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V. PERFORMANCE IN SERVICE: LOW TEMPERATURE EFFECTS

The role of residuals and alloying elements in temper embrittlement

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A brief review of the general metallurgical properties of temper brittleness in low alloy steels emphasizes that this intergranular embrittlement is sensitive to essentially two categories of independent variables: the chemical composition of the grain boundaries (segregation of the solutes on an atomic scale), as well as the 'mechanical–microstructural' parameters of the alloy (microstructure and strength of the matrix, morphology of the carbides and grain boundaries, etc.). This paper, essentially devoted to the former, reviews and discusses the available segregation data in the light of recently proposed models. The segregation potencies and embrittling powers of the various impurities are compared, and their dependence on the alloy's metallic components through chemical interaction between both types of solutes is particularly emphasized. The link between segregation and solubility in multicomponent systems and its use as a predictive means for impurity segregations is outlined. The discussion aims at showing that temper embrittlement is in no way a unique phenomenon, specific to low alloy steels, as was formerly considered, but rather a strikingly illustrative case of multicomponent segregation induced embrittlement, where some metallic alloying elements, although not embrittling *per se*, can drastically enhance the segregation of residual impurities, while some others can be used as scavengers to alleviate it.

1. INTRODUCTION

Reversible temper embrittlement (r.t.e.) has been a recognized metallurgical problem for almost a century, and has been reviewed frequently and extensively over the past decades (Woodfine 1953; Low 1964; McMahon 1968; Capus 1968; Narayan & Murphy 1973; Mulford 1974; Guttmann 1974; Clayton 1977; Briant & Banerji 1978). Before 1970 these reviews were essentially historical in style and phenomenological in nature: since there were no experimental means of getting at the basic mechanisms of the phenomena, which were therefore poorly understood, the only progress that could be made consisted in completing its metallurgical characterization in an effort to indirectly confirm tentative models. Only recently has a clearer picture begun to emerge, thanks to the advent of modern techniques, notably Auger electron spectroscopy (A.e.s.), for the chemical analyses of surfaces, and to their immediate and intensive application to r.t.e. studies. Although a complete understanding of the mechanism of r.t.e. has not yet been attained, sufficient progress has been achieved lately to allow the phenomenon to be presented in a way that will encompass both its phenomenological characteristics and its underlying mechanisms.

2. DEFINITION AND GENERAL CHARACTERISTICS OF R.T.E.

Temper embrittlement is the loss of fracture toughness which occurs when alloy steels are held in or slowly cooled through the temperature range between approximately 375 and 600 °C.

The embrittlement is manifested as an increase of the transition temperature in impact tests, accompanied by a change in the low temperature brittle fracture mode from cleavage to intergranular. This shift between a non-embrittled and embrittled condition of the same steel has become a generally accepted 'measure' of the degree of temper embrittlement.

As emphasized by Mulford (1974) and Guttmann (1974), the occurrence and extent of the embrittlement are determined by two categories of more of less independent variables:

(*a*) First, the impaired cohesion of the boundaries is induced by a considerable alteration of their chemical composition, since the simultaneous segregation of several atomic species occurs upon tempering at certain temperatures. Two types of solute atom have to be present in the steel for the phenomenon to occur in its typical form.

Certain residuals, which belong to Groups 4A to 6A of the Periodic Table (Sb, P, As and Sn essentially) are basically responsible for the embrittlement, and they possess very large segregation potencies, i.e. their enrichment ratio, β,† is of the order of 10^2–10^3. They are efficient embrittlers even at minute bulk contents, e.g. *ca.* 10 μg/g for P, *ca.* 100 μg/g for Sb and Sn, which correspond to a small atomic percentage in the grain boundaries. The time, temperature, and concentration dependences of embrittlement and segregation appear qualitatively similar: both increase with the nominal impurity concentration, and obey 'C-curve' kinetics. The 'reversibility' of the embrittlement (e.g. at 650 °C) is obviously the result of the decrease in maximum segregation as the tempering temperature is increased.

The metallic alloying additions of the transition series, although less potent segregants (β = 2–10) also segregate to the boundaries in the presence of impurities, and profoundly influence the occurrence and magnitude of the embrittlement due to the latter elements; however, their effect becomes manifest only at the 1 % (Ni, Cr, Mn) or 0.1 % (Mo) bulk level. Plain carbon steels, in which metallic additions are 'absent' (i.e. below 0.5 %), have been reported to be immune to r.t.e. even in the presence of impurities. At given impurity contents, alloying elements like Ni, Cr and Mn enhance embrittlement, the association of Ni and Cr being particularly deleterious, while the stronger carbide formers like Mo, V and W are able to reduce or retard it in certain concentration ranges. This critical role of alloying elements has conferred to r.t.e. both its mysterious and specific characters compared with other segregation phenomena, as well as its technological severity in high strength low alloy steels from which high performances in service are required.

(*b*) For a given intergranular composition, i.e. for a given loss of boundary cohesion, the fracture process is affected by the material's microstructural and mechanical properties, which, if not necessarily able to induce intergranular fracture by themselves, can profoundly modify the degree of embrittlement.

The relative importance of these parameters has not always been clearly distinguished, since the fracture response of the material integrates all of them. This is so, for instance, for the well known tendency of the prior austenite grain boundaries to fracture preferentially, which could be due either to preferential segregation or to preferential crack propagation.

In the present paper the emphasis will not be on the role of the residuals *per se* but rather on their behaviour within the framework of the interactions between them and the metallic solutes, which has recently emerged as the clue to the understanding of r.t.e.

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† β is the ratio of grain boundary to bulk concentration.

3. Experimental evidence for synergistic equilibrium segregation of residuals and metallic additions, and associated embrittlement

That the segregation of the embrittling agent(s) responsible for r.t.e. was of the equilibrium (Gibbsian) type was first suggested by McLean & Northcott (1948) and the precise nature of these impurities was identified soon afterwards (Balajiva *et al.* 1956; Steven & Balajiva 1959). By 1974, grain boundary analysis techniques had confirmed the equilibrium nature of impurity segregation (Viswanathan 1971; Glikman *et al.* 1972; Mulford 1974; Guttmann *et al.* 1974). This confirmation was based on the existence at each tempering temperature of a saturation value of the segregation, which varies inversely with temperature, in qualitative agreement with McLean's equation:

$$X_{\mathrm{I}}^{\phi}/(1-X_{\mathrm{I}}^{\phi}) \approx X_{\mathrm{I}}^{\mathrm{B}} \exp{(\Delta G_{\mathrm{I}}/RT)}, \tag{1}$$

where $X_{\mathrm{I}}^{\mathrm{B}}$ is the concentration of the impurity I in the bulk phase B, X_{I}^{ϕ} its concentration in the grain boundary ϕ, and ΔG_{I} its segregation energy (per mole), which is a constant.

The critical influence of the metallic element on the embrittlement, despite their supposedly non-embrittling character, and the occurrence of their segregation, at variance with their rather non-surface-active behaviour in iron, have led several workers to suggest that some kind of interaction between the metallic and metalloidic element was operating at one stage or the other of the segregation process (Woodfine 1953; Capus 1968; Low & Smith 1974; McMahon 1974; Guttmann 1974, 1975*a*). It is now recognized that none of the two-step and/or asymmetrical procedures assumed in the earlier models – like the presegregation of the metallic element M in the austenite (Capus 1968), its rejection by the growing carbides (McMahon, 1974), or a non-equilibrium vacancy-induced segregation of M – is necessary for the phenomenon to occur in its typical form, and that non-equilibrium effects are essentially transient.

Early qualitative A.e.s. experiments demonstrated that both the impurities and some alloying elements were segregated at the prior austenitic grain boundaries in the embrittled condition (Harris 1968; Marcus & Palmberg 1969; Joshi & Stein 1969). It was further shown that both types of solutes segregated at e.g. 500 °C and desegregated at 650 °C in a totally concomitant manner (Krahe & Guttmann 1973).

The ability of some metallic additions to enhance the segregation of metalloidic impurities appears clearly from a comparison between alloy steels and plain-C steels or FeI alloys.

Evidence for the segregation of P in pure iron, both in ferrite and in austenite, has been given by Ramasubramanian & Stein (1973) and Hondros (1965), and in plain-C steels by Inoue (1974) and Hondros & Seah (1976). However, it is seen from Seah's compilation (1977) that the enrichment ratio β_{P} of P in these systems is never in excess of 300, while in alloy steels, values of 500–2000 are obtained. As for Sn, enrichment ratios of 100–300 have been measured by Seah & Hondros (1973) in pure Fe, while a much larger value is found in alloy steels, and the same is true for Sb. Generally speaking, the alloying additions Ni, Cr and Mn, alone or in association, enhance the equilibrium segregation potencies of P, Sn and Sb by a factor of 5–10.

Another important effect of M additions is to increase the temperature dependence of the equilibrium segregation of I with respect to the binary system FeI as observed by Mulford *et al.* (1976*a*) and Guttmann *et al.* (1974).

The specific influence of Ni, Cr and Ni + Cr additions on segregation and resulting embrittlement has been extensively characterized in 3340 type steels (0.4 %C, 3.5 % Ni, 1.7 % Cr) by Mulford *et al.* (1976*a*, *b*). Figure 1 shows that Ni is much more effective than Cr in enhancing

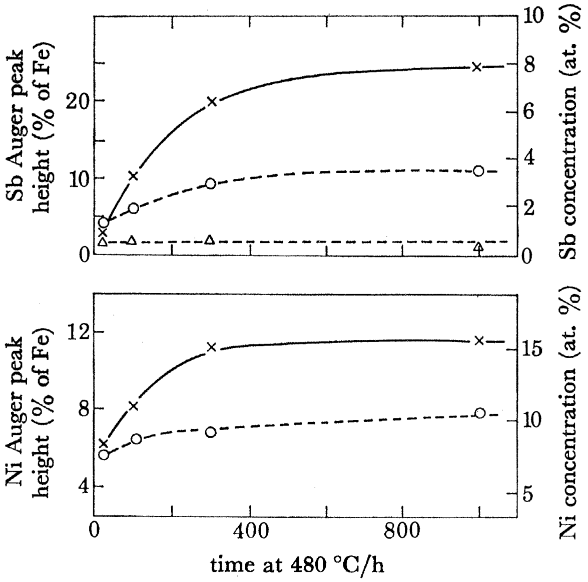

FIGURE 1. Influence of Ni (○), Cr (△) and Ni + Cr (×) additions on the segregation of Ni and Sb in 0.4 % C alloys at 480 °C, after Mulford *et al.* (1976*b*).

the segregation of Sb and associated embrittlement, the couple Ni + Cr being even more effective than would be expected from a purely additive effect. Conversely, Cr promotes the segregation of and embrittlement due to P more strongly than Ni, the effect of Ni + Cr being not very different from that of Cr alone.

