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# Non-Equilibrium Segregation in Metals and Alloys

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# Non-equilibrium segregation in metals and alloys

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[Plate 1]

The phenomenon of non-equilibrium segregation of solute and impurity atoms at interfaces in quenched materials is defined and the driving force and kinetics of the segregation are shown to differ significantly from those of reversible equilibrium segregation.

Large point defect supersaturations are produced during quenching, irradiation and sintering, and both enrichment and depletion of solute atoms at interfaces, associated with the flow of point defects to sinks, have been observed.

Some of the quantitative and qualitative experimental data on non-equilibrium segregation are described and the current understanding of the mechanisms and kinetics are summarized. Finally, some of the practical implications of non-equilibrium segregation, in terms of the effects on the deformation, fracture and mechanical properties, corrosion behaviour and structural stabilities of quenched and irradiated metals and alloys, are outlined and possible methods of inhibiting segregation are suggested.

## INTRODUCTION

The phenomenon of reversible equilibrium segregation of dilute solutes to interfaces in solids and the techniques for studying such segregation have been reviewed periodically during the past 15 years (Inman & Tipler 1963; Westbrook 1964; Hondros & Seah 1977). The driving force for this equilibrium segregation of elements to free surfaces, grain boundaries and other interfaces is the minimization of surface free energy; the segregation, particularly at grain boundaries, has been extensively studied because the mechanical and chemical properties and behaviour of metals and alloys can be dramatically affected (Hondros & Seah 1977).

A second type of segregation to interfaces was first suggested by the work of Westbrook and his colleagues who noted a marked increase in microhardness in the grain boundary regions of a number of quenched, dilute non-ferrous alloys and intermetallic compounds (see Westbrook 1964). The hardening effect was attributed to atomic segregation to the grain boundary regions during cooling, and direct experimental evidence of such segregation in quenched alloys has subsequently been obtained. This non-equilibrium segregation has only been observed during cooling at below a critical rate and the effect has been attributed to the existence of mobile solute atom–vacancy complexes at high temperatures, with the formation of a large vacancy supersaturation and the diffusion of these complexes to free surfaces and grain boundaries, where the vacancies are annihilated, during cooling.

The two main features of non-equilibrium segregation, by which it can in principle be distinguished from equilibrium segregation, are that its extent increases with increasing temperature and the alloy can be homogenized by suitably ageing it without further quenching since its lowest energy state corresponds to uniform solute distribution. In contrast, the equilibrium segregated state has, by definition, the lowest energy in a system exhibiting equilibrium segregation, and the magnitude of the effect decreases with increasing temperature.

Non-equilibrium segregation (and desegregation) of elements to free surfaces and other sinks, in binary, ternary and more complex ferrous and non-ferrous alloys, also occurs during irradiation. As in quenching, large point defect supersaturations can be produced during irradiation and the strong segregation effects observed are again related to the flow of these defects to sinks.

Some experimental observations of non-equilibrium segregation in quenched and irradiated materials are briefly described in the second section of this paper. The currently proposed mechanisms are summarized in the third section while the importance of the phenomenon in determining the mechanical, structural and chemical properties and behaviour of metallic systems are outlined in the final section.

## Experimental observations

### *Quenching*

A number of investigations of segregation during quenching have been made by directly measuring the corresponding changes of solute concentration near a vacancy sink. For example, Cundy *et al.* (1968) used electron energy loss measurements to study the segregation of magnesium to grain boundaries in Al 7 %Mg quenched at $3 \times 10^4$ K/s from 480 °C. A systematic study of solute segregation during quenching in aluminium alloys has been made by Anthony and coworkers, and reviewed by Anthony (1975). Aluminium alloys were air-cooled from near their melting point, and the resulting changes in the concentration of solute near vacancy condensation pits at the metal–oxide interface measured. Observations included enrichment, depletion and no effect.

Cadmium enrichment near the grain boundaries in Zn 0.1 at. % Cd alloys, cooled at 0.05 K/s from high temperature, has been detected by using a grain boundary dissolution – analytical technique (Bercovici *et al.* 1970). Also using scanning transmission electron microscopy – microanalysis techniques, Faulkner *et al.* (1977) have detected titanium enrichment to a level of about three times the matrix concentration in a zone 200–300 nm thick at a grain boundary in a solution treated and aged austenitic steel; this segregation has been attributed to quenching during heat treatment (R. G. Faulkner 1978, personal communication). In addition, it has been shown by using a semiquantitative autoradiographic technique, that boron segregation occurs to the grain boundary regions of a type 316 austenitic steel containing 10 μg/g boron during cooling at a rate of *ca.* 50 K/s from the higher solution treatment temperatures in the range 900–1350 °C (figure 1, plate 1); no segregation was produced on cooling at 500 K/s from the same temperatures (Williams *et al.* 1976). Essentially similar observations of grain boundary segregation in a relatively slowly cooled austenitic steel have been made by Sen (1976).

