984) alloys like modified stainless steels, ferritic steels and nimonic alloys have emerged showing reduced swelling, irradiation creep and helium embrittlement behaviour. In more advanced reactor concepts like fusion systems, the damage to the first wall by direct impingement of light and heavy ions can erode the surface besides affecting the mechanical properties (Gruen 1979). Here, along with the development of new alloys (*e.g.* V-15% Cr-5% Ti) new technologies, such as rapid solidification (to produce metallic glasses), formation of surface coatings (*e.g.* TiC), have also been investigated to ascertain their superior radiation damage resistance.

In all these developments significant contributions have come from the more basic aspects of radiation damage research. There has been a tremendous growth in our understanding about the mechanism of damage and the behaviour of vacancies; self-interstitials; their configurations and clustering kinetics; precipitation; diffusion of gases like helium; and the effect of stress and temperature on these defects (see the review of Ullmaier and Schilling 1980). This has emerged mainly from studies in pure metals, often on single crystals and by investigating simple defect structures. To some extent all this can be extended to dilute alloys but there are serious difficulties while applying these principles to concentrated alloys. Here, even the basic building blocks like vacancies and self-interstitials become diffuse and their structure and properties are not understood. Even well-established facts in pure metals like the high mobility of self-interstitials cannot be assumed since there is gradually emerging evidence that in some alloys they may be slower than vacancies and become mobile only at higher temperature. Emphasis now in basic research is shifting to radiation damage problems in concentrated alloys. This shift is encouraging since it brings basic research into contact with materials of technological importance which have so far mainly remained in the realm of metallurgical research.

Basic research efforts at understanding the radiation behaviour of alloy systems are still in the early stages. This article discusses some of the new concepts which are emerging in this field and the differences from pure metals are highlighted. In § 2 the damage mechanisms are discussed together with defects and their mobility in alloys. Section 3 deals with the secondary effects of damage; segregation and dissolution, order-disorder and damage effects in metallic glasses. The highly non-equilibrium nature of the processes involved introduces interesting possibilities of synergetic effects which could manifest as phase instabilities. These are briefly discussed in § 4. Finally, § 5 relates these structural changes in alloys with their metallurgical properties and behaviour. Accelerators are increasingly being used for such investigations and some of the recent results are presented.

2. Displacement damage and defects in alloys

The process of atomic displacements and the production of the initial damage structure can be discussed under three headings (i) primary and secondary atomic displacements, (ii) defects and their mobility and (iii) mixing effects and structural changes.

2.1 Displacement process

2.1a Primary displacements: The early stages of damage in alloys are essentially similar to those in pure metals. They involve the creation of the primary-knock on-atoms (PKAs) by the incident irradiation and secondary damage as Frenkel pairs and cascades produced in turn by the PKAs. For an incident monoenergetic radiation (neutrons/ions/electrons) with energy E , the PKAs acquire a spectrum of energies due to recoils of energy T . This energy spectrum is governed by the nuclear scattering and involves the nuclear differential cross-section $d\sigma_p(E, T)$ which depends on the masses and nuclear charges ($M_I, Z_I e$) and ($M_p, Z_p e$) of the incident (I) and target atom ($P = A, B, \dots$, for alloy atoms) respectively. In non-relativistic situations the maximum recoil energy transferred is $T_{\max}, T_{\max, p} = 4M_I M_p E / (M_I + M_p)^2$. For neutrons

due to hard sphere collision of radius R , $d\sigma_p(E, T) = R^2 dT/T_{\max, p}$ which is independent of T . In the case of charged particles, Rutherford scattering predominates and

$$d\sigma_p(E, T) = \pi Z_1^2 Z_p^2 e^4 M_1 dT / M_p E T^2. \quad (1)$$

In this case there is a strong dependence of $d\sigma_p(E, T)$ on T showing that most of the energy loss occurs with small recoil energies at approximately right angles to the incident particle direction.

Consider a binary alloy having elements with well separated masses M_A, M_B (and charges Z_A, Z_B). The strong dependence on these variables of $d\sigma_p(E, T)$ and $T_{\max, p}$ results in two well-defined PKA spectrums. In an alloy of NiAl for instance, $d\sigma_{\text{Ni}}/d\sigma_{\text{Al}} \sim 2$ at all recoil energies and $T_{\max, \text{Ni}}/T_{\max, \text{Al}} \sim 0.5$ as seen from figure 1a. An interesting situation arises in the case of irradiation by energetic electrons (≥ 0.5 MeV) and very low energy light ions (\sim keV). Due to the large difference in the maximum recoil energies it could so happen that the entire damage process is confined only to the lighter atom species constituting the alloy. A number of alloys like stainless steel which are technologically important contain a significant amount of light elements like C, Al and Si. These elements could be either dispersed or could be in the form of precipitates generically called γ' : like Ni_3Al , Ni_3Si , and are responsible for the hardening characteristics of alloys. The process of selective displacements upsets the equilibrium of the thermally formed composition resulting in the restructuring of the alloy.

The subthreshold effects dominate at low energies (except for electrons) where the scattering cross-section is high as seen from figure 1a. However at higher energies the displacement damage by the heavier masses becomes more significant as can be seen from figure 1b. There is however, another feature which becomes important in alloys even if there is no mass difference between the alloying elements. This arises from the dependence of the PKA spectrum on the local atomic concentrations $\xi_A(\mathbf{r})$ and $\xi_B(\mathbf{r})$,

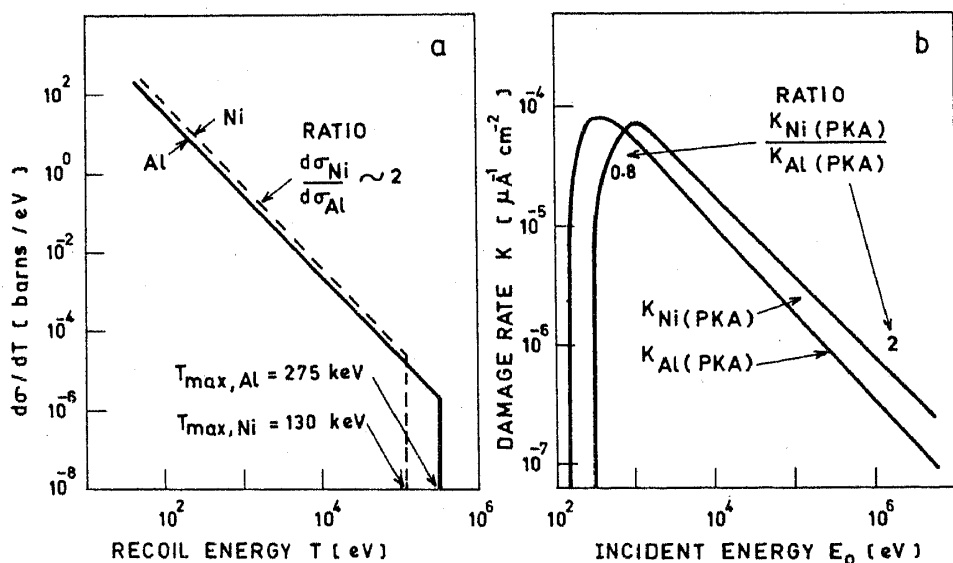


Figure 1. (a) Recoil energy spectrum of Ni and Al atoms in NiAl alloy with 2 MeV protons (b) Comparative damage rates produced by the Ni and Al PKA spectrums for different proton energies (Panigrahi 1984).

($\xi_A + \xi_B = 1$). The PKA spectrum (ignoring mixing effects) is given by

$$PKA_{A,B}(\mathbf{r}, T) = (d\sigma_{A,B}/dT) N \xi_{A,B}(\mathbf{r}), \quad (2)$$

where N is the total atomic concentration. The spatial variation in $\xi_A(\mathbf{r})$ and $\xi_B(\mathbf{r})$ arises because the distribution of A and B atoms would depend on whether the alloy has stoichiometric order, short range order (SRO), long range order (LRO) or is completely disordered. Thus even though the irradiation is completely homogeneous, inhomogeneities in the PKA spectrum lead to gradients in the defect structure introducing fluxes of atoms and defects which can restructure the alloy (Krishan and Abromeit 1984).