The interactions between Ni and P, Sn and Sb respectively can be compared with the help of figure 2, where very good correlations are obtained between the grain boundary concentrations of Ni and the impurities (McMahon 1976). According to this figure, a given amount of Sb or Sn would induce a much larger segregation of Ni than the same amount of P, which reveals a much stronger attractive interaction with the former than with the latter. However, individual

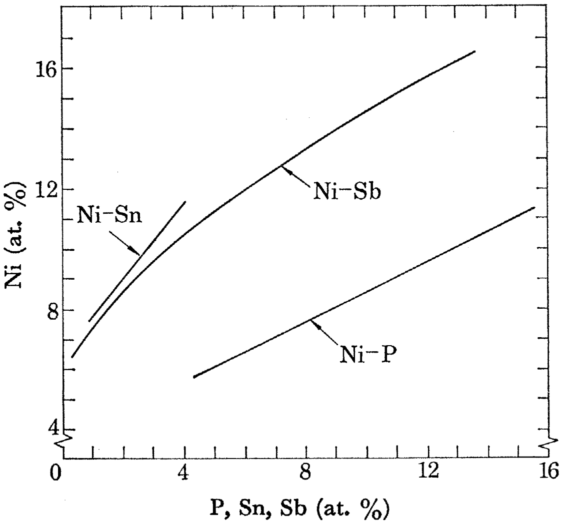

FIGURE 2. Correlations between the segregation of Ni and those of P, Sn and Sb in 3340 steels at various temperatures and for constant Ni and impurities concentrations, after McMahon (1976).

correlations of this type do not demonstrate the existence of an interaction. Only their relative positions are indicative of the different interactive strengths (Guttmann & McLean 1977).

The existence of strong M–I interactions can also be demonstrated by varying the concentration of either solute. Clayton & Knott (1977) have demonstrated that in 5 % Ni, 1.5 % Cr steels the enrichment ratios of Ni and Sb at equilibrium increase with Sb content (figure 3). This can only occur if a strong attractive Ni–Sb interaction exists, since in the absence of such an interaction β_{Ni} is constant and β_{Sb} decreases with increasing bulk Sb content, according to McLean's isotherm (equation (1)).

Manganese is in general a minor addition (less than 1 %) and its Auger peaks are not easily detected between those of O, Cr and Fe. However, its effect might be strong on Sb (Krahe & Guttmann 1973; Guttmann *et al.* 1974) and especially on P. Inoue (1974) and Inoue *et al.* (1974), who compared 3 % Cr steels, 3 % Mn steels and a plain carbon steel, have demonstrated that Mn strongly segregates and enhances the segregation of phosphorus, but somewhat less than does Cr.

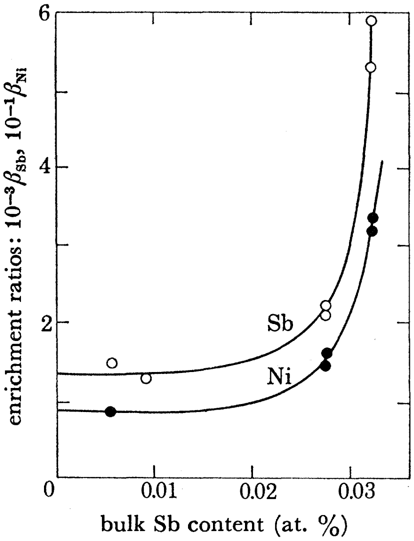

FIGURE 3. Influence of the bulk Sb content on the intergranular enrichment ratios of Ni and Sb in a 5 % Ni, 1.5 % Cr steel at 520 °C, after Clayton & Knott (1977).

The role of molybdenum is of central importance in the interpretation as well as in the prevention of r.t.e. (for a review, see Wayman *et al.* (1977)). Recent work by Guttmann *et al.* (1977) on 20CND 10–10 steels (0.2 % C, 2.7 % Cr, 1 % Ni, 0.5 % Mn, 0.4 % Mo) has unambiguously demonstrated its equilibrium segregation within a few monolayers of the boundary. In ternary FeMoP alloys, increasing the bulk Mo content from 0.5 to 2 % reduces the segregation of phosphorus and induces its partial precipitation into $\mathrm{Mo_3P}$ (Wayman *et al.* 1978): Mo acts essentially as a scavenger for P, in complete contrast to Ni, Cr and Mn. In alloy steels, Mo exhibits a more complex behaviour which cannot be understood without taking into account the role of carbon (Dumoulin *et al.* 1979). As the Mo content is increased from 0 to 1.1 %, a minimum appears in the embrittlement curve (figure 4). Sputtering experiments show that the decreasing part of the curve (from 0 to 0.7 % Mo) is associated with segregated Mo at the boundaries, indicating that at least part of the Mo is in solution within the matrix, while on the ascending part (i.e. *ca.* 1.1 %) Mo is precipitated at the boundaries (and probably also in the grain interior) in the form of carbides. Also, the kinetics of embrittlement and P segregation are considerably modified by Mo since a much longer time is needed to reach the equilibrium values of these properties in Mo-bearing than in Mo-free steels (Guttmann *et al.* 1977; McMahon *et al.* 1977).

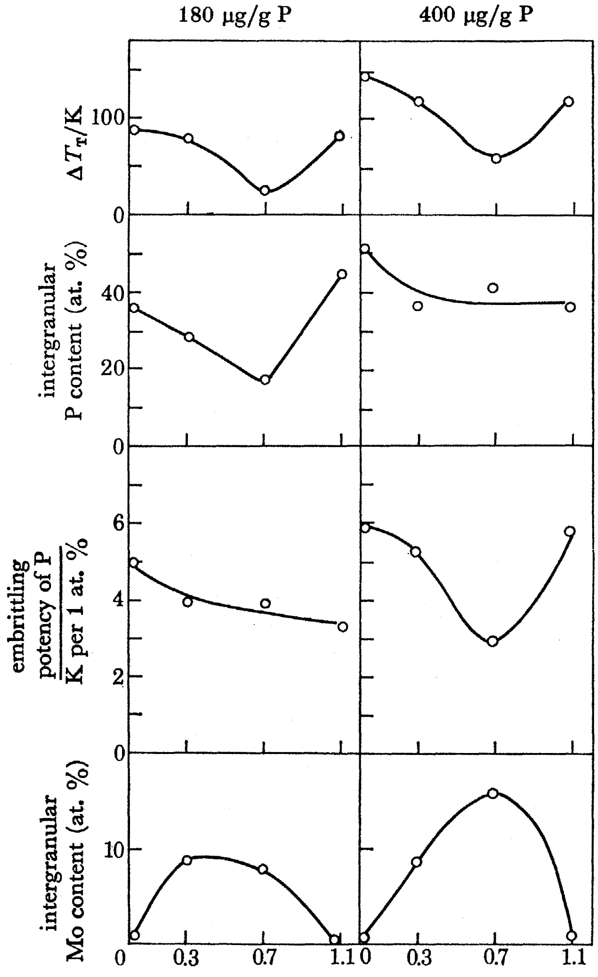

FIGURE 4. Variation of transition temperature shift ΔT_T, grain boundary P and Mo concentrations, and embrittling potency of P, as a function of nominal Mo content in 20CND 10 steels, after Dumoulin *et al.* (1979).

The grain boundary chemistry of the 20CND 10-10 steel (figure 5) strikingly illustrates the complexity of segregation processes in low alloy steels, since the majority of the solutes are found to segregate: P, Sn, Ni, Cr, Mn, Mo and Cu. Copper is somewhat special in r.t.e. Although it can be considered as an unwanted 'residual', coming from recycled scrap, it is neither a metalloid nor a transition metal. Since it does not induce intergranular brittle failure of the above alloy in the absence of other impurities, it cannot be ascertained whether it is able to segregate alone without embrittling, or whether it cosegregates with P only as a result of the strong Cu–P interaction, as also observed by Hasegawa *et al.* (1975), and participates in the embrittlement.

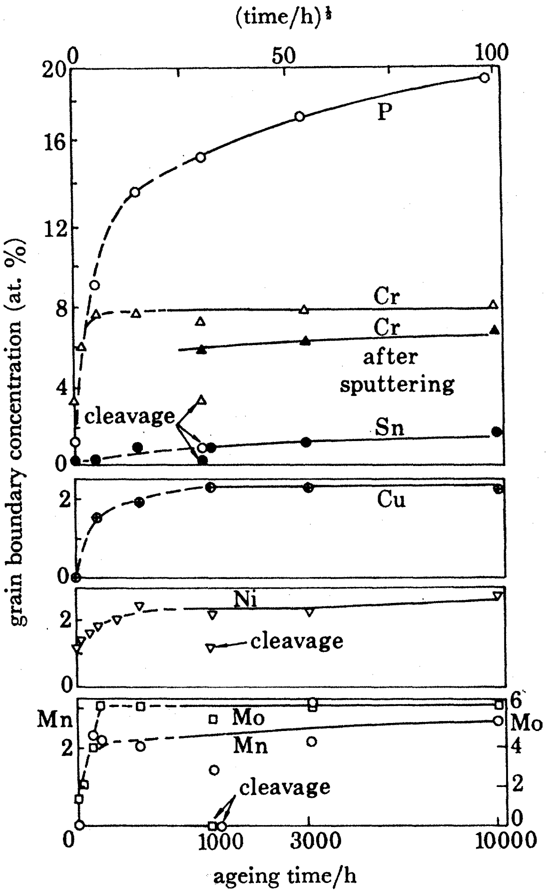

FIGURE 5. Long time segregation kinetics of 20CND 10-10 steel at 500 °C, after Guttmann *et al.* (1977).

4. THE THERMODYNAMICS OF COSEGREGATION

(*a*) *Theory*

Because of the high concentrations of both types of solutes encountered in grain boundaries, the chemical interactions between atoms cannot be neglected, i.e. the solution behaviour of the grain boundaries cannot be considered ideal as in McLean's model (equation (1)). A convenient, if not totally realistic, formalism allowing this phenomena to be handled in a straightforward way is the regular ternary solution model, in which the preferential interaction between the impurity I and the metallic element M is completely described by a single parameter which is positive when the former is attractive, i.e. when the affinity of the impurity for M is larger than for Fe.

The segregation equations of I and M keep the general form of (1), except that the segregation energies are no longer constant but depend on the M–I interaction and on the intergranular concentrations themselves. Also, a distinction has to be made between competitive and non-competitve segregation of I and M atoms.

