

## Contact conditions for gamma to alpha Transformation in Ternary Fe-C-X

### Part I: Thermodynamic Models

In the study of alloying effects on transformations in steels, one can trace the evolution of these concepts to the realization that the austenite decomposition reactions, although clearly influenced by the presence of substitutional alloying elements, often proceed at rates determined essentially by the diffusion of carbon. The diffusion coefficients of typical alloying elements (X=Mn,Ni,Cr, Mo...) in austenite are many orders of magnitude less than those of interstitial solutes (C, N).

Hultgren [1] coined the term “paraequilibrium” (PE) to describe the hypothetical case where the alloying element is essentially bypassed by the transformation interface; the situation then becomes quasi-binary, the substitutional solution behaving, in the thinking of many researchers, as a single “element”. In an internal report of the Swedish Institute for Metals, Hillert [2] developed this concept quantitatively, showing that corresponding interfacial constrained equilibria for carbon would always lie inside the true equilibrium boundaries on a ternary isotherm. Since the PE tie-lines are required to connect compositions of equal Fe/X ratio, they correspond to component rays, each passing through the carbon corner of the Gibbs triangle. Hillert also employed isoactivity lines and their extrapolations into the two phase region to show how the PE boundaries could be generated.

Aaronson and Domian [3] independently proposed a closely-related type of partial equilibrium, called “no-partition equilibrium”, which differed only in minor aspects from PE, and presented a series of ternary isotherms calculated on this basis.

There is another way in which the transformation can proceed rapidly with negligible alloying element partition: this was also anticipated by Hillert [2], and termed “quasi-paraequilibrium”. The situation requires that the interfacial contact conditions conform to a true local equilibrium tie-line, but one that corresponds to a product phase substitutional composition very close to the bulk austenite composition, so that a thin alloying element “spike” exists in the parent austenite at the interface. Kirkaldy [4], studied the full multicomponent diffusion problem, including cross-terms in the diffusion matrix, and found solutions that corresponded to local equilibrium unpartitioned growth. Subsequently, Purdy et al [5] showed that the requirement of simultaneous mass balances for the two solutes generated a regime on the ternary isotherm within which such solutions could exist, and called its limit the “envelope of zero partition”. Coates [6] explored the consequences of differences between the diffusivities of two solutes, and obtained this same envelope as a limiting case for very large ratios  $D_C/D_X$ . More recently, this condition and its limit have been termed local equilibrium with negligible partition LE-NP [7].

For a simple ternary steel containing an austenite-stabilizing alloying element, such as Fe-C-Ni, the isothermal section then divides into three regions: LE-NP, where both PE and LE-NP are

thermodynamically possible; a larger region where the only paraequilibrium contact conditions will lead to an unpartitioned product, and an even larger region (full equilibrium) where, on this basis, only partitioned product (ferrite in this case) can form.

These arguments are entirely thermodynamic; they do not explicitly contain kinetic information, nor do they account for departures from local equilibrium contact conditions. They were initially based implicitly on the concept of an infinitely thin interface; it was only somewhat later that the concepts of interfaces with separate thermodynamic (e.g. segregation, anisotropy of energy) and kinetic (transport, mobility) properties were overlaid on the earlier constructs.

The increasing widespread availability of assessed thermodynamic databases and computational thermodynamic methods has led to the quantitative evaluation of the LE-NP and PE limits for ternary and higher-order systems. In addition, thanks largely to Aaronson and his colleagues [8,9,10], the kinetics of grain boundary ferrite precipitation in high purity homogenized ternary and quaternary steels has been investigated: in many cases, the agreement between the models (often using the PE interfacial condition) and observed rates of ferrite growth is not encouraging. It is not at all clear that the PE interfacial condition, even if established, will persist throughout the precipitation event. Different researchers have attributed observed deviations from the predictions of the PE model to solute drag [11,12], cross-interface atomic transport [13] and interfacial structural inhibition [10].

The study of controlled decarburization has proven informative, in part because the structural influences are absent; the interface, once established, is essentially “incoherent”. A planar ferrite layer develops from the surface of an initially austenitic specimen, and grows at a rate determined by carbon diffusion in both ferrite and austenite. With a knowledge of the carbon diffusion coefficients in ferrite and austenite, this allows the deduction of the interfacial contact conditions. For Fe-C-Ni [14], for all compositions and temperatures investigated, the growth of ferrite was accurately parabolic in time, implying semi-infinite boundary conditions and constant interfacial compositions, and consistent with LE-NP, rather than PE conditions. For Fe-C-Mn alloys [15,16], in contrast, one finds LE-NP conditions at lower temperatures, and a surprising gradual transition to PE conditions at the highest temperatures. This behavior has been modeled on the basis of multiple discrete atomic jumps to and from a solute-enriched interfacial energy well [16].

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