2.1b Secondary displacement effects: The process by which PKAs produce secondary displacements is *via* replacement collision sequences where each atom displaces the neighbouring one along the crystallographic directions. A vacancy is generally produced at the beginning of the chain and the replacement sequence propagates 3 to 6 lattice distances (sometimes as long as 20) till the extra atom is displaced to an interstitial position. For a replacement sequence the PKA must transfer an energy between T_f and T_d where T_f is the focussing energy and T_d the minimum threshold displacement energy to form a stable vacancy-interstitial atom pair. T_d is typically 10–30 eV and depends on the crystallographic direction. The higher limit T_f arises because of dechannelling effects and for energy transfers larger than these, cascades are formed with several vacancies (≥ 1000 for typical large cascades) and the atoms are removed to peripheral interstitial sites by several replacement sequences.

The scenario of separation of vacancies from self-interstitials *via* replacement sequences to escape spontaneous correlated recombination needs to be considered more carefully in alloys. The complete transfer of energy from the moving to a stationary mass, when the masses are equal, forms the basis on which replacement sequences are formed. In alloys, where different masses are involved, there will be a large dissipation of energy during transfer and this effectively inhibits the propagation of such sequences. Figure 2 shows four different situations which can arise and these will be discussed.

Figure 2a shows an ordered FeAl alloy. In this alloy we find that channels along the $\langle 111 \rangle$ direction are blocked and no replacement sequences can propagate; on the other hand the $\langle 100 \rangle$ and $\langle 110 \rangle$ channels are free. The threshold displacement energy surface will show a high degree of anisotropy in such alloys. There have been very few detailed studies of such effects though some resistivity measurements have been made at low temperatures (Rivier and Dinhut 1981) after irradiating with electrons along various crystal orientations. Figure 2b shows a plane of atoms for a NiAl alloy. Such alloys are composed of two interpenetrating simple cubic sublattices α and β . On the A-rich side the excess A-atoms are accommodated on the β -sublattice as antistructure defects, while on the B rich side structural vacancies are formed on the α -sublattice. The existence of these vacancies which can be as much as 10% would not make it possible for any collision sequences to operate on the α -sublattice as shown in the figure 2b. Such vacancies would play a very effective role as recombination centres and therefore significant differences can be expected in the formation of the microstructure as a function of alloy composition. In another class of alloys *viz* CuZn and AuCo the lattice defects consist of A-atoms on β -sites, B-atoms on α -sites and vacancies, the behaviour of replacement sequences would be correspondingly different. A more complex

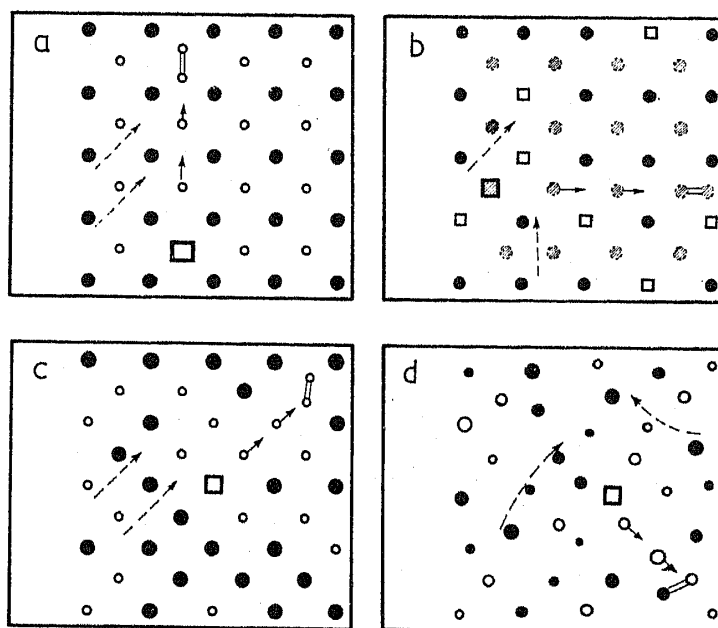


Figure 2. The blocked channel directions (broken arrows) and free channels (full arrows) along which replacement sequences can operate producing Frenkel pair damage in alloys (a) Unequal masses do not allow replacement channels to propagate along some directions like $\langle 111 \rangle$ for FeAl alloys (b) In alloys which are away from stoichiometric composition vacancies appear as structural defects on one of the sublattices blocking all replacement channels in the sublattice. The shaded dots are on a separate plane and belong to a different sublattice. (c) In a disordered alloy with unequal masses all channels would be blocked but for the short range clustering which allows replacement sequences (d) In glassy alloys the short range order is sufficient to allow short replacement sequences to occur making them also vulnerable to damage.

situation arises in cases where the alloy is disordered as shown in figure 2c. In such cases if the mass difference is large it should be very difficult for replacement sequences to operate along any direction making them ideal radiation damage resistant materials. However, this is not the case since some amount of short range ordering will persist. Since it is sufficient for chains to be a minimum of three to four lattice spacings long to form a stable Frenkel defect, a large number of chains would be possible. However, under identical conditions resistivity measurements at low temperatures do indeed show that the disordered phase is more radiation resistant than the ordered one. Finally, figure 2d shows the even more extreme situation encountered in metallic glasses. In this case besides composition disorder, one encounters spatial disorder in the atomic arrangements. Here also there is evidence (Egami 1983) for chemical sro, and on the scale of replacement sequence lengths (a few atomic spacings) the spatial disorder will not have a significant influence, particularly when one views the structure on the basis of a network model (Gaskell 1980; Krishan 1982b). However, as we will see in the next section the vacancies will collapse in about 10^{-10} sec being unstable in such amorphous systems.

2.2 Defects and their mobility in concentrated alloys

We have already encountered two defects namely 'structural vacancies' and 'antistructure' defects which exist when we move away from the stoichiometric compositions in

alloys like NiAl, CoGa, CuZn, AuCd. Interstitialcy transport *via* the dumb-bell type configuration has been identified as a possible mechanism for transport though there is only limited experimental evidence. Vacancy-interstitial complexes also appear to play an important role in some alloys like Fe-Cr-Ni containing impurities. On the other hand, in systems like metallic glasses even less is known.

2.2a Interstitialcy mechanisms: Our understanding of defects in concentrated alloys comes mainly from the experience in dilute alloys and pure metals. Here the self-interstitial is known to exist as a dumb-bell along $\langle 100 \rangle$ direction in fcc lattices. In a concentrated alloy A, B this picture would involve three possible dumb-bells A-A, A-B and B-B. If their binding energies and migration energies are about the same they would be mobile and would freely change their form as shown in figure 3. Due to such continuous exchanges the identity of the interstitial is lost though atomic mobility can take place. Identification of such a process experimentally is difficult since the behaviour is very similar to a self-interstitial in a pure metal and produces no additional structure in resistivity measurements. In principle such a complex could lead to segregation though there is no direct experimental evidence for this. Such a mechanism is believed to operate in alloys like Cu Ni (Wollenberger 1982) possibly in stainless steel Fe-Cr-Ni, and alloys of Cu with Co, Fe, Zn and Ge (Robrock 1983).

A more complex situation arises if the binding energies for the A-A, A-B and B-B complexes are relatively different and so are their migration energies. Three possibilities exist as shown in figure 4a depending on ω_t the trapping and ω_d the detrapping jump frequencies. In this case the ability of the defect to move becomes strongly dependent on the paths available as shown in figure 4b. Bocquet (1983) showed that when the trapping is infinitely deep $\omega_t \gg \omega_d$, the ability for the defect to percolate depends on the solute concentration. If the solute concentration C_B is lower than a limiting percolation value $p_c \approx 0.29$, the defect is trapped in clusters of B-atoms which are entirely surrounded by A-atoms and the long range migration of the defect becomes impossible. Internal friction experiments, done by Halbwachs and Beretz (1980), show that in AgZn the interstitial mobility is smaller than the mobility of vacancies. Generally strong trapping effects are observed when an oversized "impurity" atom is involved or an undersized 'impurity' is involved. A detailed discussion of this has been given in the review by Robrock (1983).