If the sites available at the boundary are all of the same type, I and M will compete for them in the segregation process, and the equations are (Guttmann 1974, 1975*a*):

$$X_i^\phi/(1-X_\mathrm{I}^\phi-X_\mathrm{M}^\phi) \approx X_i^\mathrm{B} \exp\,(\Delta G_i/RT) \quad \text{for} \quad i = \mathrm{I, M}, \tag{2}$$

$$\Delta G_\mathrm{I} = \Delta G_\mathrm{I}^\circ + \alpha'\, X_\mathrm{M}^\phi, \quad \Delta G_\mathrm{M} = \Delta G_\mathrm{M}^\circ + \alpha' X_\mathrm{I}^\phi, \tag{3}$$

where the X_i^{ϕ}, X_i^{B} are respectively the boundary and bulk concentration of i = I, M, the ΔG_i° (i = I, M) are the constant segregation energies in the binary ideal solutions FeI and FeM, and α' is the preferential M–I interaction coefficient.†

If I and M can segregate non-competitively, i.e. on two independent sets of sites of which the respective fractions b and a exist in the boundary (intergranular 'sublattices') the following equations are obtained (Guttmann & McLean 1979):

$$Y_i^{\phi}/(1-Y_i^{\phi}) \approx X_i^{B} \exp{(\Delta G_i/RT)} \quad \text{for} \quad i = \mathrm{I, M}, \tag{4}$$

$$\Delta G_{\mathrm{I}} = \Delta G_i^{\circ} + \beta' Y_{\mathrm{M}}^{\phi}/b, \; \Delta G_{\mathrm{M}} = \Delta G_{\mathrm{M}}^{\circ} + \beta' Y_{\mathrm{I}}^{\phi}/a. \tag{5}$$

The Y_i^{ϕ} are the concentrations of I and M in their respective 'sublattices' within the boundary, which are saturated with solute atoms when $Y_{\mathrm{I}}^{\phi} = Y_{\mathrm{M}}^{\phi} = 1$, i.e. $X_{\mathrm{I}}^{\phi} = b$, $X_{\mathrm{M}}^{\phi} = a$. β' is the preferential interaction coefficient with these variables.† The above equations (4 and 5) have been proposed by Seah (1977) although with a slightly different definition of the compositional variables.

Equations (3) and (5) obviously show that for an attractive M–I interaction ($\alpha', \beta' > 0$), the segregation energy of each solute increases with the intergranular concentration of the other solute, i.e. both segregations tend to enhance each other, as far as is allowed by competition processes.

In both the competitive and non-competitive types of segregation, the M–I affinity enhances the intergranular build up of the least surface active element, here referred to as M and defined

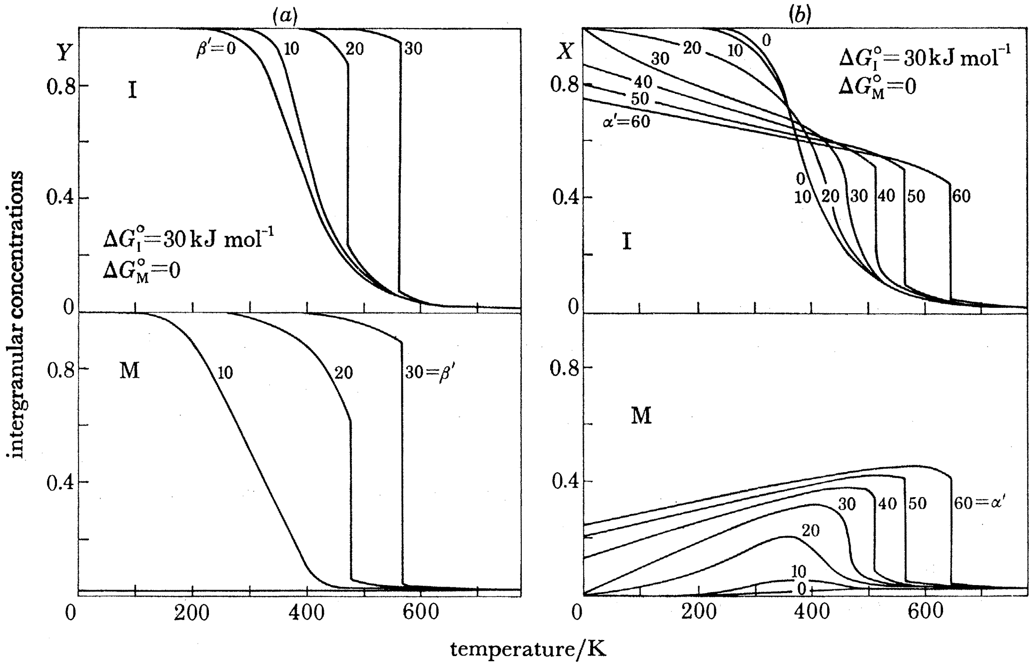

FIGURE 6. Calculated temperature dependence of grain boundary concentrations of solutes I and M in regular ternary solutions for the indicated values of the interaction coefficients α', β' (kilojoules per mole). (*a*) No competition between I and M (equations (4) and (5)). (*b*) Competition between I and M (equations (2) and (3)). $X_{\mathrm{I}}^{B} = 0.01\,\%$, $X_{\mathrm{M}}^{B} = 2\,\%$. After Guttmann & McLean (1979).

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† α' is the excess of the binary *regular* M–I interaction coefficient over the two Fe–I and Fe–M coefficients: $\alpha' = \alpha_{\mathrm{M\text{-}I}} - \alpha_{\mathrm{Fe\text{-}I}} - \alpha_{\mathrm{Fe\text{-}M}}$; $-\beta'$ is the excess standard free energy of formation of the saturated $\mathrm{M}_a\mathrm{I}_b$ solution over the $\mathrm{Fe}_a\mathrm{I}_b$ one: $-\beta' = \Delta G^{\circ}_{\mathrm{M}_a\mathrm{I}_b} - \Delta G^{\circ}_{\mathrm{Fe}_a\mathrm{I}_b}$.

by $\Delta G^\circ_{\rm M} < \Delta G^\circ_{\rm I}$ (figure 7). This can reach the point where even an element M that is not surface active, i.e. one that would not segregate if it were the only solute in iron ($\Delta G^\circ_{\rm M} = 0$), is still induced to segregate by the mere effect of the interaction ($\alpha', \beta' > 0$) with a more surface active impurity I, since its segregation energy becomes positive ($\Delta G_{\rm M} = \alpha' X^{\phi}_{\rm I}$). In effect, most of the current transition metals used as additions in low alloy steels susceptible to r.t.e. are known to be only weakly surface active in solid and liquid Fe (Hondros & McLean 1968; Kosakevitch 1970) i.e. much less than are the residuals ($\Delta G^\circ_{\rm M} \ll \Delta G^\circ_{\rm I}$).

As for the surface active element I, its segregation is also amplified by the presence of a metallic addition with α' or $\beta' > 0$ (figure 6), but in the competitive case this remains true at the higher temperatures only (figure 6*b*). Similarly an increase in the alloying element concentration increases the segregation of both elements at a given temperature (figure 7).

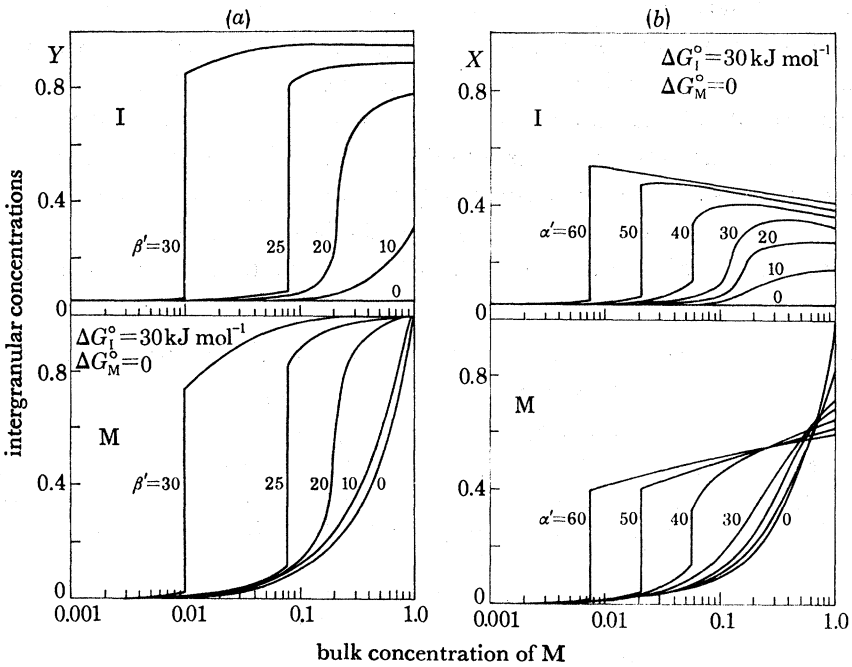

FIGURE 7. Calculated grain boundary concentrations of I and M as a function of the bulk M concentration in regular ternary solutions for the indicated values of α', β' (kilojoules per mole): (*a*) no competition; (*b*) competition. $T = 573\,\rm K$, $\Delta G^\circ_{\rm I} = 30\ \rm kJ\ mol^{-1}$, $\Delta G^\circ_{\rm M} = 0$, $X^{\rm B}_{\rm I} = 0.01\,\%$. The same curves hold for any set of proportional values of T, ΔG°_i, α', β'. After Guttmann & McLean (1979).

This type of model therefore demonstrates that if a preferential attractive interaction exists between the residuals responsible for r.t.e. and the normal metallic additions, a synergistic cosegregation of equilibrium type will naturally occur in susceptible steels for couples of solutes I and M, when their mutual affinity assumes reasonable values (e.g. less than 1 eV).

Other types of interactive segregations have been formalized by Guttmann & McLean (1979). The same general patterns of cosegregation are predicted independently of the type of interaction chosen, and the regular solution models are well fitted for semi-quantitative evaluations of the interactions (α', β') and their comparison with experiment.

(*b*) *Evaluation of the interaction coefficients*

Their order of magnitude can be estimated from the thermodynamic properties of bulk phases. Since essentially the same basic atomic interactions exist in the bulk and in the interface, it is reasonable to consider that at least a valid classification of the interactions in the boundaries can be obtained in this way. The bulk interactions can be studied either in the ternary Fe base solid solution (i), or in the binary (ii) and ternary (iii) intermetallic compounds of Fe, M and I.