In addition, there is a wealth of indirect experimental evidence for non-equilibrium segregation in quenched alloys. The results of microhardness traverses across grain boundaries and adjacent grains in lead with minor additions of tin, indium and gold (Westbrook & Aust 1963; Aust & Westbrook 1965; Aust *et al.* 1966), and in ZnAl and SnPb alloys (Aust *et al.* 1968) show considerable grain boundary quench-hardening extending for many micrometres on either side of the grain boundaries (figure 2).

Chemical concentration profiles in the regions of the grain boundaries and their correlation with increases in microhardness have not been directly measured. Nevertheless, all these observations have been interpreted on the basis of a vacancy–solute interaction which is positive

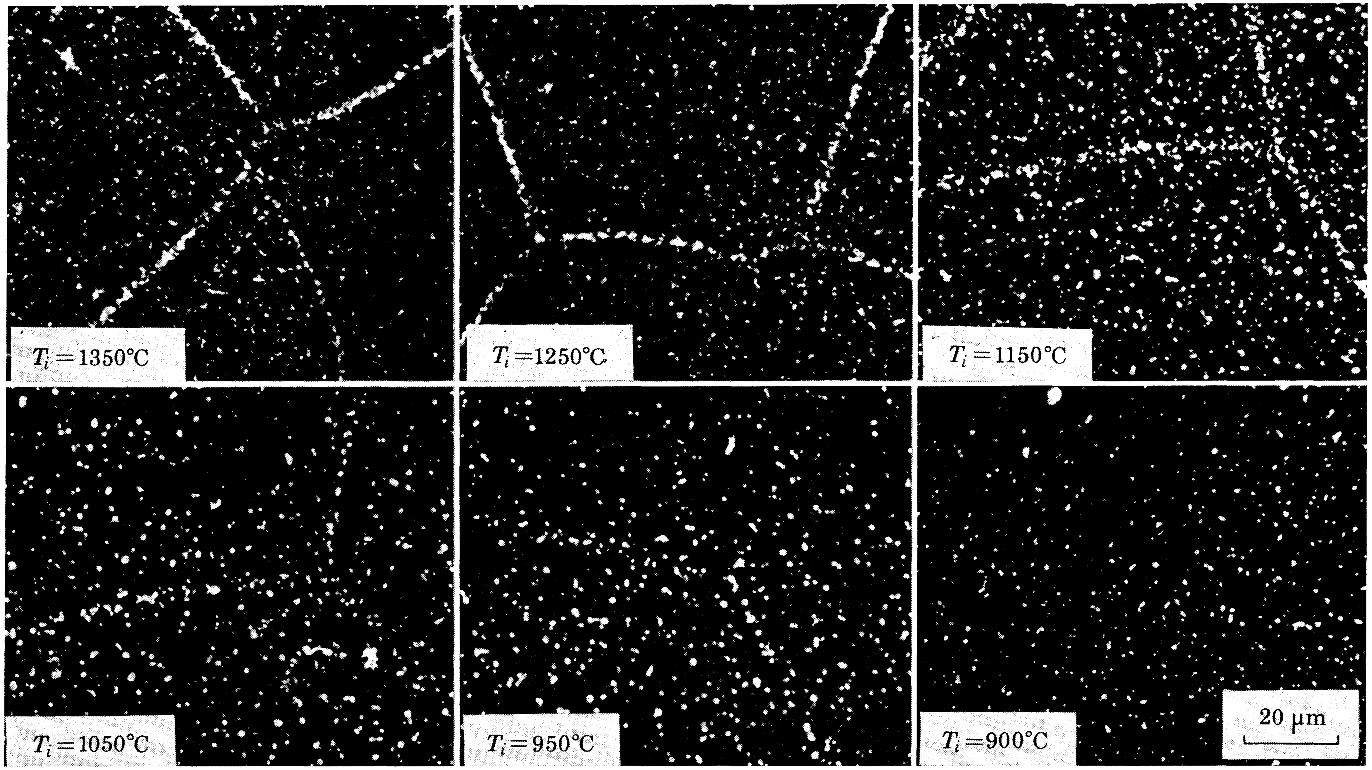

FIGURE 1. Optical autoradiographs of type 316 steel specimens solution heated at 1350 °C for 0.5 h, furnace cooled to a temperature $T_i$ in the range $900° \leqslant T_i \leqslant 1350$ °C, held for 0.5 h and cooled at 50 K $s^{-1}$ to room temperature (Williams *et al.* 1976).

and large relative to the thermal energy, $kT$, and a relatively mobile atom–vacancy pair which allows solute enrichment at grain boundaries during the quench (Bercovici *et al.* 1970; Aust *et al.* 1968; Anthony 1969; Hanneman & Anthony 1969; Williams *et al.* 1976). Hardening was attributed to the formation of solute-rich metastable or stable clusters (Aust *et al.* 1968) or vacancy loops stabilized by the solute atoms (Hanneman & Anthony 1969) near the grain boundaries.