2.2b Minor alloying addition in Fe-Cr-Ni alloys: Fe-Cr-Ni alloys are technologically important and elements like Ti, Si, Mo have been used to control their swelling behaviour. Sharma *et al* (1978) and Dimitrov *et al* (1981) have obtained some

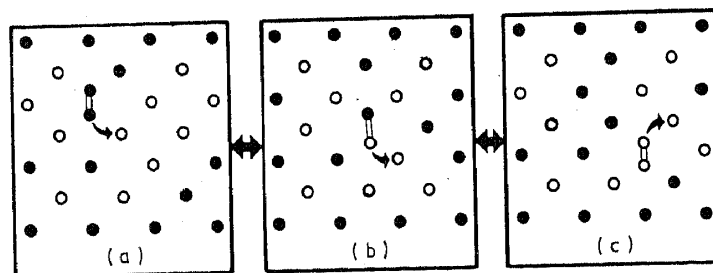


Figure 3. Changes in the dumb-bell configurations as it migrates (a) B-B dumb-bell changing to (b) A-B dumbbell and (c) A-A dumb-bell. Transport by such interstitialcy mechanism also causes structural rearrangements.

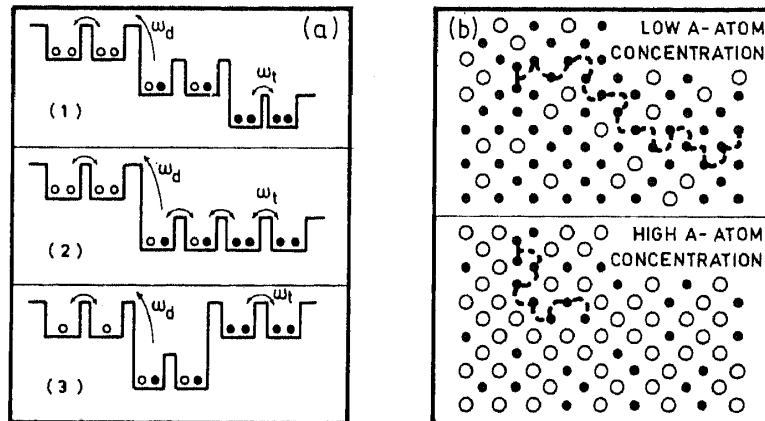


Figure 4. (a) Relative binding and migration energies which can lead to transport by (1) B-B (2) A-A & A-B and (3) A-B dumb-bells ω_d and ω_t are the dissociation and trapping frequencies. (b) Percolation of a B-B dumb-bell at low A-atom concentrations and no percolation at high A-atom concentrations. Percolation paths depend on the alloy concentration and effect the atomic mobility by interstitialcy mechanism.

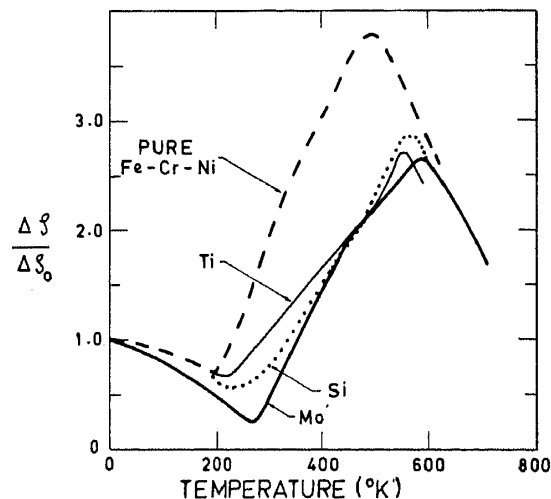


Figure 5. Resistivity change by minor alloy elements indicating different trapping processes (Sharma *et al* 1978).

information about defect trapping mobilities with these solutes, using low temperature resistivity technique. The main results are shown in figure 5. At low temperatures till 190 K the decrease in the resistivity is due to the recombination of close pair Frenkel defects. Between 190 K and 260 K the transport by the interstitialcy mechanism is postulated in pure Fe-Cr-Ni. However, from the shift in the temperature for Si and Mo, it follows that they strongly trap the interstitials while Ti does not. In the temperature range 260 K to 460 K, vacancies also become mobile and are strongly trapped by Ti and weakly by Si and Mo. At temperatures above 460 K the release of interstitials and vacancies from Si and Ti atoms is responsible for the resistivity decrease. These features are in general agreement with the swelling behaviour in these alloys. It is perhaps worth pointing out that the contribution to resistivity in concentrated alloys comes from the defect concentrations and structural changes.

2.2c Defects in amorphous alloys: There is even less understanding about defects in amorphous alloys more commonly known as metallic glasses. The glassy phase always has a density lower than the crystalline phase indicating that there should be a large free volume available. Experiments have failed to show any presence of large atom sized holes which could be called 'vacancies' and it is therefore thought that this free volume is distributed amongst the atoms. Irradiation would produce instantaneous 'vacancies' due to displacement of atoms but such vacancies exist for only $\sim 10^{-10}$ sec as shown by computer simulation (Bennett *et al* 1979) and this volume gets distributed (figure 6a). However very low temperature resistivity experiments show some structure and the possibility that they may be stable in some complex form cannot be ruled out. Cahn (1978) on the basis of diffusion data argued that a duality picture involving both distributed volume and atom-sized holes may be required. A theoretical justification for this has been given by Krishan (1982b) on the basis of a random network model where the distributed volume could exist as a configurational lock which could be thermally activated to form an atom-sized hole (figures 6b and c). Such a 'hole' would migrate but would not be detectable since it would collapse into a configuration lock in $\sim 10^{-10}$ sec. The presence of such 'holes' is required to explain atomic transport which appears to have the same temperature dependence as in crystalline metals where the vacancy mechanism is involved. On the other hand, there is not so much difficulty in identifying interstitials since they would reside in the interatomic spaces of the disordered network (shown in figures 6b and c). They cannot form a part of the network since such a process would make the local atomic density to become more than that of the crystalline solid, and there seems to be no evidence for this. Though the structure and properties of interstitials are not understood, the diffusion constant for light gases like He seems to be very similar to that in crystalline solids.

There is no evidence at all for any extended defects and electron microscopy does not reveal any structures which could be equivalent to dislocations, precipitated phases or grain boundaries. Theoretically the possibility of disclinations as stable defects has been postulated by Rivier (1979) but there is no experimental evidence for this. However slip bands have been observed in mechanically deformed metallic glasses.

2.3 Atomic mixing and restructuring in alloys

Besides displacement of atoms, irradiation also rearranges the atoms during replacement sequences since atoms get shifted in the process. This rate is often even greater

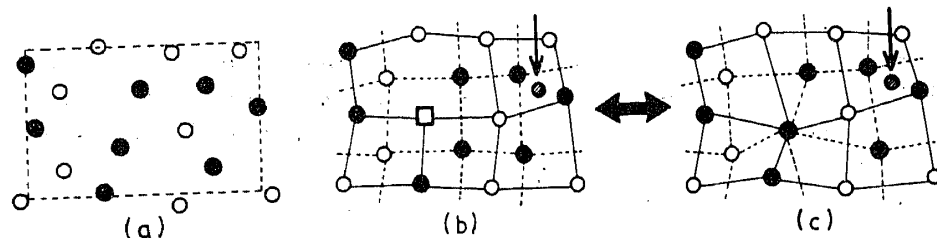


Figure 6. Schematic diagram showing (a) lower density of the glassy phase (b) The same atoms are shown on the basis of an interpenetrating network model with a displacement event a 'vacant site' and an interstitial (arrow) in the internetwork position (c) The vacant site collapses in $\sim 10^{-10}$ sec forming a configuration lock distributing the vacant volume. Structure in (c) by thermal activation can produce the structure in (b) showing the duality behaviour of the 'atom sized hole' and distributed volume (Krishan 1982b).

than the displacement rate; the ratio ε being about 2 for electron irradiation and 80 for fast neutron irradiation in Ni_3Mn . Also such rearrangements can be caused by cascades since the atoms during the collapse of the cascade will be rearranged. The extent of rearrangement or disorder depends on the state of the alloy. In case there is only short range clustering, then the changes can be quantified in terms of the Warren-Cowley short range ordering (SRO) parameters α_i . These parameters express the number of like atoms which on an average would be in $i = 1, 2, \dots$ neighbouring shells. On the other hand if the original state is ordered with atoms prescribed to fixed α, β sublattices in the ideal state, then the degree of order is quantified by the Bragg-William LRO parameter S defined by

$$S = (f_{A\alpha} - X_A)/(1 - X_A), \quad (3)$$

f_A is the probability of finding an A -atom on an α -sublattice and X_A is the average A -atom concentration. From purely statistical considerations the disordering rate for LRO is

$$(dS/dt)_{\text{irr}} = -\varepsilon KS, \quad (4)$$

where K is displacement rate. The changes in SRO and LRO by irradiation are studied by diffuse and small angle x-ray and neutron scattering techniques. Such measurements reveal the basic mechanisms operating in the alloy. The irradiation effect can be seen in terms of the average distance an interstitial atom is moved from its vacancy in a replacement sequence. This can be expressed by $W(\mathbf{r} - \mathbf{r}')$ which is the normalized probability for producing A (or B) interstitial at a distance $(\mathbf{r} - \mathbf{r}')$. The spatially dependent dose rate $K_A(\mathbf{r})$, $K_B(\mathbf{r})$ for interstitial production is given by

$$K_{A,B}(\mathbf{r}) = \alpha \sigma_{A,B} \int W(\mathbf{r} - \mathbf{r}') \xi_{A,B}(r') d^3r', \quad (5)$$

where $\sigma_{A,B}$ is the displacement cross-section for A, B atoms and α the proportionality constant. One can get an idea about the restructuring of the alloy if we take the Fourier transform $W(\mathbf{k})$ of $W(\mathbf{r} - \mathbf{r}')$ and decompose it into correlation effects of different wavelengths. This gives some idea about the state of LRO which will be most affected since these would have a wavelength comparable to the dominant wavelength in $W(\mathbf{k})$ (Abromeit and Krishan 1984).