(i) Evidence for preferential M–I interactions in dilute FeMI solid solutions have recently been obtained at the Laboratoire de Structure Electronique des Solides in Strasbourg, with the help of various solid state physics techniques. Residual resistivity and lattice parameter measurements in binary and ternary alloys (I = Sb, Sn or As; M = Ni or Cr) exhibit strong departures from the linear laws of mixture (respectively the Vegard and Mathiessen rules) in FeNiSb, which is consistent with a strong preferential grouping of Ni and Sb atoms (Biolluz 1977; Biolluz *et al.* 1978). The Cr–Sb interaction is weaker. The behaviour of Sn is very similar to that of Sb, while As exhibits much less affinity for Ni and none for Cr. Nuclear magnetic resonance and neutron scattering experiments have confirmed the existence of short-range order (Maurer *et al.* 1978; Edwards *et al.* 1977) and the latter technique will allow a determination of the short-range order parameter from which interaction energies can be derived.

TABLE 1. VALUES OF THE INTERACTION COEFFICIENTS α', β' (KILOJOULES PER MOLE), AFTER GUTTMANN & McLEAN (1979)

(*a*) Fe+M+P system, $a = \frac{3}{4}$ $b = \frac{1}{4}$

M	Ni	Mn	Cr	V	W	Mo	Ti	Zr
β'	5.6	12.5	18.8	27.0	32.0	34.5	41.4	48.1
α'	30.1	66.9	100.3	143.8	170.7	184.0	221.0	256.4

(*b*) Fe+M+Sb system, $a = b = \frac{1}{2}$

M	Cr	Ni	Ni+Cr
β'	8.4	14.2	14.2
α'	33.6	56.8	56.8

(ii) A comparison of the heats of formation of the various binary FeI and MI intermetallic compounds (Guttmann 1974, 1975*a*) shows that, for the M and I elements concerned in temper brittle steels, the MI compounds are always more stable than the corresponding FeI of similar structure, indicating an M–I interaction stronger than the FeI one.

(iii) A much more precise estimation is obtained through solid solubility data (Guttmann 1976). When increasing either the concentration of the metallic element M, or the interaction coefficient by changing the nature of M, the solubility of the impurity is decreased and its segregation potency increased. This inverse relation between solubility and segregation ratio is the extension to ternary alloys of the correlation which exists for a wide variety of binary systems (Hondros & Seah 1972; Seah 1975). An estimation of the preferential M–I interactions in the ternary FeMI precipitates has been obtained (table 1) by applying regular solution models to the solubility data of Kaneko *et al.* (1965) (I = P), and of Nageswararao *et al.* (1974) (I = Sb). Table 1 shows that the moderate interaction of P and Sb with the metals known to enhance the segregation of impurities (Ni, Cr and Mn) is of the order of magnitude deduced from the segregation data by fitting to them the above theoretical equations (2) and (3) or (4) and

(5), e.g. 26 kJ/mol for the Ni–P interaction (Mulford 1974; Seah 1976; Clayton 1977). These results also show that, at the normal concentrations of residuals present in steels (i.e. much less than 0.1 at. % each) these elements remain totally in solution at the embrittling temperature for low alloy contents.

As for the more reactive metals (Mo, V, W, Ti and Zr) the data show that they are able to reduce the solubility of P to such an extent that it falls within the concentration range of commercial steels. Figure 8 shows the calculated solubility limits in ternary FeMoP at 500 °C. The composition of many low alloy steels lies in the vicinity of this line or even above it: scavenging effects are then to be expected,† and a much more complicated segregation pattern arises.

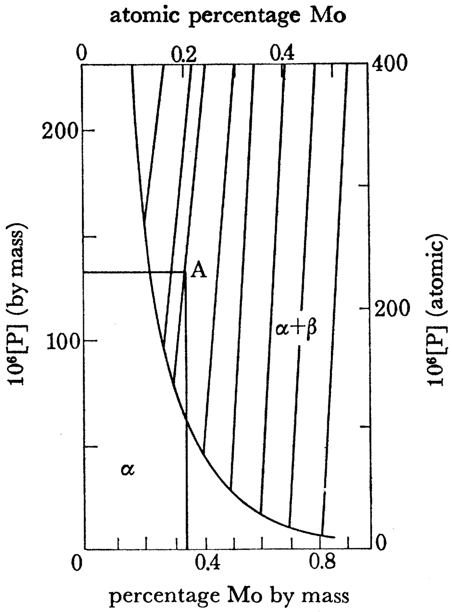

FIGURE 8. Calculated solubility line in FeMoP at 500 °C, after Guttmann (1976). Point A corresponds to the commercial 20CND 10-10 steel studied by Guttmann *et al.* (1977).

5. THE COMPARATIVE BEHAVIOUR OF THE SEGREGATING SPECIES

The above models provide us with a comprehensive interpretation of the general trends in the cosegregation behaviours of the embrittling residuals and alloying elements, according to the values of their respective segregation energies (ΔG_i°) and interaction coefficients (α', β').

(a) *The residuals of Groups 4A–6A*

(i) P, Sn, Sb, (As)

These elements, chiefly responsible for typical r.t.e. behave quite similarly. They segregate extensively to the grain boundaries of Fe but their segregation ratios are appreciably raised by the transition metals. The only differences are that P segregates appreciably more and at higher temperatures than Sb and Sn in alloyed and unalloyed ferrite, and that it segregates in

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† Even if precipitation does not occur extensively, large preferential interactions between M and I give rise to short-range order in the Fe matrix, where MI clusters have already been shown to occur even with less reactive metals like Ni; see § 1.

austenite, whereas the two other elements do not (Smith & Low 1974; Guttmann *et al.* 1974). However, these discrepancies can be rationalized on the basis of purely quantitative differences, and it cannot be asserted that their segregation mechanisms are different, as is sometimes suggested (Edwards *et al.* 1976), but the segregation energy $\Delta G_{\mathrm{I}}^{\circ}$ is appreciably larger for P (50–60 kJ/mol) than for Sb or Sn (20–40 kJ/mol). As for As, only small values of its segregation energy and affinity for transition metals can explain that its segregation has never been detected even at bulk concentration levels as high as 400 µg/g (Guttmann *et al.* 1977; Lemblé *et al.* 1979 and this symposium).

(ii) O, S, Se, Te

The more reactive chalcogens are extremely surface active and would therefore segregate with very large enrichment ratios, provided their solubilities are not so low that they virtually disappear from the solution.

Oxygen is not soluble enough in pure iron (less than 1 µg/g) to segregate to any appreciable extent in the grain boundaries (Pichard *et al.* 1976).

Sulphur segregates more strongly than P and at a higher temperature ($\Delta G_{\mathrm{S}}^{\circ} \gg \Delta G_{\mathrm{P}}^{\circ}$) in pure Fe – even at the 5 µg/g bulk level (Pichard *et al.* 1976) – but owing to its strong interaction with most alloying elements, in particular Mn ($\alpha'_{\mathrm{MnS}} \simeq 220$ kJ/mol), it is in general completely precipitated in steels, which always contain a certain amount of Mn precisely for that purpose. This is why S does not participate in temper embrittlement. Se and Te behave like S, only they are much less common in steels.

N is also very surface active in Fe_{α} and Fe_{γ} (Tauber & Grabke 1978). In steels, it is in general partially scavenged by Al or Si additions, but some free N often exists and some segregation is possible. Manganese, from its relatively strong interaction with nitrogen ($\alpha'_{\mathrm{MnN}} \approx 155$ kJ/mol) can be expected to enhance the effect considerably, and this is confirmed by experimental evidence (Guttmann 1975, unpublished; B. C. Edwards & H. E. Bishop 1976, unpublished). It has been suggested that this phenomenon may give rise to 500 °F embrittlement, but recent work by Tauber & Grabke (1978) indicates that N rather improves the cohesion of grain boundaries.

(*b*) *Carbon*

Carbon also strongly segregates to the grain boundaries of Fe_{α} (Papazian & Beshers 1971), and interacts with many metallic elements, but it does not embrittle the grain boundaries, see below (§ 7*a*). In steels its behaviour is extremely complicated since its concentration, much larger than that of the above impurities, is well in excess of the solubility limit, and both the soluble and precipitated carbon are involved in the segregation and mechanical properties.

It is now well established that carbon is not necessary for reversible temper embrittlement to occur, since this phenomenon has also been observed in very low-C alloys: FeNiCrP and FeNiCrSb (Ohtani *et al.* 1976*a*, *b*; Mulford *et al.* 1976*a*, *b*), FeMnSb (Guttmann 1975*b*) and FeMoP (Wayman *et al.* 1978).

Carbon does not have any influence *per se* on the segregations of Ni and Sb, since they remain unchanged when removing the carbon from a 0.4 % C 3.5 % Ni steel, (Mulford *et al.* 1976*b*). This shows that the C–Ni and C–Sb interactions are negligible. However, carbon can profoundly alter the segregation behaviour of other M (and therefore I) elements, by precipitating reactive metals M as carbides, as discussed in § 5*c*. This decreases appreciably the soluble M content when the nominal M content is comparable with the concentration of carbon (*ca.* 1 at. %). Depending on the nature of M, carbon can therefore have two opposite effects: with Mo or Ti, the decreased amount of soluble scavenger will release the deleterious impurities into the solution, allowing them to segregate and embrittle the steel; conversely, with Cr, the smaller amount of the metallic cosegregant will reduce the segregation of both solutes and the resulting embrittlement.

Segregated carbon might also enhance the segregation of carbide forming elements which in turn would enhance that of I. Conversely, Glikman *et al.* (1973) have invoked competition effects between C and P whereby P would be expelled from the boundary; these hypotheses have not, however, been substantiated by segregation measurements.

(*c*) *Metallic additions of the transition series*

(i) Ni, Cr, Mn

Considering first the moderately active elements which intensify impurity segregation, we have seen in § 4*b* that P interacts more strongly with Cr than with Ni, while exactly the reverse is true for Sb. The Mn–P interaction is intermediate between Ni–P and Cr–P. The effect of a carbide-forming element like Cr is often obscured by its concurrent reaction with carbon. When the C content is decreased in a 3340 steel, the segregation of Ni and Sb are drastically increased (figure 9) (Mulford *et al.* 1976*a*). Since carbon does not have any influence on the segregation of Ni and Sb (§ *b*), this result can be rationalized only on the basis of the attractive Cr–Ni interaction, which is manifested only when Cr is dissolved in the low-C heat. Conversely, in the 0.4 % steel, the major part of the Cr is precipitated in the form of Cr-rich carbides and the matrix is depleted in Cr.