Grain boundary quench-softening can also occur. Both relatively pure metals (lead, zinc and tin) and dilute alloys of ZnAu, ZnCu, PbCa, PbU and SnSb exhibit this effect (Westbrook & Aust 1963; Aust & Westbrook 1965; Aust *et al.* 1966; Aust *et al.* 1968) (figure 2). It has been suggested that in these binary alloys, depletion of the solute atoms near vacancy sinks occurs because of a weak or negative solute–vacancy binding energy and a solute diffusivity greater than the solvent diffusivity (Aust *et al.* 1968; Anthony 1969; Hanneman & Anthony 1969). In the pure metals and in binary alloys depleted in solute atoms in the zones adjacent to the grain boundaries, defects resulting from quenched-in vacancies cannot form and grow, and hence softening occurs in these regions.

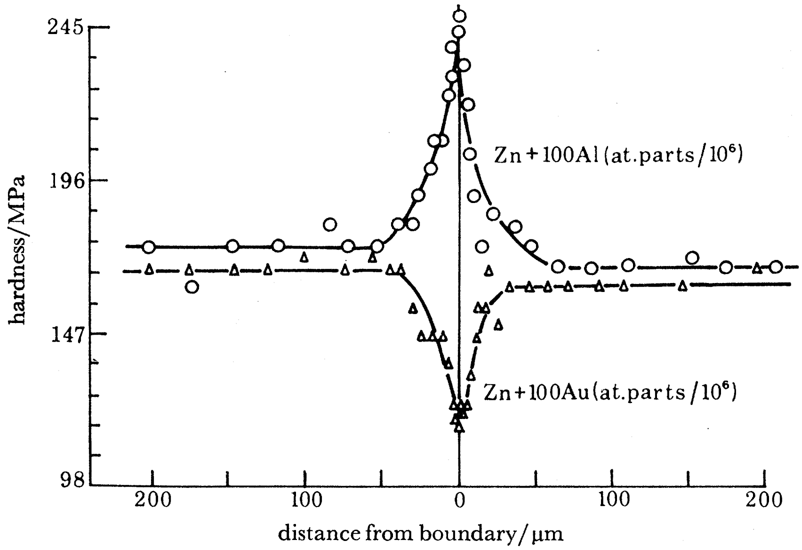

FIGURE 2. Hardness–distance profiles near a grain boundary in ZnAl and ZnAu alloys, 1 g load (Aust *et al.* 1968).

Segregation may well be more complicated in ternary or commercial alloys containing a variety of alloying and impurity elements; in such cases, there is a possibility of interaction between two or more solute or impurity atoms such that the segregation characteristics of one are affected by the other(s). Some evidence for such an interaction has been reported (Westbrook 1964; Aust *et al.* 1968).

### *Observations of segregation under irradiation*

Under irradiation, as in quenching, strong point defect fluxes are induced in the neighbourhood of point-defect sinks. The most accessible sink is the surface, so that by using sputter profiling together with a surface analysis technique such as secondary-ion mass spectrometry (s.i.m.s.) or Auger electron spectroscopy (A.e.s.), a composition profile of the segregating element can be obtained. Typical results of such an experiment are shown in figure 3 for a very dilute nickel alloy containing manganese and silicon irradiated at 500 °C to a surface dose of 46 displacements per atom (d.p.a.) (Marwick & Piller 1977; Piller & Marwick 1978). The composition of the alloy was initially uniform, but as a result of irradiation the inhomogeneity shown has developed, with the silicon and manganese atoms having moved in opposite directions. The explanation for the shape of the profiles is that under irradiation the quasi-steady-state point defect profile has a sharp peak at *ca.* 20 nm, falling steeply to almost zero at the surface, and tailing off into the bulk of the crystal. It follows that the measured profiles are a result of manganese atom movement against the flow of point defects, whereas silicon atoms have migrated out of the defect-rich region. The atomic mechanisms by which these movements are thought to take place are surveyed in the next section.