3. Structural changes in alloys

Alloys under irradiation are essentially non-equilibrium systems. They develop concentration gradients in point defects and complexes formed by irradiation. These gradients cause fluxes of atoms and violate the thermodynamic requirement that, at equilibrium, the chemical potential of each species is constant throughout the system. Thus these fluxes produce segregation and restructuring of the alloy resulting in development of new phases, changes in the short range and long range order and new types of sinks to maintain a steady state. In this section we give examples of these effects.

3.1 Process of segregation and precipitation

Radiation-induced segregation has been extensively studied because of its important technological implications. For example, austenitic grains of stainless steel can transform entirely into ferritic during neutron irradiation (Potter 1983), because of Ni

segregation towards and chromium segregation away from grain boundaries. Also despite small concentration of silicon in stainless steels, it tends to segregate to grain boundaries to form intermetallic silicide phases like γ' -Ni₃Si which have a profound influence on the in service performance of components. Segregation essentially occurs *via* two processes. The inverse Kirkendall effect where a gradient in vacancy concentration near a sink results in a reverse flux of *A* and *B*-atoms, the atom diffusing faster leaves behind a region rich in the slower atomic species. The second process involves the diffusion *via* the defect-solute complex. The complex diffuses in its own concentration gradient which could be opposite of that of the solute. A criteria for such a process is that

$$E_b^{\text{complex}} + E_m^{\text{defect}} > E_m^{\text{complex}} \quad (6)$$

where E_b and E_m refer to the binding and migration energies of the defects involved.

Converse processes like the dissolution of existing precipitates are also known to occur. This has been observed in Ti-modified stainless steel containing γ' precipitates by Lee *et al* (1980) after neutron irradiation. The electron micrograph in figure 7 (Varatharajan *et al* 1982) shows another example of dissolution of γ' precipitates Ni₃(Al, Ti) after 50 keV helium ion irradiation where the fragmentation effects are clearly evident. There are various processes by which dissolution can occur. For example a phase with a positive volumetric mismatch with respect to the matrix will tend to have a bias for vacancies and hence will establish a gradient of those atomic species which migrate by vacancy-mechanism. Another mechanism of dissolution has been postulated by Nelson *et al* (1972) where the solute atoms are ejected from the precipitates by impinging energetic PKA's. The recoil-induced concentration of solutes may exceed the equilibrium concentration and thus would start a new nucleation for the precipitate. Thus it appears that the original precipitate is fragmented. The different stages of this process are schematically shown in figure 8.

3.2 Short-range clustering and long-range decomposition of Ni-Cu alloy

The Ni-Cu alloy has been extensively studied and shows complete miscibility in the solid state at temperatures well above 600 K where thermal diffusion is high for mass transport. At around 600 K thermally-activated mass transport becomes sluggish and

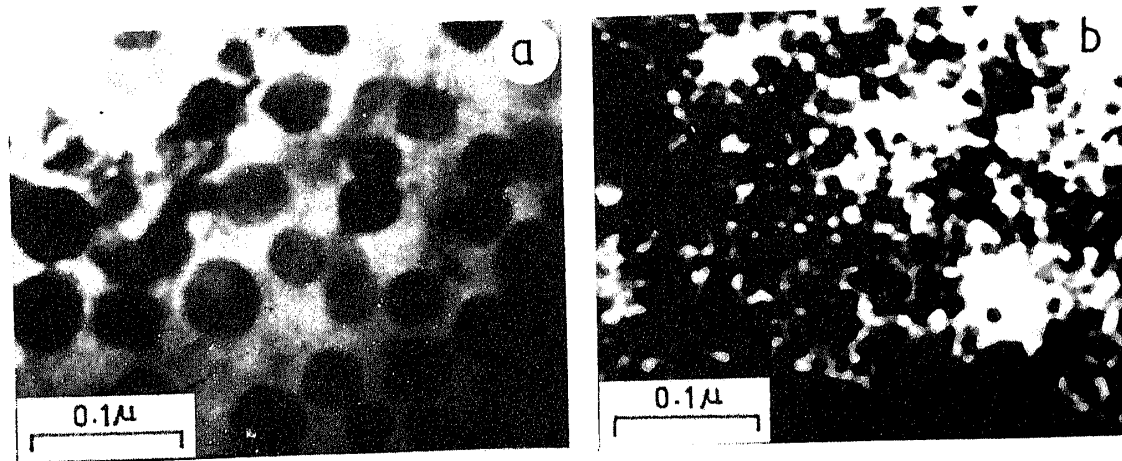


Figure 7. Dissolution and fragmentation of γ' precipitates Ni₃(Al, Ti) produced by low energy α particles. (a) unirradiated (b) irradiated in nimonic 90 alloy (Varatharajan *et al* 1982).

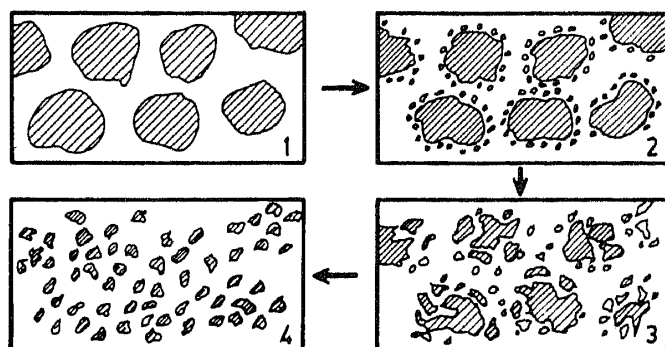


Figure 8. Schematic representation of fragmentation and reprecipitation of precipitates at different stages.

has a tendency to show short-range clustering (Vrijen 1977). On the basis of this spinodal decomposition (see the review by de Fontaine 1979) is predicted but has never been observed because of low atomic mobility. Wagner *et al* (1980, 1982) have shown by small-angle neutron scattering experiments on ^{62}Ni -41% ^{64}Cu alloy that in the temperature range 373–480 K a long-range periodic composition fluctuation can be produced by electron irradiation, with a wavelength of about 45 Å. Two points of view can be adopted. The role of the irradiation is only to enhance diffusion but the kinetics is determined by the Cahn (1966) and Cook (1970) theory of spinodal decomposition. In this theory the increase in the intensity of the fluctuation of wavevector \mathbf{k} is governed by the 'amplification factor' $a_{\text{therm}}(\mathbf{k}^2)$. This is positive inside the spinodal due to a change in sign of the second derivative of the free energy. Such a model however is not completely consistent with the experimental results (Wagner *et al* 1982).

The second point of view is to consider the decomposition as a radiation-induced process. This possibility has been examined by Krishan and Abromeit (1984) and Abromeit and Krishan (1984). In the presence of irradiation there is radiation-enhanced vacancy and interstitial diffusion. It would appear that the vacancy mechanism will contribute to an enhancement of the thermodynamic decomposition while the interstitial diffusion would effect the irradiation-induced processes. In the simplest case where point defect annihilation is only by recombination, the vacancy concentration would be the same order as that for interstitials. However due to the much higher diffusion constant of the latter, the interstitialcy transport mechanism will dominate. The thermodynamic amplification factor will now be replaced by a new effective amplification factor.

$$a_{\text{eff}}(\mathbf{k}^2) = a_{\text{therm}}(\mathbf{k}^2) + a_{\text{irr}}(\mathbf{k}^2). \quad (6)$$

The contribution to $a_{\text{irr}}(\mathbf{k}^2)$ comes from two effects which have already been discussed, *viz*, the spatial dependence of $\xi_{A,B}$ which produces fluxes of A and B atoms contributing to restructuring of the alloy and the mixing effect discussed in § 3.3 which influence fluctuations of wavevector \mathbf{k} depending on $W(\mathbf{k})$.