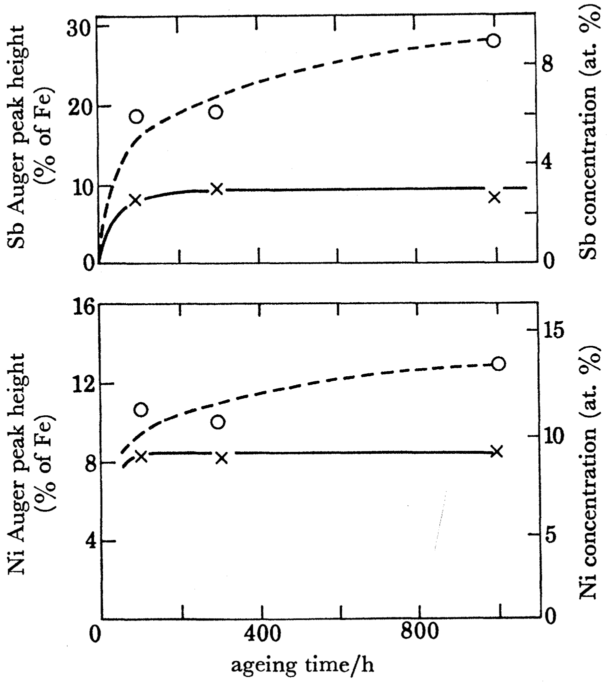

FIGURE 9. Influence of C on the segregation of Ni and Sb in a 3340-based steel at 520 °C; ○, 0.008 % C; ×, 0.4 % C. After Mulford *et al.* (1976*b*).

(ii) Ti, Zr

These very reactive metals exhibit much stonger interactions with P and Sb. They can precipitate the metalloid and reduce its solubility to so low a level that its equilibrium segregation vanishes. It has been suggested (Guttmann 1976) that this scavenging mechanism is responsible for the inhibition of P and Sb segregation by Ti observed by Ohtani *et al.* (1976*b*) in a low-C, NiCr steel.

(iii) Mo, V, W

As for the intermediate metals, Mo, V and W, their behaviour is expected to be more complicated since they are able to play two opposing roles. Owing to its high interaction with them, the impurity may have its segregation ratio considerably raised, and in this sense these metallic elements favour segregation. Conversely, these metals can also reduce the solubility of the residuals and, in this sense, they hinder their segregation. Such a scavening effect of Mo on P, observed in ternary FeMoP alloys and in commercial steels up to 0.7 % Mo (figure 4) (Wayman *et al.* 1978; Dumoulin *et al.* 1979; Jin Yu 1978 and personal communication), is in qualitative agreement with the calculated solubility curve of figure 8.

However, the increase in embrittlement at Mo contents larger than 0.7 % in figure 4 reveals that in steels the real situation is much more complicated than in ternary alloys, owing to the presence of carbon and the strong carbide forming tendency of the reactive metals. The effect of Mo on the embrittlement will now be primarily dictated by the quantity of free Mo left in solution by the precipitation of the alloy carbides, and can therefore vary throughout the embrittling cycle in accordance with the kinetics of the latter reaction. At low Mo contents (i.e. not more than 0.7 %) the incorporation of Mo into the carbides is very slow at 500 °C (Viswanathan *et al.* 1972; Palmier *et al.* 1972) and enough Mo remains in solution after 240 h to segregate to the boundaries together with P (figure 4). In the low-P steel (180 μg/g) the P segregation is decreased by a factor of 2 at 0.7 % Mo nominal content, which shows that the solubility of P is reduced by *ca.* 90 μg/g. At higher P contents (400 μg/g) this effect is of secondary importance: since the boundaries are almost saturated with P, an equivalent decrease in dissolved P has virtually no effect on its segregation. The major contribution to de-embrittlement is now due to the segregation of Mo itself, as discussed in § 7*a* below, and this segregation is amplified by the very large P segregation, owing to the strong Mo–P interaction. At higher concentrations (1.1 %) the precipitation of Mo-rich carbides becomes very rapid in particular at the temperature of the initial temper, 650 °C (Baker & Nutting 1959), during which most of the Mo is removed from solution, and its segregation cancels out. The embrittlement and P segregation are then allowed to become similar to those in the Mo-free steel (figure 4).

Similarly, for prolonged tempering at 500 °C (3000–10000 h) or for higher tempering temperatures (e.g. 550 °C), the Mo content in the carbide phase increases, decreasing that of the matrix. The impurity bound to Mo is therefore released and its segregation can increase again, while that of Mo vanishes.† The beneficial effect of soluble Mo is progressively annihilated, which explains the slow segregation kinetics of the impurities in low-Mo steels. This mechanism supports the idea (Capus 1968) that Mo merely slows down the kinetics of embrittlement but since the equilibrium properties can be affected as well, both the transient and equilibrium effects of Mo on P depend on the kinetic and equilibrium properties of the carbide transformation reactions in each particular steel.

† This effect can in some cases give rise to S-curve kinetics as discussed in §6.

(iv) *Higher alloy steels*

Although traditionally considered as specific to low alloy steels, r.t.e. also occurs in its typical form in alloys with quite large M contents, like the 13 % Cr martensitic stainless steels, and the behaviour in such systems can be rationalized on the basis of the same models (Guttmann & McLean 1979; Lemblé *et al.* 1979 and this symposium).

Considering an element, e.g. chromium, which enhances segregation in low alloy steels, these models predict that upon increasing its concentration, the segregation ratio of the impurity as well as its own should be raised (figure 7) and the temperature range in which segregation occurs should be extended towards higher temperatures (figure 6). Considerable amounts of phosphorus and chromium do, in fact, build up at the boundaries of a commercial 12 % Cr heat containing 0.02 % P; even at 675 °C a P concentration of 20 % has been observed (Lemblé *et al.* 1979 and this symposium). However, the segregation ratios have smaller values than in many low alloy steels. The Cr segregation, although significant (a small percentage in excess of the bulk nominal content), corresponds to an enrichment ratio less than 2, and that of P is *ca.* 700 at 500 °C and 550 °C.

Actually, Cr at large bulk contents can play the same role as Mo does at smaller ones, in decreasing the solubility of P below the alloy's nominal P content. When allowance is made for this effect, the segregation ratios are raised to 4500 and 2000 at 500 °C and 550 °C respectively, these values being now much in excess of those encountesed in low alloy steels, in agreement with the theory.

(*d*) *Competition for sites and the structure of the segregated boundary*

Competition effects between two segregating solutes become significant only when interfacial saturation is approached. The few observations available are therefore concerned with elements, essentially the metalloids, which segregate powerfully to the boundaries and/or the free surfaces, the behaviour being incidentally quite different for the two types of interface. Sulphur, for instance, expels many elements from surface sites of iron, in particular Sn (Lea & Seah 1975), while it does not compete with Sn in the boundaries of Fe, and is even expelled from them by N and C (Tauber & Grabke 1978).

In the boundaries of temper brittle steels, no competition effects have yet been observed directly, either between impurities themselves or between one impurity and the alloying elements, because in all the alloys examined there has been in general at most one element whose intergranular concentration reached the order of half a monolayer. However, the problem of site competition between M and I atoms is important from the theoretical point of view because it leads to that of grain boundary structure. Structural aspects of grain boundaries with particular reference to segregation have been reviewed by Baluffi (1979), and the related thermodynamics by Guttmann (1977).

It has been proposed (Guttmann 1977) that when the solute build up at the boundary approaches saturation, some similarity may exist between the composition and atomic structure of these concentrated two-dimensional (2D) 'phases' and those of the 3D phases which are known to exist in the bulk alloy at similar concentrations, as for many 2D saturated phases formed by adsorption on the free surfaces. In particular when I is a metalloid, its maximum segregation may correspond to the composition of one of the bulk stoichiometric Fe_aI_b compounds, i.e. $(X_I)_{max} = b/(a+b)$. The unambiguous evidence for saturation behaviour in the grain boundary segregation of Te and Se in high purity Fe (Pichard *et al.* 1974) can be quantitatively interpreted in these terms (Guttmann 1977). In temper brittle steels, the metallic solutes M substitute for Fe atoms in the bulk solid solution and compounds. The latter phases are therefore of the type $(\mathrm{Fe, M})_a\mathrm{I}_b$, and it has been suggested that this might also be so for saturated boundaries. In other words, M atoms would segregate 'substitutionally' on grain boundary sites formerly occupied by Fe atoms, while I atoms would fill another set of independent ('interstitial') sites, the maximum segregations attainable being $(X_\mathrm{I})_\mathrm{max} = b/(a+b)$ and $(X_\mathrm{M})_\mathrm{max} = a/(a+b)$. Such a non-competitive segregation can occur by a progressive filling of the boundary sites, as described by equations (4) and (5), or through a genuine first-order 2D phase transition whereby the boundary abruptly assumes a completely different composition and atomic configuration, as discussed in detail elsewhere (Hart 1968, 1972; Guttmann 1977; Guttmann & McLean 1979). Even the simple binary and ternary regular solution models predict that discontinuous transitions can occur in the form of 2D miscibility gaps (without a change in atomic configuration) as the interaction or the bulk solute content are increased, as shown by the steps in some curves in figures 6 and 7. Experimental evidence for 2D phases and phase transitions in the grain boundaries of temper brittle steels has not yet been obtained since, as the available data show, absolute saturation should occur below 500 °C and would therefore require prohibitively long tempering times. However, the very steep increase in cosegregation of M and I with bulk Sb concentration in a 4 % Ni steel (figure 3) strongly suggests that a 2D transition may occur in this alloy (Clayton 1977). Glikman *et al.* (1974) have also suggested the possibility of 2D phase transition in grain boundaries but they invoked this 'condensation' to explain the de-embrittlement that they observe at low temperatures, according to a suggestion by Hart (1968). The embrittling nature of such 2D 'compounds' seems more probable (see § 7*a*).

(*e*) *Anisotropy of segregation and the problem of the prior austenite boundaries*

That the prior austenite grain boundaries in martensitic and bainitic steels become selectively embrittled compared with the other boundaries of the structure has remained a puzzling property of r.t.e. for quite a long time, and earlier theories had difficulty explaining this on the basis of initial segregation in austenite. However, such a segregation would not be inherited by the tempered structure and lead to preferential embrittlement since the intermediate temper at elevated temperatures achieves complete and rapid desegregation in low alloy steels.

Also, direct evidence for segregation in boundaries other than the former γ ones has been obtained, e.g. in completely recrystallized ferrite (Guttmann *et al.* 1974), or in structures where only massive ferrite, upper bainite and recrystallized ferrite exist (Ohtani *et al.* 1975, 1976*a*). As for the quenched and tempered structures where the prior γ grain boundaries exist along with the boundaries between the packets of laths, indirect evidence of segregation in both types of boundary was obtained by etching techniques as early as 1953 (Woodfine 1953). These results confirm that cosegregation of M and I occurs to all the disordered high angle boundaries existing in the α phase (Guttmann & Krahe 1973).