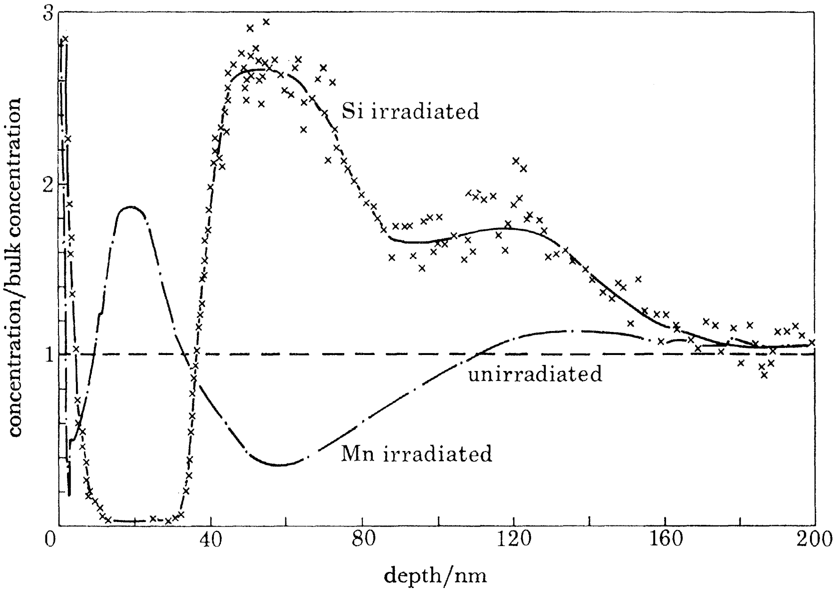

FIGURE 3. The depth distribution of manganese (—·—) and silicon (×) concentration as measured by s.i.m.s. in a dilute nickel alloy after irradiation at 500 °C (Marwick & Piller 1977). Manganese atoms have moved into, and silicon atoms out of, the defect-rich region centred on 20 nm depth. The concentrations of both solutes in an unirradiated control sample are indicated by the dashed line.

The segregation of silicon in nickel and FeCrNi alloys has been intensively studied because of its importance as an element which reduces void swelling in fast-reactor steels (Harries 1978*a*). As a consequence of the segregation behaviour illustrated in figure 3 silicon is strongly enriched at sinks. For example, enrichment of silicon at the surface of an experimental 18Cr8Ni1Si steel irradiated to 15 d.p.a. at 600 °C has been observed by Okamoto & Wiedersich (1974), while the temperature dependence of the enrichment in Ni 1 at.% Si has been studied by Rehn *et al.* 1978. The largest amount of segregation occurred at 560 °C (figure 4), and a layer of $Ni_3Si$ was formed on the surface, enrichment of silicon having been sufficient to induce a phase change.

The behaviour of solutes in nickel falls into two classes, with beryllium behaving like silicon (Pronko *et al.* 1977), and other solutes being depleted at the surface, like manganese in figure 3.

For example, figure 4 shows results for molybdenum, titanium and aluminium as well as the silicon data at 560 °C already referred to. These results have been confirmed by low energy ion irradiation (Marwick & Piller 1978), which also shows that chromium behaves in a similar way.

At internal sinks in a metal, depletions are experimentally harder to measure, although depletion of $\gamma'$ precipitates around interstitial loops in Ni 6.35 % Al has been reported by Potter & Hoff (1976) and Potter & Ryding (1977). Segregation to sinks, on the other hand, has been intensively studied. Kenik (1976), using s.t.e.m. analysis, was able to show enrichment of silicon at faulted loops in a modified 316-like steel containing 1 % silicon, irradiated to 1 d.p.a. at 626 °C. At higher doses, copious precipitation of $Ni_3Si$ was observed in such materials with *ca.* 1 % Si (well below the solubility limit). It appears to be associated with dislocation loops (Barbu & Ardell 1975) with silicon enrichment at the loops exceeding the solid solubility limit.

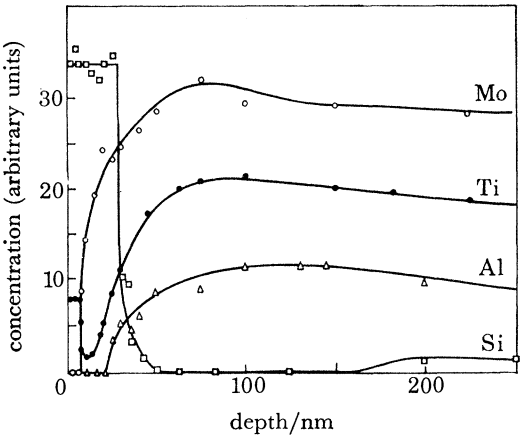

Figure 4. A.e.s. measurements of the depth distributions of the solutes in a series of 1 % nickel alloys after ion irradiation at the following doses and temperatures: Mo, 11.2 d.p.a. at 617 °C; Ti, 8.5 d.p.a. at 560 °C; Al, 10.7 d.p.a. at 620 °C; Si, 8.5 d.p.a. at 560 °C. (Rehn *et al.* 1978). Si has been enriched at the surface to a concentration in excess of the solubility limit, while Mo, Ti and Al have all been depleted.

