The Thermodynamics of Interactive Co-Segregation of Phosphorus and Alloying Elements in Iron and Temper-Brittle Steels

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The thermodynamics of co-segregation and precipitation of P and alloying elements (transition metals M and carbon) involved in temper embrittlement of steels are studied quantitatively on the basis of the regular solution model for co-segregation. The equations of this model are fitted to the available Auger data for grain boundary segregation in high purity iron-base alloys and commercial steels, allowing the determination of the intrinsic segregation energies $\Delta G_i$ and of the binary $\beta_{ij}$, $\beta_{ij}^c$ and ternary $\beta_{ijk}$, $\beta_{ij}^{cb}$ interaction coefficients in the grain boundaries. This analysis shows that Ni, Cr, and Mo do not segregate per se in iron whereas Mn does weakly, and that the segregation of these elements is essentially driven by that of P through the strong $\beta_{iph}$ attractive interaction energy at the boundaries. This energy, which increases in the order Ni, Mn, Cr, Mo, is remarkably close to the bulk values $\beta_{iph}$ in the corresponding phosphides as calculated on the basis of solubility data. The scavenging of P by M elements with large bulk M-P interactions is shown to play a determining role in low Mo and high (12 pct) Cr steels. The beneficial role of carbon is complex since it drives Mo to the grain boundaries due to the large Mo-C attraction, but it also strongly opposes P segregation due to the large repulsive P-C interaction.

I. INTRODUCTION

Reversible temper embrittlement (RTE) of low-alloy steels was the first metallurgical phenomenon to be attributed to the interfacial co-segregation of dissolved elements.\(^1\) It was initially suggested and then experimentally confirmed by Auger Electron Spectroscopy (AES) that not only residual nonmetallic impurities (hereafter referred to as I) but also metallic additives (M) can segregate simultaneously to the grain boundaries of these materials. Later it was demonstrated on the basis of thermodynamic considerations using the simple regular solution approximation, that the major specific characteristics of RTE were due to the existence of preferential attractive interactions between M and I atoms, and that the manifestations of these interactions in the grain boundary and in the matrix had antagonistic effects. Thus, attractive interactions in the boundaries enhance the segregation of both types of elements,\(^1\) whereas in the bulk the attractions hinder segregation due to the scavenging of I by M in the matrix.\(^4\) The initial formalism, further developed,\(^5\) allowed a consistent comparison between models which assumed that competition for sites was\(^6\) or was not\(^7\) taking place at the interface, and, most importantly, it strongly emphasized the basically amplifying effect of the interfacial M-I interaction on the segregation of M and I.

Reviews of the co-segregation data available up to 1977\(^6,7\) qualitatively confirmed the model but did not allow their systematic quantitative analysis, because of the scarcity of quantitative segregation data, the wide range of alloys and experimental conditions used by the various workers, and because this early research had essentially aimed at obtaining unambiguous evidence for interaction effects rather than a systematic quantitative characterization.

Such a systematic investigation was therefore undertaken in our laboratory on a number of iron-base alloys, including high-purity ternary Fe-M-I alloys,\(^8,9\) low-alloy,\(^9,10,11\) and high-Cr\(^12,13,14\) martensitic steels. Both grain boundary,\(^9,14\) and free-surface\(^6\) segregations were considered, while the physics of the M-I interactions in the matrix of the same systems was concurrently being studied at the Laboratoire de Structure Electronique des Solides in Strasbourg.\(^5\) Not only did these investigations quantitatively confirm the validity of the proposed model, but they allowed a preliminary assessment of the various thermodynamic parameters (segregation and interaction energies at the free surface, in the grain boundary and in the matrix) to be proposed. In view of the importance of the co-segregation phenomena in a wide variety of engineering properties of iron-base and other alloys,\(^11,16,17\) it is worthwhile at this point to discuss these segregation results comprehensively and to compare them with those available in the literature in order to establish a first picture of interfacial segregation thermodynamics in iron and steels.* The interactive effects of co-segregated elements on the mechanical behavior of grain boundaries in temper brittle steels is discussed elsewhere.\(^19\)