This does not exclude the possibility that the solute content of the various types of grain boundaries may be different. This is suggested by the widely varying etching responses of the various packet boundaries and former γ boundaries in a given sample, (Krahe & Guttmann 1974; Ogura *et al.* 1978), and by the scanning Auger electron images performed by Joshi (1979) on fracture surfaces.

In any event, such anisotropy of intergranular segregation might play only a minor role in the choice of the fracture propagation path, and an explanation for the preferential embrittlement of the prior γ boundaries with respect to those between packets of laths may be found not in a differential segregation mechanism but rather in the fracture process itself, as explained in § 7*b*.

6. The kinetics of cosegregation

It is in general admitted that the kinetics of impurity segregation are satisfactorily described by the equation derived by McLean (1957) for binary alloys, which assumes local equilibrium between a boundary layer and the neighbouring bulk material (figure 10). At a given time t, the intergranular concentration X_{I}^{ϕ} is given by

$$X = \{X_{\mathrm{I}}^{\phi}(t) - X_{\mathrm{I}}^{\phi}(0)\}/\{X_{\mathrm{I}}^{\phi}(\infty) - X_{\mathrm{I}}^{\phi}(0)\} = 1 - \exp(s^2)\,\mathrm{erfc}\,(s), \tag{6}$$

with $s = 2\sqrt{(Dt)}/\beta d$, where D is the bulk diffusion coefficient of I, β its equilibrium enrichment ratio ($\beta = X_{\mathrm{I}}^{\phi}(\infty)/X_{\mathrm{I}}^{\mathrm{B}}$) and d the boundary thickness. At the beginning of segregation, this equation approximates to

$$X \approx 2s/\sqrt{\pi} = 4\sqrt{(Dt)}/\beta d\sqrt{\pi}, \tag{7}$$

and from the initial slopes of the experimental segregation curves, values of D can be deduced which are in agreement with available diffusion data within one order of magnitude.

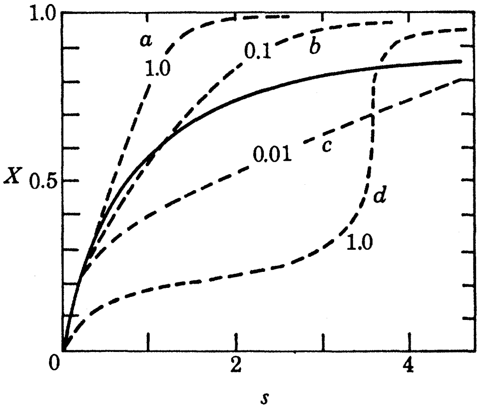

Figure 10. Calculated segregation kinetics. Solid line, after McLean (1957) (equation (6)). Broken lines, after Tyson (1978) for indicated values of $(D_{\mathrm{M}}/\beta_{\mathrm{M}}^2)/(D_{\mathrm{I}}/\beta_{\mathrm{I}}^2)$: (*a*), (*b*), (*c*), $\Delta G_{\mathrm{I}}/RT = 5.21$, $\Delta G_{\mathrm{M}}/RT = 1.30$, $\alpha'/RT = 6.51$, $X_{\mathrm{I}}^{\mathrm{B}} = 0.027\,\%$, $X_{\mathrm{M}}^{\mathrm{B}} = 1.2\,\%$; (*d*), $\Delta G_{\mathrm{I}}/RT = \Delta G_{\mathrm{M}}/RT = 4.53$, $\alpha'/\Delta G_{\mathrm{I}} = 1.2$, $X_{\mathrm{I}}^{\mathrm{B}} = X_{\mathrm{M}}^{\mathrm{B}} = 0.1\,\%$.

Some of the earlier theories of r.t.e. considered that the effect of the alloying elements was purely kinetic in nature, Cr increasing the diffusivity of the impurities while Mo decreased it. Seah (1977) has applied the two above kinetic equations without modification of either the theory or the diffusion coefficients, to cosegregation in three-component systems where the equilibrium values of the M and I segregations are as predicted by equations (4) and (5). This allowed him to generate a complete set of C-curve kinetics for the segregation of P in the 3140 steel studied by Carr *et al.* (1953) (figure 11), which appeared to be in very good agreement with those describing the kinetics of embrittlement in the original paper (the link between embrittlement and segregation in a given steel being linear as discussed in § 7*a*), and to illustrate numerically the original claim (Guttmann 1974, 1975) that the interactive cosegregation models allow for a steeper temperature dependence than that predicted by the McLean equation, (1).

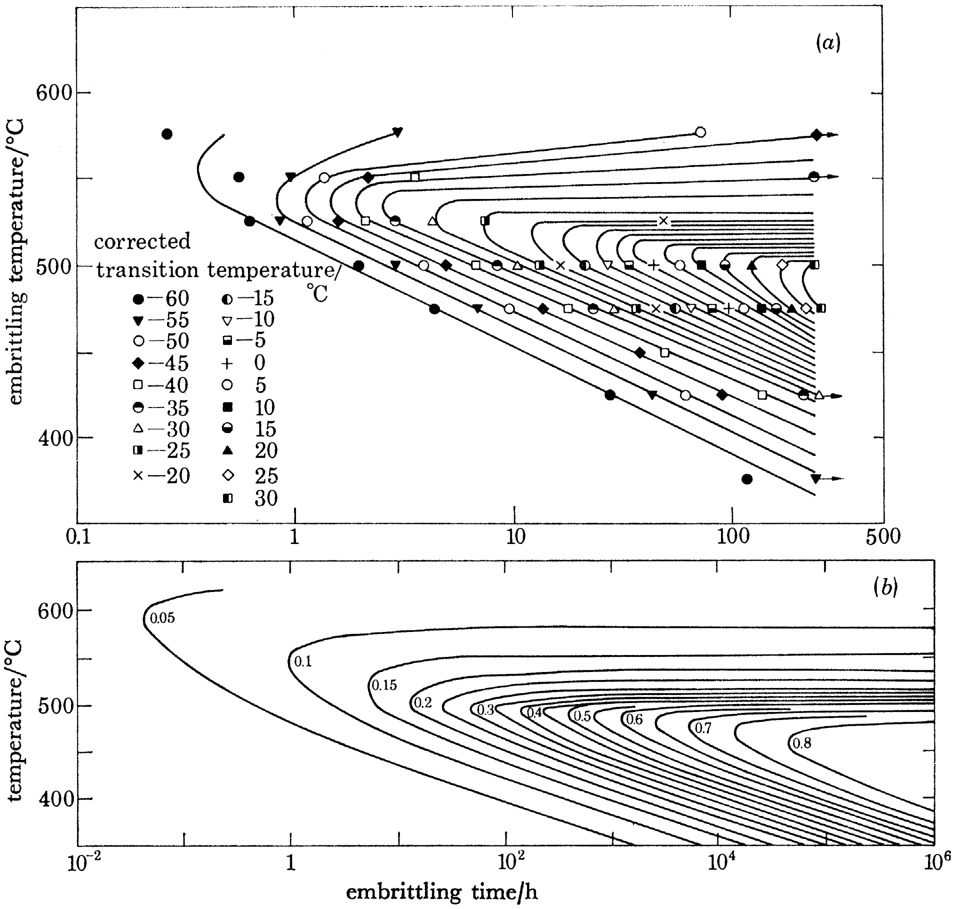

FIGURE 11. C-curve kinetics in r.t.e.: time–temperature diagrams for: (*a*) embrittlement, experimental values from Carr *et al.* (1953); (*b*) phosphorus segregation, after Seah (1977). The numbers on the curves indicate the values of P segregation calculated in terms of Y according to equation (4).

Also, the calculation allowed extrapolations to be made to lower temperatures and longer times, which predict that for instance in a rotor steel operating at a temperature as low as 350 °C, considerable segregation and embrittlement are to be expected after 10 years.

Tyson (1978) has demonstrated that the M–I interactions are efficient during the transient process as well. He pointed out that the enrichment ratios are not constant as implied in (6), but decrease while segregation proceeds; according to (5), for example,

$$\beta_i(t) = Y_i^{\Phi}(t)/X_i^{\mathrm{B}}(t, x = 0) = (1 - Y_i^{\Phi}(t)) \exp(\Delta G_i/RT); \quad i = \mathrm{I, M}. \tag{8}$$

In this case, equilibrium is reached much more abruptly than predicted by (6), even though the initial slopes are similar (figure 10). This conclusion is valid for both the binary and ternary alloys, but in the latter, Tyson's model allows for dynamic effects of the M–I interaction during the transient process: the alloying element can accelerate the segregation of the impurity – as predicted by curves *a* and *b* in figure 10, and observed experimentally by several workers (King & Wigmore 1977; Lemblé *et al.* 1979 and this symposium) – or retard it (curve *c* in figure 10). Curve *d* in figure 10 shows that for some values of the parameters, a two-step process may occur. The first plateau in the S-shaped curve corresponds to the case where, during segregation, a state of metastable equilibrium is nearly reached. This phenomenon could be partly responsible for the quite similar kinetics encountered in Mo-bearing steels, but we have seen in § 5*c* that this behaviour was essentially due to the temporary trapping of I by Mo atoms.

Nevertheless, the important point here is that both effects arise directly from the existence of a strong preferential interaction between Mo and I. These theories therefore revitalize the earlier contention that the alloying elements alter the kinetics of impurity segregation, although this does not result merely from modified diffusivities, but rather from a complex scheme involving chemical interaction effects. These therefore appear of central importance in controlling both the equilibrium segregation values and the kinetics of the approach to equilibrium.

7. THE RELATION BETWEEN SEGREGATION AND INTERGRANULAR FRACTURE

The problem of grain boundary fracture in the presence of segregated atoms appears very complex, since in metallic materials, this mode of failure results from a competition between two processes, decohesion and plastic deformation. The condition for fracture initiation is not merely that the concentrated normal stress σ exceeds the cohesive stress σ_c at the boundary, $\sigma > \sigma_c$, but also that relaxation of shear across the boundary plane does not occur, i.e.:

$$\sigma/\tau > \sigma_c/\tau_c, \tag{9}$$

where τ is the concentrated shear stress at the boundary and τ_c the shear resistance of the bulk material (McLean 1975; Hondros & McLean 1976). An atomically sharp crack will develop only if it is stable against blunting by dislocation emission, and Rice (1975) has analysed this condition in terms of the energy necessary to nucleate a dislocation at the crack tip, which depends on the work of separation of the boundary, the lattice surface energy, and the dislocation core cut-off radius.