In addition to changes in the distribution of minor alloying elements, segregation of major constituents of alloys has been observed. For example, enrichment of nickel and depletion of chromium at the surface of Fe18Cr8Ni1Si following irradiation to 15 d.p.a. at 600 °C was noted by Okamoto & Wiedersich (1974). Johnston *et al.* (1977) were able to depth-profile the zone of altered composition beneath an ion-bombarded surface, as did Marwick (1978). Bloom *et al.* (1973) and Clausing & Bloom (1975) found enrichment of nickel and iron and depletion of chromium in a narrow (*ca.* 3 nm) zone at grain boundaries in type 304 stainless steel irradiated in EBR-II at doses up to $10^{24}$ neutrons $cm^{-2}$. Sklaad *et al.* (1976) have made similar observations in reactor-irradiated Nimonic PE16, where nickel was enriched and chromium and iron were depleted at grain boundaries. Similar segregation at voids in another high-nickel alloy has recently been measured by Marwick *et al.* (1978). These results show that even the base composition of an alloy can be altered near sinks.

### *Other observations of non-equilibrium segregation*

There are several additional situations in which vacancy fluxes may be induced, and a few observations of solute segregation have been made in these cases. For example, for sintering necks between dissimilar alloys, Kuczynski *et al.* (1960) found evidence for solute segregation in copper and silver alloys. Whittenberger & Dayananda (1970) found enrichment of manganese and depletion of zinc at pores that grew in a copper diffusion sample annealed at 850 °C. In general, the growth or shrinkage of pores must be associated with a vacancy flow, and segregation of alloy components is then a possibility. A related observation is that of Jorgensen & Westbrook (1964) who measured segregation of nickel and magnesium to grain boundaries in sintered $Al_2O_3$.

## MECHANISMS AND KINETICS

In this section the present understanding of the microscopic mechanisms and the kinetics of non-equilibrium segregation will be surveyed. Space does not permit an exhaustive presentation of the theory; rather the physical understanding which has been developed will be emphasized. Segregation under irradiation is in some ways conceptually simpler than in quenching, because the concentrations of defects (self-interstitials and vacancies), and hence the defect fluxes, reach a quasi-steady-state soon after the beginning of irradiation in a typical experiment at 300–700 °C (Sharp 1969). The concentration profiles of the defects, and the resulting solute segregation, can be readily calculated numerically by using suitable physical models (see for example Yoo & Mansur 1976; Johnson & Lam 1976).

### *Vacancy fluxes*

Solute movement in a vacancy flux can be simply regarded as resulting from two effects. The first is due to the diffusion coefficient of solute atoms being different from that of solvent atoms (Anthony & Hanneman 1968; Anthony 1969). In an irradiation-induced vacancy flux $J_v$ the solute flux $J_u$ due to this mechanism alone, relative to the surface of a sink, can be written for the case of negligible solute–vacancy binding in a dilute alloy as

$$J_u = -C_u (D_u^* - D_s^*) J_v / D_v C_v, \tag{1}$$

where $C_u$ and $C_v$ are the concentrations of solute and vacancies, $D_u^*$ and $D_s^*$ are the solute and solvent tracer diffusion coefficients, and $D_v$ is the vacancy diffusivity. The equation shows that a fast diffusing solute with $D_u^* > D_s^*$ moves counter to the vacancy flux. It is believed that this is the explanation for the depletion of solutes at sinks shown in figures 3 and 4.

Opposing any tendency to move against the vacancy flux, and especially effective at lower temperatures, is the propensity of some solutes to form bound complexes with vacancies. If dissociation of the complex is sufficiently improbable, it can be thought of as diffusing independently. At a sink the vacancy is lost and the solute atom remains. Thus, the net flow of solute by this means is towards the sink (Anthony 1969).

A comprehensive description of solute segregation in a vacancy flux is provided for dilute alloys by the theory of Howard & Lidiard (1968). The key parameter in this theory that decides the direction of segregation is the ratio $W_3/W_1$ where $W_3$ and $W_1$ are the jump frequencies of a vacancy away from and around a solute atom. This ratio can in principle be determined from extensive diffusion measurements (see the review by Le Claire (1978)) but very few alloys have been sufficiently studied for this to be possible. $W_3/W_1$ ratios were derived from the aluminium quenching measurements already referred to (Anthony 1975).

In concentrated alloy systems, where solute–defect binding can be neglected, segregation under irradiation is thought to take place by an inverse Kirkendall effect (Marwick 1978) with slowly diffusing alloy components being enriched at sinks. A similar model has been put forward to explain segregation in the sintering of dissimilar alloys (Kuczynski *et al.* 1960).