3.3 Order-disorder transformations in Ni_4Mo

The alloy Ni_4Mo shows a wide range of order-disorder transformations and is therefore a good example of such processes. It has been extensively studied by Banerjee *et al* (1984) over a wide range of temperatures $50 \text{ K} \leq T \leq 1050 \text{ K}$ in a high voltage

electron microscope. During irradiation we have already discussed some of the replacement processes by which the alloy disorders and loses its short range and long range order. The process of irradiation is non-equilibrium in nature and eventually there are competing ordering mechanisms, and the alloy attains some equilibrium structure depending on temperature. Interestingly, the final state to which an alloy develops seems to be very sensitive to the initial state of the alloy as shown by figure 9 where the transition from the long range ordering stage to short range ordering is forbidden. An ordering mechanism map which has been developed in terms of the long range ordering parameters and the experimentally determined short range ordering reflection intensity ratio R is shown in figure 10, which gives the broad features of the effects in this alloy.

A detailed understanding of all the processes responsible for these order-disorder effects is not available. However, the formation of the different regions appear to be related to the different processes by which atomic mobility can occur. At temperatures

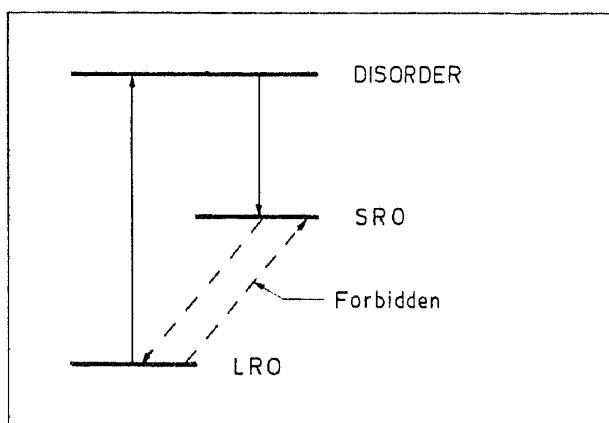
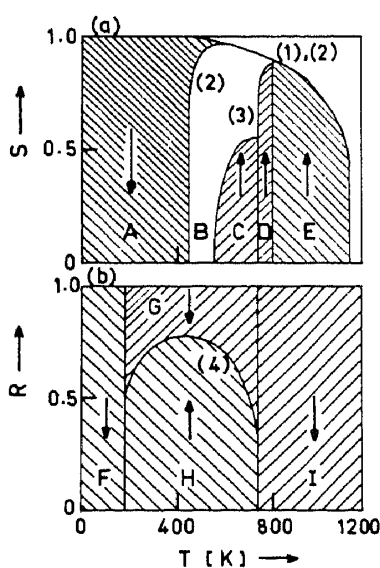


Figure 9. Allowed and forbidden transitions in order-disorder transformations.



Region A = destruction of LRO.

Region B = no significant change if initial state corresponds to $S = 1$ or $S = 0$.

Region C = continuous ordering by decay of the SRO waves and simultaneous amplification of the LRO waves.

Region D = initially as in Region C. After SRO is destroyed completely the degree of LRO increases further by domain formation and growth.

Region E = nucleation and growth of D_{1a} domains.

Region F = destruction of SRO.

Region G = reduction of the degree of SRO and at $T > 550$ K transition to LRO.

Region H = development of SRO. Data for the build-up of SRO in the completely disordered material is so far only available for $200 \text{ K} < T < 450 \text{ K}$.

Region I = destruction of SRO and transition to LRO.

Figure 10. Radiation ordering Map in Ni_4Mo by electron irradiation. S is the long range order parameter and R a measure of short range order (Banerjee *et al* 1984).

$T < 200$ K there is very little mobility of atoms apart from that provided by radiation-induced diffusion. The next two critical temperatures from the alloy ordering map in figure 10 are T_c^* (SRO) $\simeq 200$ K and T_c^* (LRO) $\simeq 450$ K. It appears that above T_c^* (SRO) the short range ordering processes are restored in the alloy due to diffusion *via* an interstitialcy mechanism involving Mo atoms. This is conjectured from the fact that the Mo atom is considerably larger than the Ni atom which is known to be mobile at somewhat lower temperature. The temperature T_c^* (LRO) is connected with mobility of atoms *via* the vacancy mechanism. Banerjee and Urban (1984) have done a detailed calculation based on this process where they have considered the various jump mechanisms from the β - β , β - α and α - α sub-lattices which are occupied by the Ni and Mo atoms. These jumps lead to ordering of the alloy and provide an explanation of the high temperature behaviour in ordering mechanism map.

3.4 Irradiation effects in metallic glasses

Metallic glasses are a rather extreme example of alloys where the structure is both spatially and compositionally random. Though a large number of alloys have been produced in the glassy phase, metal-metal glasses like $\text{Ni}_{60}\text{Nb}_{40}$ and $\text{Ni}_{64}\text{Zr}_{36}$ are better suited for radiation environments because of the low neutron capture cross-sections and high crystallization temperatures. Also they are expected to show high radiation damage resistance because practically no restructuring effects would influence these alloys!

These expectations have to some extent been borne out by experiments. For example there has been no direct observation of void formation for which the existence of biased sinks like 'dislocations' are required. Rehtin *et al* (1978) have studied $\text{Ni}_{60}\text{Nb}_{40}$ using 3 MeV Ni^+ ions and have reported a high stability of the amorphous phase and no observation of voids using TEM. Also Cahn *et al* (1981) reported on neutron irradiation of Ni-Zr glasses, they found $\text{Ni}_{64}\text{Zr}_{36}$ to be highly stable whereas alloys with higher Zr concentrations ($\text{Ni}_{33}\text{Zr}_{67}$) partially crystallized. Detailed studies have been made of the partial atomic structure factors of metallic glasses after irradiation using x-ray scattering. Also other techniques like positron annihilation and resistivity have been used but nothing specific could be concluded regarding the damage structure (see the review by Nandedkar and Tyagi 1984).

The situation under low energy irradiation using gaseous ions is somewhat different. These irradiation conditions broadly fall in the domain of fusion reactors. Here one finds that though metallic glasses are more resistant to damage effects than crystalline alloys, their behaviour shows a similar pattern (Tyagi *et al* 1983a, b, 1984). Gases like helium, hydrogen and argon have been found to precipitate into gas bubbles which ultimately leads to blistering and flaking. Figure 11a shows the precipitation of helium into bubbles 20–50 Å in size at a very high density of $\sim 10^{19}$ cm^{-3} in $\text{Ni}_{60}\text{Nb}_{40}$ glass. Figure 11b shows blistering in $\text{Fe}_{40}\text{Ni}_{40}\text{P}_{14}\text{B}_6$ and figure 11c shows flaking in $\text{Ni}_{60}\text{Nb}_{40}$ glasses. Measurements of the critical dose for blistering show that it is 50–100% higher in the glassy phase than in the corresponding crystallized phase.