Very little is known for the moment on the physics of grain boundary cohesion, i.e. on the stress σ_c necessary for elastically breaking atomic bonds. Metallurgists concerned with fracture have therefore generally envisioned the problem in terms of the cohesive energy concept, i.e. the work of reversible separation of the interface surface tension, γ, as discussed by Hondros & McLean (1976) and by Hirth (this symposium). Here $\gamma = 2\gamma_s - \gamma_b$ where γ_s is the surface tension of the freshly formed surface, and γ_b that of the boundary before fracture. In this approach, care must be taken as to the meaning of γ_s which is *not* the value at equilibrium, but at the moment of crack opening (Seah 1975). A definite contribution to the thermodynamics of interfacial separation has been made by Rice (1976) who showed that γ depends on whether the segregating solute is mobile enough to segregate to the new surface – and decrease γ_s – while the crack tip opens up. The loss of cohesive energy is larger in this condition (e.g. creep fracture, hydrogen induced cracking, etc.) than in the case where the solute is not mobile (typically brittle fracture). In both cases, however, γ decreases with increasing segregation, provided the equilibrium enrichment ratio of the unstressed boundary is smaller than that of a pair of equivalent free surfaces (Mason 1977; Asaro, this symposium). The cohesive stress $\sigma_c \approx (E\gamma/b)^{\frac{1}{2}}$ (where E is the Young modulus and b the lattice parameter) is thereby decreased.

Recently, McMahon *et al.* (1978, 1979) have criticized the attempts to calculate the work of brittle fracture by using the laws of equilibrium thermodynamics, since fracture is essentially an irreversible process. They have also demonstrated that when segregation lowers the work for ideal brittle failure by *ca.* 12 %, the plastic work accompanying crack propagation in a real steel can be decreased by *ca.* 96 %, which would explain the influence of impurities on the fracture of semi-brittle materials. In addition to cohesion controlled by grain boundary chemistry (§ 7*a*), the fracture behaviour is also determined by the plastic properties (such as τ_c, strain hardening coefficient, energy for nucleating a dislocation) which are controlled by microstructural parameters (§ 7*b*).

(*a*) *The embrittling potency of segregated elements in iron and steels*

(i) *Non-metals*

It has been observed that the change in transition temperature ΔT_T increases steadily with the impurity content at the boundary (see, for example, Viswanathan 1971; Smith & Low 1974; Ohtani *et al.* 1976*a*). The fact that this relation is roughly linear does not have a known physical basis but does allow an easy definition of the embrittling potency, P_e in terms of ΔT_T per 1 % of the segregated monolayer. According to Marchut & McMahon (1978) (figure 12), P_e increases considerably from P to Sn and Sb (respectively 26, 40 and 72 K per 1 % of the monolayer), while the segregation potency is in the reverse order (§ 5*a*). The P_e values found by different workers may vary considerably owing to the different coefficients used in calibrating Auger peak heights. Guttmann *et al.* (1977) give 3 and 20 K per 1 % of the monolayer for the P_e of P and Sn respectively.† However, if the calibration coefficients of Marchut & McMahon are used, these values become respectively 10 and 15. It is striking that both Marchut & McMahon (1978) and Guttmann *et al.* (1977) found the relative P_e of Sn to be *ca.* 1.5 times that of phosphorus even though two different steels were studied.

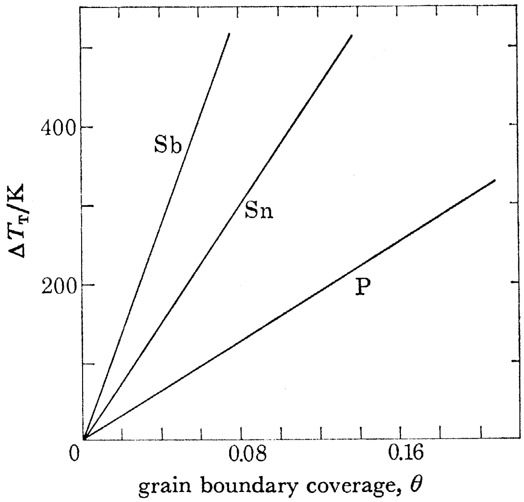

FIGURE 12. Embrittling potencies of the main impurities for 3.5 % Ni 1.7 % Cr (285 d.p.h.; A.S.T.M. no. 3–5), after Marchut & McMahon (1978).

Several attempts have been made to relate the embrittling potency of the residuals to a physical property at the atomic scale. Seah (1975) has shown that P_e increases with atomic size, atoms of Sb and Sn being much larger than those of P and As, in qualitative agreement with the P_e data, and atoms of C, B and Be being much smaller, which would explain the beneficial effect of C on boundary cohesion. Alonso & Girifalco (1977) have calculated that the charge

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† Seah (1977) has obtained $P_e \approx 2.75$ K per 1 % of the monolayer for P with a similar calibration.

transfer from I to Fe atoms increases for I in the following order: P, As, Sn, Sb; Marchut & McMahon (1978) have suggested that P_e increases with charge transfer.

All of these calculations do not take into account the nature of the bonds and of the electrons involved in them. However, as the concentration of non-metallic elements increases in the interface, the bonding cannot remain purely metallic and becomes more covalent and/or ionic (Guttmann 1974). It may even reach that existing in the intermetallic compound of similar composition as saturation is approached. Such bonds are in effect stronger than metallic ones, and this would therefore *increase* boundary cohesion, were it not for the strongly directional and localized character of non-metallic bonding; as the impurity concentration increases in the interface, electron orbitals become increasingly confined to the boundary plane, resulting in decreased electron density in the direction normal to this plane, i.e. between boundary atoms and those in the adjacent layer, and cohesion is thereby weakened.

(ii) *Metallic additions*

It can be expected (Guttmann 1974) that boundary cohesion is not controlled solely by impurity atoms and that the role of metallic elements is not merely to modify their segregation but also to participate in the complex state of bonding at the boundary, as suggested by the strong M–I interaction energies and the wide variety of bond types encountered in the various series of MI compounds (see, for example, Robinson & Bever 1967). Recently, Machlin (1978) has proposed an analysis of intergranular embrittlement in susceptible steels in terms of the elastic constants of the MI intergranular 2D 'phases'.

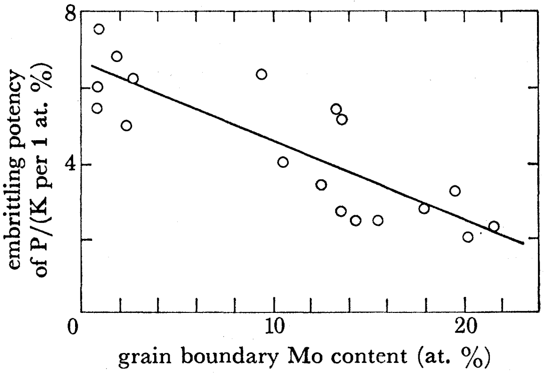

FIGURE 13. Variation of the embrittling potency of P as a function of segregated Mo content, after Dumoulin *et al.* (1979).

Experimentally, Dumoulin *et al.* (1979) have shown that the embrittling potency of the impurity decreases considerably as the intergranular segregation of Mo increases. In a series of CrNi steels where only the P and Mo contents are varied (figure 13), the P_e of P can be lowered by a factor of 3. It is not yet known whether the Mo atoms really oppose the embrittling effect of the impurities at the boundaries (owing to the strongly attractive Mo–P interaction, the segregation of Mo is observed only in association with that of P), or intrinsically improve boundary cohesion – either *per se* or via their interaction with carbon (see § iii) – or favour crack blunting, etc. In any event the important conclusion here is that the segregation of this alloying element is able to reduce temper embrittlement significantly, not only by combating impurity segregation, but also by exerting a beneficial effect on the intergranular fracture process, as summarized in figure 4.

Similar data for other transition additions are not available yet, but it can be expected that some of them will enhance the embrittling power of some impurities, and this might well be the case of Mn and of the particularly deleterious combination of Ni and Cr.

(iii) *Carbon*

Pichard *et al.* (1974, 1976) have demonstrated that below the solubility limit, carbon alleviates the intergranular embrittlement induced by the segregation of S, Se and Te, without altering the segregation of at least Se and Te. Whether or not carbon segregates competitively with the embrittling agents, its intrinsic beneficial influence on boundary cohesion must be important in steels, where its segregation is expected to vary through its interaction with alloying elements (Glikman *et al.* 1972). For instance, it is possible that Mo improves cohesion merely by attracting more carbon to the interface. Unfortunately, a reliable technique for carbon segregation measurements is not yet available, as Auger results are in general ambiguous for this element.

(*b*) *The influence of bulk material properties*

At a given grain boundary composition and cohesion, intergranular fracture and toughness will depend critically on the microstructure and related mechanical properties of the bulk material, controlled by the composition (carbon and alloying elements) and the heat treatment, through for instance hardenability, precipitation and tempering resistance.

(i) *Strength*

Mulford *et al.* (1976*a*, *b*) have shown that at a given segregation level in a given steel, the change in transition temperature, ΔT_T, increases considerably with hardness (figure 14). Therefore, during the embrittling temper, the measured ΔT_T, which reflects both the segregation and hardness levels, can go through a maximum ('overageing'), if segregation has reached equilibrium while softening is still in progress, as depicted by the broken lines in figure 15. If the structure is more completely softened by prolonged initial tempering to maintain constant hardness upon subsequent tempering, the increase in ΔT_T follows closely that of segregation and the overageing effect vanishes (solid lines in figure 15).

Intergranular failure is therefore favoured as the yield strength, i.e. the shear resistance τ_c of the material, is increased, in agreement with (9). As with transgranular cleavage fracture, this deleterious increase can be brought about by solid solution strenthening, strain hardening, precipitation, etc.

An important consequence is that at comparatively small segregations (e.g. 1–3 at. % P), embrittlement should appear only above a certain strength level. Thus the virtual absence of r.t.e. in plain-C steels results from both their smaller segregation and their lower strengths compared to alloy steels, in which the alloying elements increase both properties concurrently. Grain refinement can increase their strength, but it also improves their toughness.