### *Interstitial fluxes*

The presence of self-interstitials (Dederichs 1977) in an irradiated metal can lead to solute migration by the formation of an unstable mixed-dumbbell (Dederichs *et al.* 1978; Johnson & Lam 1976). For every diffusion process involving vacancies, there is an analogue in diffusion by this interstitialcy mechanism. However, solutes with interstitialcy diffusion coefficients higher than that of the solvent move parallel to the interstitial flux (Marwick & Piller 1977) and tightly bound interstitial – solute atom complexes move in the same direction. This is thought to be the reason for the special behaviour of silicon and beryllium (see preceding section) which, being undersized, tend to attract interstitials (Okamoto & Wiedersich 1974). However, silicon may also segregate as a result of vacancy binding (Piller & Marwick 1978). This is a special case of the general point that vacancy and interstitial fluxes need to be simultaneously taken into account in modelling segregation under irradiation, and their effects cannot yet be distinguished experimentally. The kinetics of segregation are complex, but one generally expects the greatest amount of segregation at the peak void swelling temperature (Wiedersich *et al.* 1977).

### *Quenching*

In quenching one has the possibility of any or all of the vacancy effects already mentioned, including both enrichment and depletion of solute at sinks, with the added complication of time-dependent vacancy flux and temperature. A complete treatment probably requires numerical solution of the diffusion equations. This has not yet been done, but a number of studies have identified the main features (Hanneman & Anthony 1969; Williams *et al.* 1976). Solute enrichment at sinks appears to be of particular interest technologically, and the picture that has emerged for the corresponding case of strong vacancy–solute binding will now be summarized.

At the initial (high) temperature, thermal equilibrium is established between three species: free vacancies, solute atoms and bound solute–vacancy pairs. All of these species are distributed uniformly, within the specimen. When the temperature is suddenly lowered, vacancy emission at sinks is reduced, so that the concentration of vacancies and solute–vacancy pairs nearby is also reduced, and therefore vacancies and pairs start to flow towards the sink. As pairs break up at the sink, the local solute concentration is increased. While quantitative predictions as to the amount of segregation under given conditions cannot yet be made, the conditions for solute segregation to occur have been given by Williams *et al.* (1976) in terms of a dimensionless parameter $\Lambda$ for each diffusing species:

$$\Lambda = kT_i^2 D(T_i)/\Theta E_m d^2. \tag{2}$$

Here $k$ is Boltzmann's constant, $T_i$ the quench temperature, $D(T_i)$ the diffusion coefficient at the quench temperature, $\Theta$ the initial quench rate in kelvins per second, $E_m$ the migration energy of the species of interest, and $d$ some characteristic length, for example the grain size, or the spatial resolution of a measuring technique. The necessary conditions for segregation can be stated as:

(1) There must be sufficient time for solute–vacancy pairs to diffuse a distance $d$ to the sink during the quench, i.e.

$$\Lambda_p > \Lambda_0,$$

where $\Lambda_0$ is a constant of order unity which depends on the details of geometry and the quench programme.

(2) Vacancies must be sufficiently slowly diffusing for appreciable vacancy gradients to be set up during quenching;

$$\Lambda_v < \Lambda_0.$$

(3) A similar condition is needed for impurity atoms. This only applies where the impurity can diffuse by some other means than formation of a solute–vacancy pair. For example, it might diffuse interstitially, in which case back-diffusion of solutes may considerably reduce the amount of segregation.

(4) For segregation to be appreciable, new solute–vacancy pairs must form as existing pairs flow away to sinks.

$$2\Lambda_p(D/D_p)\ (d^2/l^2) > 1,$$

where $D$ is the larger of the diffusion coefficients of vacancies and isolated impurity atoms at $T_i$, and $l$ is the mean vacancy – impurity atom spacing.

(5) In addition to the conditions above, for the strong binding model to be applicable, the lifetime of a solute–vacancy pair should be at least comparable with the time it takes to diffuse to a sink. This leads to the condition

$$\exp\ (E_B/kT_i) > \alpha\nu_0 d^2/D_p,$$

where $\alpha$ is a numerical factor *ca.* 1, $E_B$ is the binding energy of the pair, and $\nu_0 \approx$ the vacancy jump frequency.

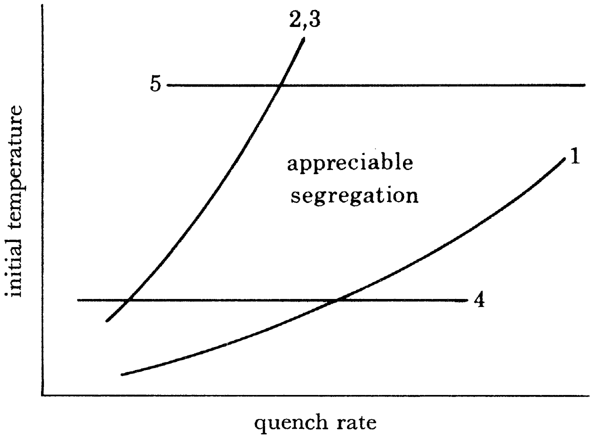

FIGURE 5. Schematic indication of the conditions in which appreciable segregation to sinks during quenching will occur, according to the model of Williams *et al.* (1976). The numbered curves correspond to the necessary conditions given in the text.