The reasons for this increased resistance of metallic glasses are not very clear and why the damage structure should eventually be so similar to crystalline materials during gaseous ion bombardment only is also rather surprising in some respects. The higher resistance of metallic glasses to gaseous ion implantation effects appears to be related to the lower ability of such glassy materials to retain insoluble gases like helium as

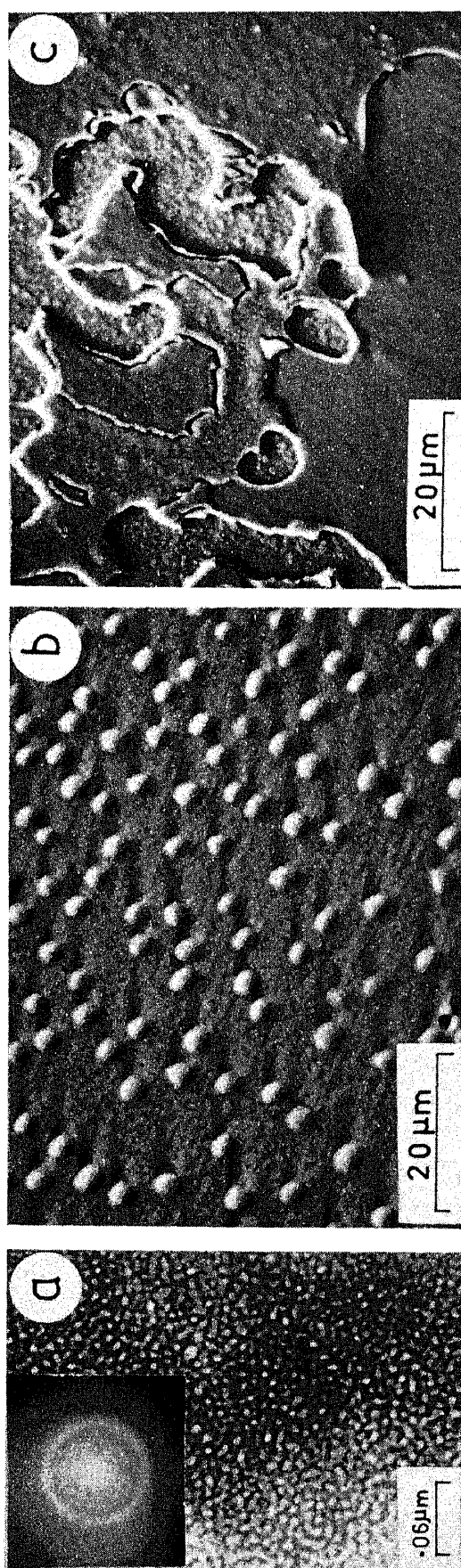


Figure 11. Electron micrographs showing gaseous implantation damage in metallic glasses (a) Helium bubbles ($\text{Ni}_{60}\text{Nb}_{40}$). (b) Blisters ($\text{Fe}_{40}\text{Ni}_{40}\text{P}_{14}\text{B}_6$) (c) Erosion ($\text{Ni}_{60}\text{Nb}_{40}$) (Tyagi *et al* 1983, 1984).

compared to crystalline materials where they can be easily trapped in vacancies. Though metallic glasses have 1–2% more free volume (equivalent of $\sim 10^{20}$ – 10^{21} vacancies!) than the crystalline phase, this as we have discussed, is distributed over several atoms and is not effective in trapping helium which seeks 'atom-sized holes'. However since gaseous ion implantation is accompanied by the production of 'vacant sites' and 'displaced atoms' the helium could be trapped into some of these 'vacant sites' before they collapse in $\sim 10^{-10}$ sec. Once of course helium is trapped into such a site in a dynamic process, it would stabilize the 'vacancy'. Such a kinetic trapping model has been examined and the main effect of the vacancy collapse is to reduce the rate of 'helium-vacancy' complex formation (Krishan *et al* 1984a). This explains the higher critical doses for blistering which are observed. Our understanding of the basic damage processes in these glasses is slowly improving.

4. Phase instability by irradiation

For a variety of reasons materials in radiation environments must be looked upon as non-equilibrium systems even though they may be in a steady state condition. This is because they are open systems, continuously subjected to a flux of energetic particles across boundaries, with energies often 10^7 times more than the thermal energies of the atoms in the solid. Such a system clearly cannot be viewed as a thermodynamic system whose final equilibrium state is governed by minimum entropy or energy considerations but not the path it takes to reach this state. Also the processes involved in irradiation are basically irreversible since irradiation produces point defects which are 'dissipated' at sinks with no reverse fluxes. Thus the basic principle of detailed balance, where microscopic processes must proceed at the same rate both ways, is violated.

4.1 Mechanism of instability

Application of non-equilibrium methods to the behaviour of metals under irradiation is of relatively recent origin. Non-equilibrium systems maintained at steady-state can undergo non-equilibrium transitions when some control parameter crosses a certain critical value. The view that all irradiation effects like segregation, precipitation and ordering are simple consequences of growth or shrinkage by point defect fluxes cannot be maintained, since the highly nonlinear nature of the processes could drive the system to new nonequilibrium states.

As a simple illustrative example consider the growth of 'defects' like precipitate or voids due to a steady flux of 'point defects' which is sustained by the irradiation. In such a situation, a balance will be maintained between the steady-state concentration of 'point-defects' and the size and concentration of 'defects' as it evolves. It is important that this balance should be a stable one *i.e.* if we change one of these variables, the system must attempt to come back to its earlier steady state. This can be quantified in terms of the time τ_i or frequency $|\omega_i| = 1/\tau_i$, it takes for it to return to equilibrium, i being the variable which is disturbed, or the degree of freedom of the system. If this disturbance is localized then it could be decomposed into a disturbance involving several wave lengths or wave vectors by Fourier expansion. Each of these wave vectors will have its own response time or frequency $|\omega_i(\mathbf{k}^2)|$. These frequencies of course depend on the basic system parameters like the sink strengths, recombination constants, dose rate, mixing effect etc and this can be explicitly shown as a dependence on the system variable s by

$|\omega_i(s, k^2)|$. Near the steady state the approach to equilibrium is exponential in time t so that the system will re-establish its equilibrium as

$$\sim \exp[\omega_i(s, k^2)t] . \quad (7)$$

An interesting situation can arise if for a given k value $\omega_i(s, k^2)$ becomes zero for $s = s_c$, a critical value. This would mean that the time $\tau_i(s, k^2)$ taken for wavelengths fluctuations k to return to their original steady state would be infinite. In short the system would never return to its original steady-state but will bifurcate to a new non-equilibrium state and a new structure will evolve. For a stable system all $\omega_i(s, k^2)$ are negative implying a decay to steady state.

4.2 Physical systems

Several examples of such processes have been considered in recent years. Barbu *et al* (1981) discussed a precipitation instability in undersaturated Ni-Si alloy. They found that there is a threshold value of dose rate which depends on temperature.

A similar instability has also been reported in AlZn alloy by Cauvin and Martin (1983). Another interesting application of this theory is the void-lattice formation. Voids are initially disordered but after certain time orders into a lattice with the same symmetry as that of the host matrix. Besides pure metals this is formed in a number of alloys including stainless steel. In this case the disorder to order transition occurs at a critical value of the sink densities (ρ_s)_c and (ρ_v)_c for voids and dislocations like vacancy loops respectively.

Taking into account the various rate processes it is found that $\omega_i(s_c, k_c^2) = 0$ for $s_c = [(\rho_s)_c, (\rho_v)_c]$ and this is shown in figure 12. The value of the wavelength $\lambda_c = 2\pi/k_c$ in this model depends on the mean free path of point defects before they are absorbed.

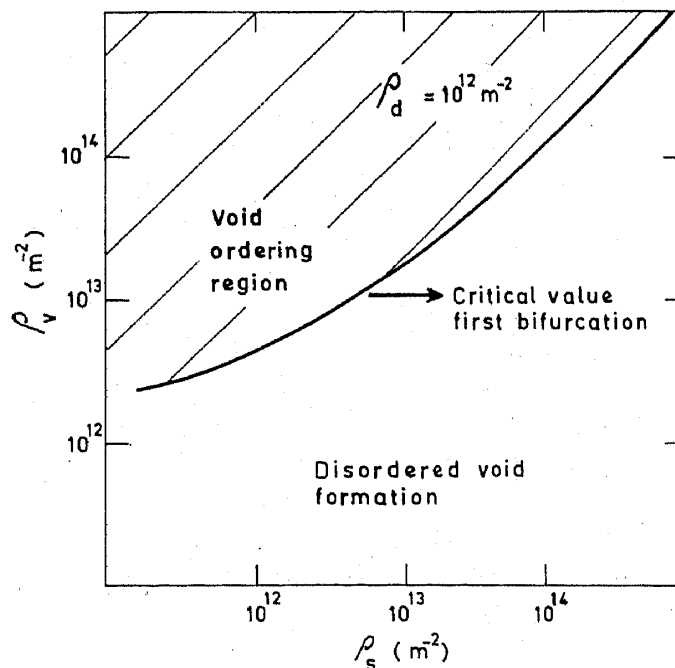


Figure 12. Critical sink densities ρ_s, ρ_v for void ordering in stainless steel (Krishan 1980, 1982a).