(ii) *Grain size*

Capus (1962) has shown that for a given embrittling treatment, the embrittlement in terms of ΔT_T increases with prior austenitic grain size d_γ (figure 16). Segregation itself does not vary with grain size (Guttmann *et al.* 1974) and a simple calculation shows that it could do so only at

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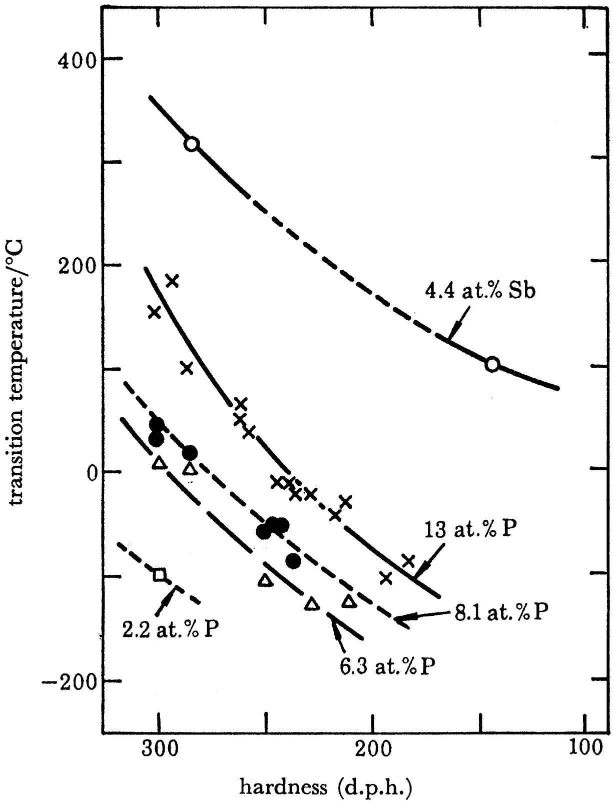

FIGURE 14. Influence of hardness on transition temperature at constant segregation levels in a 3340 steel, after Mulford *et al.* (1976*a*).

very small impurity contents and grain sizes (Guttmann 1974). Capus rather interpreted the results shown in figure 16 in terms of the energy necessary to deflect a propagating crack at a triple junction: the larger the grain size, the less frequent the deflexions and the smaller the total propagation energy. Conversely, transgranular pseudo-cleavage is much less sensitive to γ grain size – as demonstrated by the high purity alloy, which is the only one in figure 16 to exhibit this mode of failure – because this fracture process is now controlled by the size d_α of lath packets ('α grains') which are smaller than the γ grains. Since, according to the data of Roberts (1970), d_α varies as $d_\gamma^{\frac{1}{2}}$ the cleavage transition temperature varies only slightly with d_γ, i.e. as $d_\alpha^{-\frac{1}{2}} \approx d_\gamma^{-\frac{1}{4}}$ (Guttmann 1974).

(iii) *Morphology of grain boundaries*

Fracture propagation is expected to be easier along a planar and smooth boundary than along a twisted and rough one. With increasing tempering time before embrittlement, recovery of the lath substructure induces a progressive roughening of the prior austenite grains which acts to decrease the transition temperature after embrittlement. However, compared with softening the influence of this type of interface roughness is of secondary significance in high strength heavily embrittled alloys, like 4340 and 3340 steels (Ohtani & McMahon 1975).

The choice of the prior austenite boundaries as the preferred fracture path in embrittled martensite and bainite has been attributed by several workers (Guttmann & Krahe 1973; Ohtani & McMahon 1975) to the morphological differences between the α and γ networks in

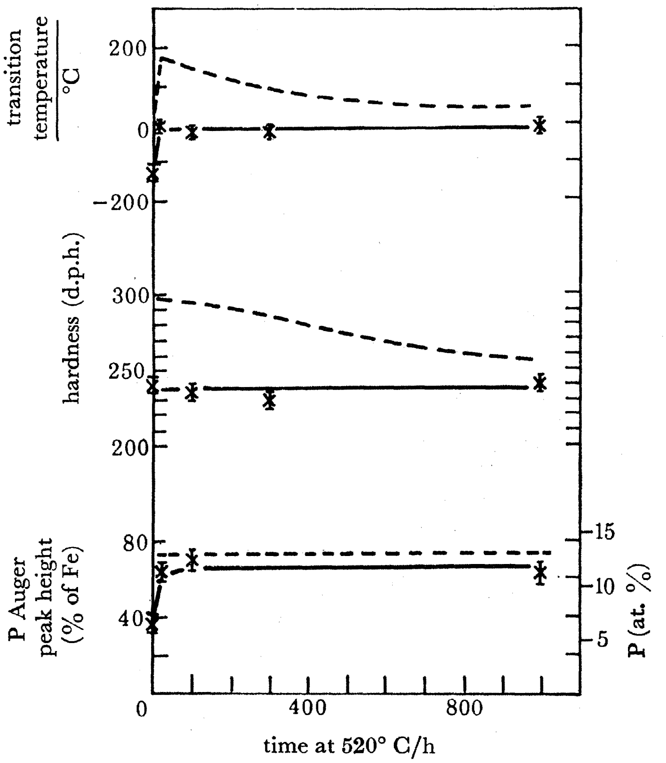

Figure 15. Effect of prior tempering treatment at 650 °C on embrittlement and segregation behaviour at 520 °C in a 3340 steel, NiCr 0.4 C 0.06 P: solid line, tempered for 20 h; broken line, tempered for 1 h. After Mulford *et al.* (1976*a*).

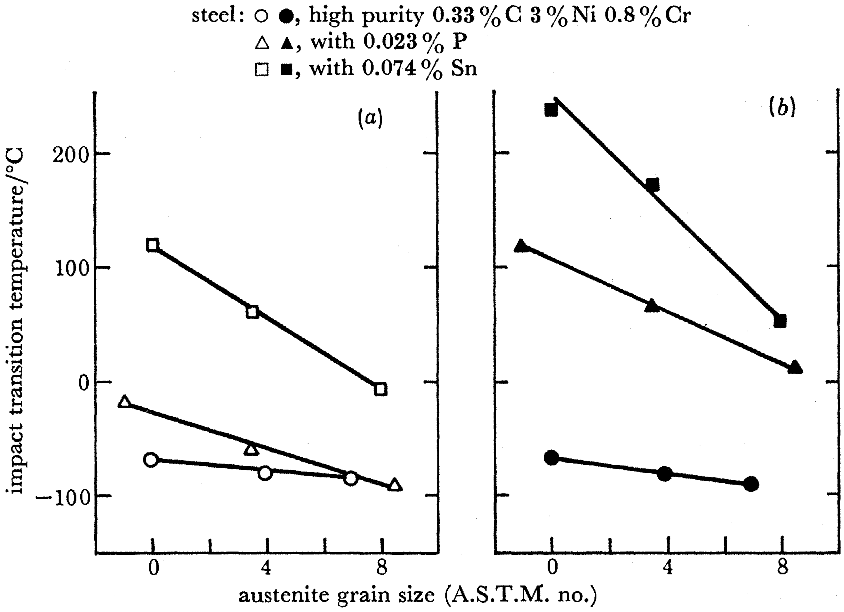

Figure 16. Influence of prior austenite grain size on transition temperature in the non-embrittled (*a*) and embrittled (*b*) conditions. (*a*) As quenched and tempered for 1 h at 600 °C; (*b*) 168 h at 450 °C. After Capus (1962).

these structures. The α boundaries, formed by the impingement of different packets of laths, are very ragged and meet each other at various angles, some of which are *ca.* 90°. Continuous fracture propagation along them is therefore much less favoured than along the relatively coarse network of smooth and nearly planar γ facets, between which a propagating crack needs to be deflected by only *ca.* 60° on the average.

(iv) *Type of microstructure*

It has been known for a long time that the susceptibility to temper embrittlement in terms of transition temperature changes increases in the order: ferrite, bainite and martensite, while the absolute transition temperature and toughness of the unembrittled conditions are improved from ferrite to martensite. The latter property can be understood in terms of the microstructural components which control transgranular quasi-cleavage fracture (Naylor 1975, 1979; Naylor & Blondeau 1976), while the former can be partially explained in terms of the above considerations on the effect of matrix strength and intergranular fracture path morphology. Also, the kinetics of segregation might be slower in structures where the density of short-circuit diffusion paths (dislocations, lath boundaries) is smaller.

8. Conclusion

This overview has attempted to re-evaluate the earlier picture of r.t.e. as a unique phenomenon, emphasizing on the contrary its general and representative character among segregation-induced embrittlement phenomena. Its complex features actually arise from the fact that not a single species, but two groups of elements, both exhibiting a wide range of segregation and interaction patterns, are closely associated in the mechanisms of segregation and of embrittlement.

Undoubtedly, the embrittling agents are the dissolved residual metalloids, and not the metallic additions, but the segregations and embrittling potencies of the former are drastically modified by the latter. Experimental evidence has firmly established the simultaneous and equilibrium character of the segregation of both types of atom, the synergism between them affecting the equilibrium as well as the kinetic properties of the segregation process. A thermodynamic approach to the problem demonstrates that the mere existence of moderately attractive preferential interactions between the two species is able to enhance and accelerate their buildup at the boundaries, and this formalism is substantiated by the existence of such preferential interactions in all the iron-based systems concerned. This same type of interaction also provides a means of combating r.t.e. with the help of the more reactive metals (Mo, V, W, Ti and Zr), which not only scavenge the impurities, but also decrease their embrittling power by segregating with them at the boundaries. It must be kept in mind, however, that owing to their even higher affinity for carbon, these elements may take part in the carbide precipitation pattern of the alloy, which may interfere with their healing action, either immediately or in the long term, as illustrated by the complex case of molybdenum. Theory also suggests competition effects and repulsive interactions (as with the segregation of C and Si at the surface of Fe; Marchut & McMahon 1978) could be used to counteract the segregation of embrittlers, but no candidate element has yet been recognized to be efficient in steels.

A further factor of complexity that r.t.e. shares with most embrittlement phenomena is that its specific fracture characteristics are determined not only by the embrittling mechanism, here segregation, but also by the independent mechanical–microstructural properties, both being the intricately combined consequence of the alloy's thermal history and composition.

R.t.e. is often concealed beneath other embrittlement mechanisms, and although it is not always clear yet whether the effects are additive or synergistic, the practical result is a severe impairment of the steel's resistance to stress corrosion cracking (Cabral *et al.* 1965), hydrogen embrittlement (McMahon *et al.* 1977*b*), creep cavitation and rupture (Tipler & Hopkins 1976), stress relief cracking (Brear & King 1976) and fatigue crack growth (Ritchie 1977). The large number of papers devoted to these subjects in the present Conference demonstrates that r.t.e., far from being the limited problem of low temperature toughness in low alloy steels, has emerged as an ubiquitous phenomenon in structural alloys from which increasingly stringent performance in service is required.

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