These conditions place limits on the range of quench rates and temperatures for which segregation will occur, as shown schematically in figure 5. The centre region corresponds to conditions in which segregation will occur, and the numbered curves correspond to the limits imposed by the conditions applying to the strong binding case. For weak binding, depletion at a boundary is more likely, at least for fast diffusing solutes (Hanneman & Anthony 1969). The conditions are less restrictive for this case, and correspond to 1, 2 and 3 above.

## Practical implications

Equilibrium segregation can affect a wide range of metallurgical properties and processes. Hondros & Seah (1977) have classified the effects into two broad categories, namely (i) mechanical phenomena such as temper embrittlement in steels in which the segregation modifies the grain boundary bonding or cohesion, and (ii) processes such as surface and intergranular corrosion and precipitate growth in which the segregation effects the kinetics. It is evident that non-equilibrium segregation can similarly affect the properties and behaviour of materials. Thus, surface and grain boundary energies of type 316 steel are reduced as a consequence of boron segregation (Mortimer 1975), and non-equilibrium segregation enhances the intergranular corrosion of ZnAl alloys (Hanneman & Aust 1968) and austenitic steels (Aust *et al.* 1967), accelerates precipitation in austenitic steels (Aust *et al.* 1967; Faulkner & Caisley 1977; Faulkner 1978, personal communication) and inhibits the grain growth of $Al_2O_3$ during sintering (Jorgensen & Westbrook 1964).

While the equilibrium segregation of solute is restricted to, for example, the width of the grain boundary, the non-equilibrium segregation can extend a considerable distance from the interface. Thus the non-equilibrium segregation may effect processes such as deformation not only at the interface but a significant distance away as reflected in the increases in microhardness referred to earlier (figure 2).

Extensive quantitative data are obviously required on the effects of non-equilibrium segregation at interfaces on the properties and behaviour as a function of both material and heat-treatment parameters. However, non-equilibrium segregation can be minimized and possibly avoided by maintaining a low solution treatment temperature and fast cooling rate. Alternatively, a 'low' temperature heat-treatment can be applied to allow diffusion of the species away from the interface or the formation of a precipitate which removes the segregating element (for example, $M_{23}(C, B)_6$ precipitation eliminates boron segregation in austenitic steel) (Williams *et al.* 1976). If heat-treatment control is not possible, the segregation tendencies of the principal solute or impurity atoms may be suitably modified by other additions to the material (Westbrook 1964; Aust *et al.* 1968; Hanneman & Aust 1968).

Non-equilibrium segregation produced during irradiation is an important phenomenon in determining the void swelling behaviour of alloys (Harries 1978*a*). It has been observed (Johnston *et al.* 1977) that void swelling, enhanced by factors of 5–10, occurs in subsurface regions and just beyond the void-free zone adjacent to grain boundaries in Ni ion irradiated austenitic steels and alloys. The enhanced subsurface void swelling was associated with regions depleted of nickel and silicon and enriched in chromium, that is compositions with inferior void swelling resistance compared with the bulk alloys. In addition, it has been considered theoretically (Mansur 1977) that the observed plating of elements on void surfaces and dislocations modifies the sink strengths and bias terms respectively for vacancies and interstitials. Furthermore, the segregation of elements such as silicon reduces their concentrations in solution where they are effective in limiting void swelling by acting as defect or inert gas atom traps.

The effects of non-equilibrium elemental segregation during quenching or irradiation on mechanical properties and fracture behaviour at high temperatures have not been systematically studied. It is considered, however, that segregation of elements to grain boundaries may affect their ability to act as perfect sources and sinks for vacancies; in addition, the surface ($\gamma_s$) and grain boundary ($\gamma_{gb}$) energies and, hence, the effective surface energy for grain boundary fracture ($2\gamma_s - \gamma_{gb}$) could be significantly reduced. Both of these factors would affect intergranular crack nucleation and growth, and hence the creep–rupture ductilities in unirradiated and irradiated alloys (Harries 1978*b*).

Finally, the hardening and embrittlement of pure iron and commercial low alloy, light water reactor pressure vessel steels produced by neutron irradiation at 280 °C increases with increasing copper, phosphorus, vanadium and nickel contents (Smidt & Watson 1972; Smidt & Sprague 1973). While it has been demonstrated that the addition of 0.3 % copper to pure iron increases the number density and reduces the average size of the irradiation induced defect clusters, the possibility that plating of atoms of copper and/or the other elements occurs on the vacancy clusters or dislocation loops, thereby increasing their stability, has hitherto not been considered.

## CONCLUSIONS

Segregation and desegregation of alloying elements due to quenching or irradiation, and in some other non-equilibrium situations, have been demonstrated in a variety of alloy systems. The common feature of the circumstances in which non-equilibrium segregation occurs is that fluxes of vacancies and (for irradiation) interstitials are present. Since not all of the components of alloys respond to the point defect fluxes in the same way, net segregation can result from the atomic movements which accompany the defect fluxes. While the basic mechanisms are fairly well understood, a full quantitative description of the segregation is only available for a few alloys, and even then only for segregation due to the action of a vacancy flux.