The long range ordering under electron irradiation in NiCu alloy which was discussed earlier would involve a similar process since the initial short range clustering eventually gives way to long range ordering which is characteristic of such dissipation structures. In this case the mixing effect of interstitials is identified as the order parameter (Abromeit and Krishan 1984).

5. Changes in properties of alloys

Besides radiation, alloys used in reactors are subjected to high stresses and temperatures. Their stability under all these three influences must be ensured. We have already seen a number of structural changes which alloys undergo during irradiation. These changes influence the mechanical behaviour and generally have a degrading influence. It is therefore not sufficient to understand the changes in the alloy structure by irradiation but also to correlate these with its changes in properties like creep, swelling, ductility and fracture behaviour. In table 1 some of these features have been tabulated. One of the problems in such studies in neutron environments is the difficulty in monitoring under controlled conditions parameters like stress and temperature. Therefore, accelerators are being increasingly used for such metallurgical investigations (Krishan *et al* 1984b) and we will give a few illustrations of such studies.

In §3 we had seen from resistivity studies, the influence on defect mobility of elements like Si, Mo and Ti (figure 7). Gessel and Rowcliffe (1977) discussed the

Table 1. Effects of phase changes on the properties of structural materials

Phase change	Affected properties	Mechanism
Formation of finely dispersed precipitates (e.g., γ')	Flow properties such as yield strength, ultimate strength and work hardening rate	(a) Precipitation hardening (b) loss of solid solution hardening and (c) changes in the kinetics of recovery and recrystallisation processes.
	Swelling and irradiation creep	(a) Dislocation pinning (b) removal of 'swelling inhibitors' from solution (c) precipitate collector effect.
Formation of 'massive' phase	Flow properties such as yield strength, tensile strength and work hardening rate	(a) Second phase strengthening (b) changes in the kinetics of recovery and recrystallisation processes.
	Swelling and irradiation creep	(a) Loss of 'swelling inhibitors' from the parent phase.
(a) Formation of semicontinuous or continuous films along grain boundaries or interphase boundaries	Impact toughness, fracture toughness and ductility	Propagation of cracks along paths having low interfacial energy.
(b) Segregation along grain boundaries or interphase interfaces		

influence of these and other elements like W, Al, Nb and C on Fe-7.5% Cr-20% Ni alloy. Their results are shown in figure 13a and show a marked reduction in the swelling. This is ascribed to the trapping of vacancies and interstitials by the impurity additions. However, these effects can manifest in a complex way since segregation and precipitation. The formation of γ' -Ni₃(Ti, Al) could for instance, remove Ti and Al which would result in high swelling rates at higher doses. This is demonstrated from the work of Bajaj *et al* (1980) where the peak swelling is shown to increase with the volume fraction of γ' in nimonic PE16 alloy (figure 13b).

The influence of stress on swelling has been a matter of considerable concern. It had so far been difficult to establish this effect and to make a systematic study because of the complex loading patterns encountered in reactors. Such effects have been recently studied by Khera *et al* (1982) and Sahu and Jung (1984) using light ion irradiation from cyclotrons in the energy range 7–10 MeV. The studies on 'pure stainless steel' are at low doses where the influence on the early stages of void growth can be studied. Under tensile stresses ~ 100 MPa the results show (figure 14) a marked increase in the void density. It is interesting to conjecture the effect of a compressive and a tensile stress on void nucleation. As seen from figure 14 the void size distribution is significantly influenced there, being larger number of voids with larger diameters. This is presumably because under a compressive stress void nucleation is inhibited while a tensile stress aids it.

Similar studies on the irradiation creep behaviour under both compressive and tensile stress have been done by Sahu and Jung (1984) in 'pure stainless steel' and the results for compressive stress are shown in figure 15. The strain rate attains a steady state value after approximately 10 hrs of irradiation. This is presumably because in the early stages of irradiation the alloy restructuring takes place and sinks like voids develop. This region is the primary irradiation creep region.

As a final example we discuss some results on Fe-3.5% Ni ferritic steel (A 203 grades). This steel has been irradiated at the CIRUS reactor to a neutron fluence of 3.5

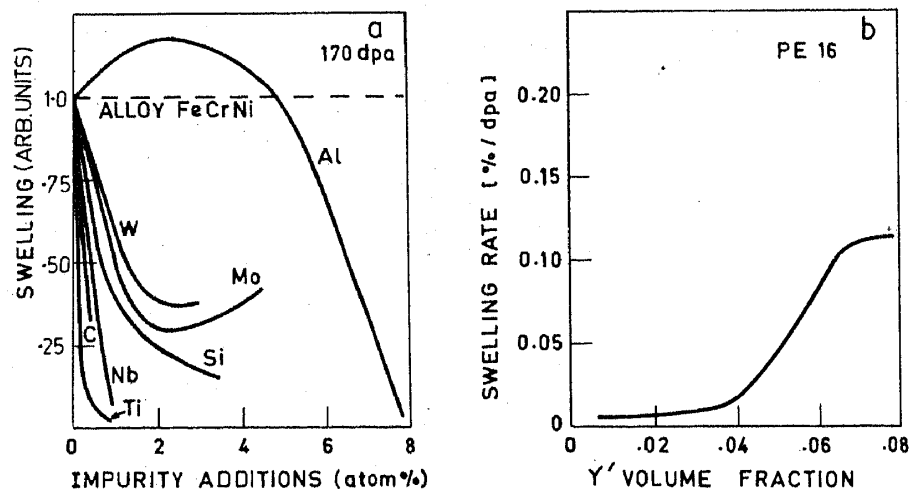


Figure 13. (a) Influence of minor alloying elements on swelling. The swelling ratio is normalized with respect to the 'pure' alloy taken as unity (after Gessel and Rowcliffe 1977) (b) Effect of γ' precipitation on swelling due to removal of minor alloying elements (after Bajaj *et al* 1980).

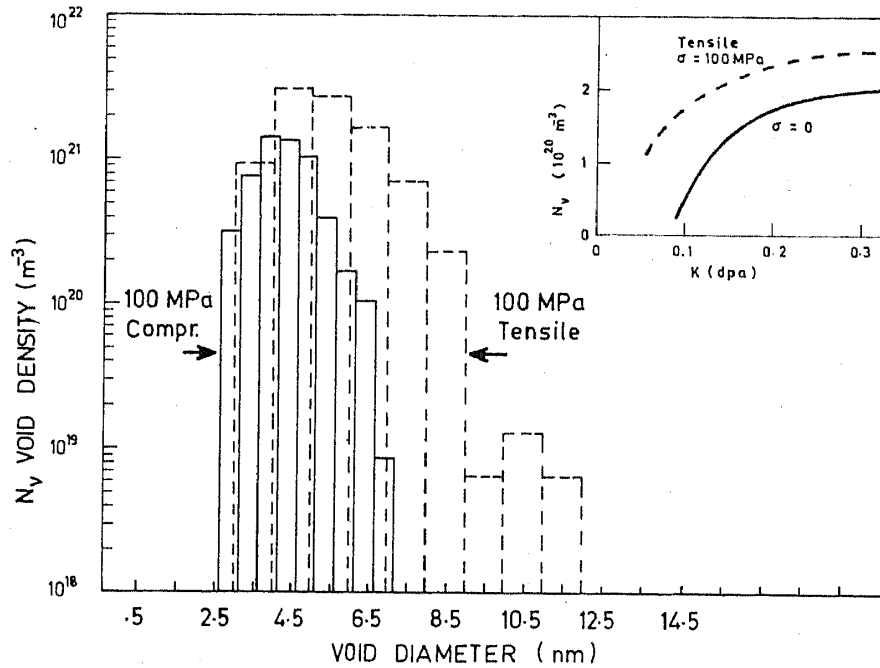


Figure 14. Comparison of void size distribution during compressive and tensile stress (Sahu and Jung 1984) Inset shows the effect of dose and tensile stress on void swelling (Khera *et al* 1982). Experiments have been done using light ion beams at 10 MeV with accelerators.