II. THE BASIC EQUATIONS OF THE MODEL

If two elements $i = 1$ and M segregate independently, i.e., without competing for sites at an interface $\Phi$ which can be a grain boundary ($\Phi = gb$) or a free surface ($\Phi = s$),
the equilibrium value of their interfacial concentration $X_i^*$ is related to their concentration $X_i^0$ in the solid solution $\alpha$ by a McLean type of equation:\textsuperscript{5,6}

$$\frac{Y_i^*}{1 - Y_i^*} = \frac{(X_i^0/X_i^{*\text{sat}})}{1 - (X_i^0/X_i^{*\text{sat}})} = \frac{X_i^*}{1 - X_M^* - X_i^*} \exp\left(\frac{\Delta G_i}{RT}\right)$$ \[1\]

where $Y_i^*$ is the partial coverage in the interfacial "sublattice" available for $i$ atoms, $X_i^{*\text{sat}}$ the maximum value of $X_i^*$ at absolute saturation, and $\Delta G_i$, the segregation free energy of $i$. If there is only one type of sites available for $I$ and $M$ in the interface, competition is unavoidable and the segregation equations read:

$$\frac{X_i^*}{1 - X_M^* - X_i^*} = \frac{X_i^*}{1 - X_M^* - X_i^*} \exp\left(\frac{\Delta G_i}{RT}\right) \quad i = I, M$$ \[2\]

In the case of the Fe-M-I systems where $M$ is a transition metal chemically similar to Fe, the noncompetition hypothesis implies that $M$ segregate substitutionally in the place of Fe atoms, whereas $I$ atoms can find another set of different "interstitial" sites. Strong competition would be expected between nonmetallic elements such as C, S, P, especially at "interstitial" sites. A competition occurs only if there is more than one type of sites available for $I$ and $M$ atoms, respectively (a $\alpha + c^* = 1$);

$$\beta_M^I < \beta_M^I \quad \text{and} \quad \Delta G_{M < 0}$$

For high attractive M-I interaction energies and for large $M$ concentrations, the impurity can be partially precipitated in the matrix into an (Fe,M)$_{1-x}$ intermetallic compound ($B$). This equation is then in equilibrium with a solution $\alpha$ where the amount of dissolved $I, X_i^*$, may become considerably smaller than its nominal content. The solubility of $I$ at equilibrium between $\alpha$ and $B$ is given by:

$$\frac{(X_i^0)_{\text{eq}}}{1 + \sum M X_i^0} \exp\left(\frac{\beta_M^I}{a_M^I RT}\right) - 1 \right)^{\alpha c}$$ \[6\]

where $(X_i^0)_{\text{eq}}$ is the equilibrium solubility of $I$ in unalloyed $\alpha - Fe$, and $\beta_M^I$ is the preferential M-I interaction energy in the bulk compound $B$. This equation assumes that Fe and all the $M$ atoms are mutually soluble in the metallic sublattice of a single form of compound $B$.

Whereas the decrease in dissolved $M$ content due to precipitation of $M-I$ compounds is negligible, other elements can drastically reduce $X_M^*$ by precipitation processes: the role of carbon which precipitates Cr and Mo-rich carbides is particularly important in the case of steels. It is also noteworthy that precipitation is often slow compared to interfacial segregation—as the bulk $\alpha-B$ equilibrium is approached, $X_i^*$ is slowly depressed toward its equilibrium value and the interface-solid solution equilibrium is displaced. This considerably complicates the quantitative interpretation of segregation data.

The concentration of element $i$ remaining in solid solution also controls the kinetics of its segregation. These kinetics are classically analyzed in terms of the law derived by McLean for binary alloys\textsuperscript{21,22} which, in its approximate form, is valid for the initial linear part of the segregation-(time)\textsuperscript{10,12} plot:

$$\frac{Y_i^*(t) - Y_i^*(0)}{Y_i^*(0) - Y_i^*(0)} = 2 \left(\frac{X_i^0}{d}\right) (D t / \pi)^{1/2}$$ \[7\]

where $Y_i^*(t)$ is the interfacial coverage of $i$ at time $t$, $Y_i^*(0)$ its initial value, and $Y_i^*(0)$ its equilibrium value as defined by Eq. [1]. $D$ is the bulk diffusivity of $i$ and $d$ the interface thickness. This simplifies to:

$$Y_i^*(t) = 2(X_i^0/d)(D t / \pi)^{1/2}$$ \[8\]

when the initial segregation $Y_i^*(0)$ is negligible. Although Tyson\textsuperscript{23} has criticized the validity of McLean's equation and demonstrated that not only the equilibrium but also the kinetics of segregation were very sensitive to M-I interaction.