The consequences of non-equilibrium segregation have been most extensively investigated for the case of irradiated metals, where void swelling and possibly other properties are affected by the distribution of certain alloying elements, especially silicon. Segregation due to quenching of unirradiated metals also can affect the mechanical properties and corrosion resistance, possibly by altering the composition and structure of alloys near grain boundaries.

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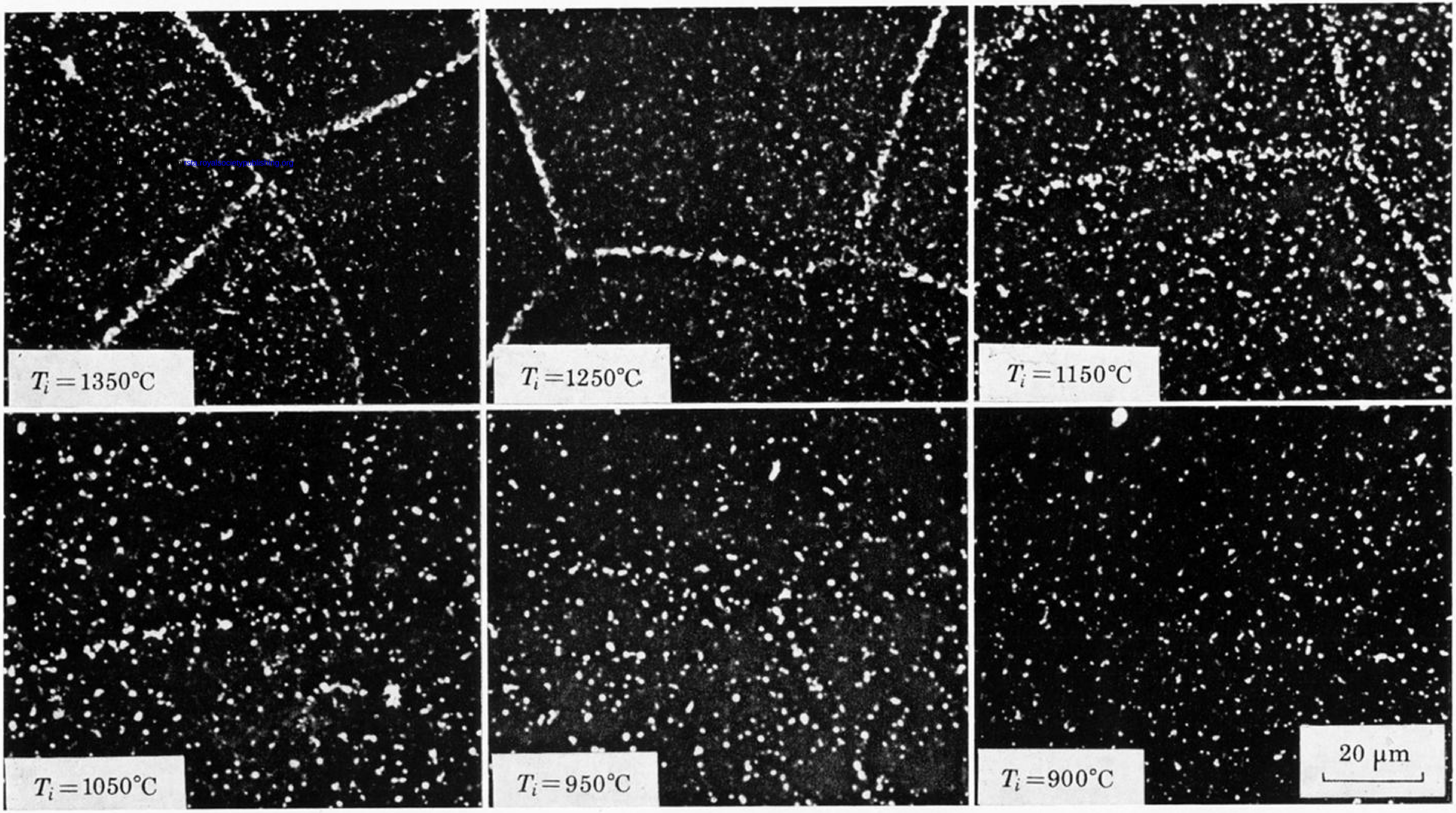

FIGURE 1. Optical autoradiographs of type 316 steel specimens solution heated at 1350 °C for 0.5 h, furnace cooled to a temperature $T_i$ in the range $900° \leqslant T_i \leqslant 1350$ °C, held for 0.5 h and cooled at 50 K s$^{-1}$ to room temperature (Williams *et al.* 1976).