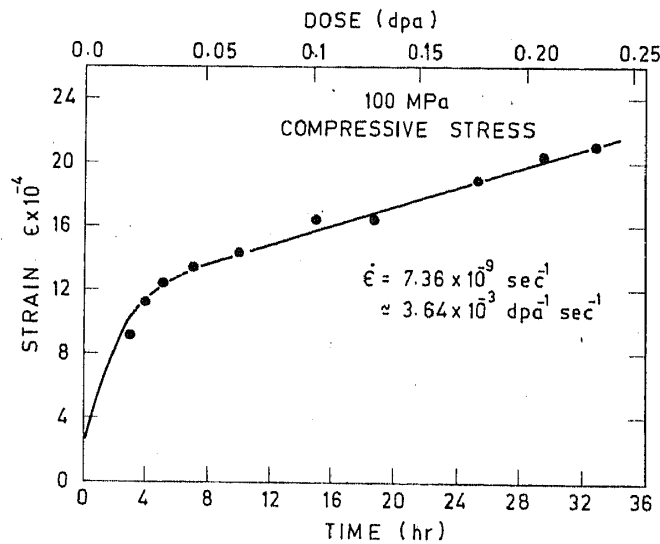


Figure 15. Strain due to irradiation creep produced by compressive load using 7 MeV protons (Sahu and Jung 1984).

$\times 10^{19} \text{ ncm}^{-2}$, and investigated for its ductility and impact toughness under irradiation. The nil ductility transition temperature $NDTT$ should remain nearly 40°C below the operating temperature of any component. $NDTT$ was measured by impact energy experiments and the results are plotted in figure 16 for the irradiated and unirradiated sample (Baldev Raj *et al* 1983). A significant increase in the $NDTT$ is observed from a value of -91°C to 149°C . Due to irradiation the flow stress of a

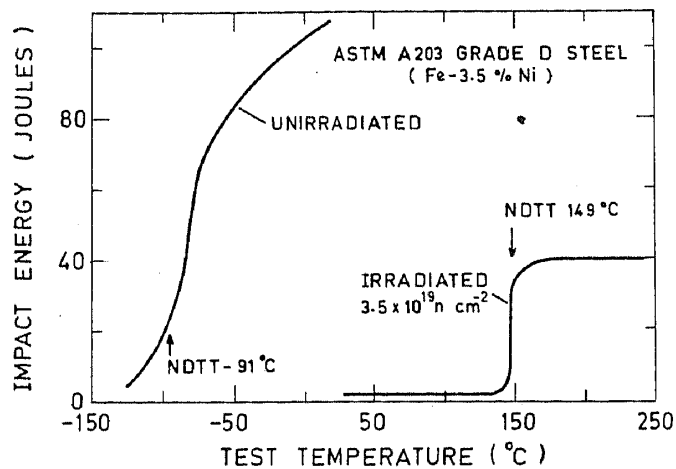


Figure 16. Shift in the NDTT temperature by low dose irradiation in CIRUS reactor of Fe-3.5% Ni alloy (Baldev Raj *et al* 1983).

material is increased while the fracture stress is reduced. Field ion microscope studies show nucleation of very small loops probably arising out of the interaction of solute atoms with irradiation produced interstitials.

References

- Abromeit C and Krishan K 1984 to be published
- Bajaj R, Diamond S, Chickering R W and Bleiberg M L 1980 in *Effects of radiation on materials* (eds) D Kramer, H R Brager and J S Perrin (ASTM-STP 725) p. 541
- Baldev Raj, Kasiviswanathan K V and Rodriguez P 1983 Reactor Research Centre, Kalpakkam report RRC-60
- Banerjee S, Urban K and Wilkens M 1984 *Acta Metall.* **32** 299
- Banerjee S and Urban K 1984 *Phys. Status. Solidi* **A81** 145
- Barbu A, Martin G and Chamberod A 1981 *J. Appl. Phys.* **51** 6192
- Bennett C H, Choudhari P, Moruzzi V and Steinhart P 1979 *Philos. Mag.* **A40** 484
- Bocquet J L 1983 *Philos. Mag.* **47** 547
- Cahn J W 1966 *Acta Metall.* **14** 1685
- Cahn R W 1978 C R 21 Colloque de Metallurgie Speciale, Saclay, France
- Cahn R W, Tolovi B, Akhtar D and Thomas M 1981 in *Proceeding 4th International conference on rapidly quenched metals*, Sendai, Japan p. 749
- Cauvin R and Martin G 1983 *J. Nucl. Mater* **83** 67
- Cook H E 1970 *Acta Metall.* **18** 297
- de Fontaine 1979 *Solid State Phys.* **34** (New York: Academic Press)
- Dimitrov C, Tenti M and Dimitrov O 1981 *J. Phys.* **F11** 753
- Egami T 1983 in *Amorphous metallic alloys* (ed.) F E Luborsky (London: Butterworth) p. 100
- Gaskell P H 1980 *Nature (London)* **289** 474
- Gessel G and Rowcliffe A F 1977 in *Radiation effects in breeder structural materials* (eds) M L Bleiberg and J W Bennett (TMS-AIME) p. 431
- Gruen D M 1979 in *Materials science in energy technology* (eds) G G Libowitz and M S Whittingham (New York: Academic press) p. 325
- Halbwachs M and Beretz D 1980 in *Third European conference of internal friction and ultrasonic attenuation in solids* (Manchester) p 139
- Khera S K, Schwarger C and Ullmaier H 1982 *J. Nucl. Mater* **92** 299
- Krishan K 1980 *Nature (London)* **287** 420

- Krishan K 1982a *Radiat. Eff.* **66** 121
- Krishan K 1982b *J. Non-Cryst. Solids* **53** 83
- Krishan K and Abromeit C 1984 *J. Phys.* **F14** 1103
- Krishan K, Rodriguez P and Sundaram C V 1984 *Indian J. Phys.* (in press)
- Krishan K, Tyagi A K and Nandedkar R V 1984 (to be published)
- Lee E H, Maziasz P J and Rowcliffe A F 1980 in *Phase stability during irradiation* (eds) J R Holland L K Mansur and D I Potter (Pittsburgh: Metallurgical Society of AIME) p 191
- Nandedkar R V and Tyagi A K 1984 in *Metallic glasses: production properties and applications* (ed.) T R Anantharaman (Switzerland: Trans Tech Publications Ltd.) p 165
- Nelson R S, Hudson J A and Mazey D J 1972 *J. Nucl. Mater.* **44** 318
- Panigrahi B 1984 Private communication
- Potter D I 1983 in *Phase transformations during irradiation* (ed.) F V Nolfi (London: Applied Science Publishers) p 213
- Rechtin M, Sande J V and Baldo P M 1978 *Scripta Metall.* **12** 639
- Rivier N 1979 *Philos. Mag.* **40** 859
- Rivier J P and Dinhut J F 1981 in *Point defects and defect interactions in metals* (eds) J I Takamura, M Doyama and M Kiritani (Tokyo: University of Tokyo Press) p. 619
- Robrock K H 1983 in *Phase transformations during irradiation* (ed.) F V Nolfi (London: Applied Science Publishers) p 115
- Rodriguez P, Krishnan R and Sundaram C V 1984 *Bull. Mater. Sci.* **6** 339
- Sahu H K and Jung P 1984 (to be published)
- Sharma B D, Sonnenberg K, Antesberger G and Kesternich W 1978 *Philos. Mag.* **A37** 777
- Sinha R K and Kakodkar A 1983 in *Proceedings of radiation effects in solids* (Bombay: Bhabha Atomic Research Centre) in press
- Sundaram C V 1984 Sixth IAEA RCA Working Group Meeting, Reactor Research Centre, Kalpakkam-603 102
- Tyagi A K, Nandedkar R V and Krishan K 1983 *J. Nucl. Mater* **114** 181
- Tyagi A K, Nandedkar R V and Krishan K 1983 *J. Nucl. Mater* **116** 29
- Tyagi A K, Nandedkar R V and Krishan K 1984 *J. Nucl. Mater* **122 & 123** 732
- Ullmaier H and Schilling W 1980 in *Physics of modern materials* (Vienna: IAEA publication SMR-46/105) p 301
- Varatharajan K, Tyagi A K and Nandedkar R V 1982 in *Proc. DAE symposium on nuclear physics and solid state physics* **25C** 562
- Vrijen J 1977 E C N Petten Report ECN-31
- Wagner W, Poerschke R, Axmann A and Schwahn D 1980 *Phys. Rev.* **B21** 3087
- Wagner W, Poerschke R and Wollenberger H 1982 *J. Phys.* **F12** 405
- Wollenberger H 1982 in *Point defects and defect interactions in metals* (eds) J I Takamura, M Doyama and M Kiritani (Tokyo: University of Tokyo Press) p 339