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New insights into the limit for non-partitioning ferrite growth

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Abstract—The limiting conditions for non-partitioned ferrite growth were investigated under controlled decarburization conditions. An abrupt change in the growth kinetics and morphology of ferrite was observed when the temperature increased above the limit defined by the local equilibrium no-partitioning (LENP) model. The ferrite layer formed below the LENP limit consisted of columnar grains and showed continuous, parabolic growth kinetics. In contrast, ferrite growth above the LENP limit showed two distinct stages. Initially, a thin layer of columnar ferrite grains formed and grew rapidly for a short period of time. In the second stage, the ferrite layer appeared to increase in thickness at a very low rate. The slow growth of the ferrite layer was associated with a strong depletion of carbon content in austenite as well as the formation of new ferrite grains as opposed to the growth of existing grains. The evolution of the carbon concentration in austenite was used to infer the operating interfacial contact conditions as a function of time. The evolution of the interfacial austenite conditions is suggested to penetrate deep into the two-phase region as predicted by ferrite growth theories that account for free-energy dissipation during the austenite-to-ferrite phase transformation.

Keywords: Ferrite growth; Kinetic transitions; Local equilibrium; Paraequilibrium; Decarburization

1. Introduction

The partitioning and segregation of substitutional atoms during ferrite growth play a critical role in determining the phase transformation kinetics in alloy steels. Of particular interest is the transition from rapid growth kinetics controlled by carbon diffusion to slow growth kinetics controlled by the diffusion of the substitutional elements. An upper estimate of the maximum temperature or substitutional alloy content for which rapid ferrite growth can take place is given by the paraequilibrium (PE) model [1,2]. In this model the substitutional elements are assumed to be immobile and as a result the parent and product phases have the same ratio of solute (X) to solvent (Fe) atoms in the substitutional sublattice. The interstitial carbon, on the other hand, is assumed to be in equilibrium across the interface. An alternative is to identify an equilibrium tie-line under which non-partitioning growth can proceed. This leads to the local equilibrium non-partitioning (LENP) model [2–4]. An important feature of the LENP model is the existence of an alloying element spike in the parent phase. The two limits (indicated by Paraequilibrium and Zero Partition, respectively) are compared in Fig. 1a for the Fe–Ni–C system and Fig. 1b for the Fe–Mn–C system.

Ferrite growth has traditionally been studied by cooling a specimen having a fully austenitic microstructure into the ferrite + austenite two-phase region and observing the nucleation and growth of the ferrite (classical precipitation experiments). Oi et al. [5] employed this method to determine the temperature above which fast, non-partitioning, ferrite growth stops. The experimental results appear to lie between the LENP and PE limits for both Fe–Ni–C (Fig. 1a) and Fe–Mn–C (Fig. 1b). Similarly, Hutchinson et al. [6] found using a diffusion couple containing a gradient in Ni that the limit for non-partitioned growth in Fe–Ni–C is slightly above the LENP limit.

Another method of deducing the operating interfacial conditions is to examine ferrite growth under controlled decarburization conditions. In this method, the initial alloy content lies within the single-phase austenite region. Carbon removal from the surface (e.g. using a flow of wet hydrogen) leads to the formation of a ferrite layer that isothermally grows into the austenite. The kinetics of ferrite growth can then be measured very accurately, in quenched specimens, with minimal complications from nucleation, stereology, crystallography or impingement of the carbon diffusion profiles.

Decarburization experiments on the Fe–Ni–C system indicate that the kinetics of ferrite growth closely follow the predictions of the LENP model over a wide range of conditions [7,8]. Phillion et al. [8] also conducted a series of decarburizing experiments using specimens with a controlled Ni concentration gradient. Based on X-ray microanalysis in the scanning electron microscope, it was concluded that the growth of the ferrite layer terminates

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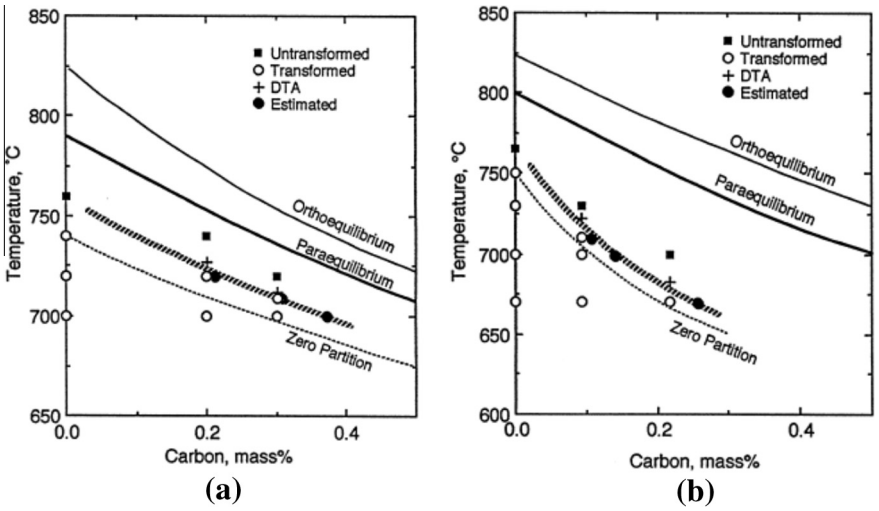

Fig. 1. Isopleths showing experimentally obtained limits (using classical precipitation technique) for transition from fast growth rate to slow growth rate in comparison with the theoretical limits calculated for different boundary conditions: (a) isopleth for Fe–Ni–C alloy containing 2.5 wt.% Ni; (b) isopleth for Fe–Mn–C alloy containing 2.0 wt.% Mn [1].

at the solubility limit for Ni in pure Fe which corresponds to the LENP limit at zero carbon content. A micrograph of the ferrite layer in one of these gradient specimens after 16 min of decarburization is presented in Fig. 2. Interestingly, some ferrite formation above the LENP limit is visible in Fig. 2. Phillion et al. [8] attributed this thin layer to "ferrite formation during quenching in the carbon-depleted region of the austenite" as opposed to ferrite formation above the LENP limit at the decarburization temperature.

Decarburization of Fe–Mn–C alloys, however, appears to suggest that the limit for non-partitioning ferrite growth is close to that predicted by the PE model. Zurob et al. [9,10] reported kinetics faster than the predictions of the LENP model during decarburization of Fe–0.94Mn–0.57C (wt.%) at 1079 K (806 °C). At higher temperatures, 1098 K (825 °C) and 1114 K (841 °C), a uniform ferrite layer is formed in spite of the fact that LENP solutions do not exist at these temperatures. These observations are puzzling because high temperature should promote the diffusion of the substitutional alloying elements, leading to the formation of at least a partial alloying element spike. As such, the observation of a long-lived PE state at high temperature is unexpected. In addition, it is difficult to rationalize the difference between the behaviors of the Fe–Ni–C and Fe–Mn–C systems under decarburization conditions. A possible explanation of these unexpected observations was offered by Zurob et al. [11], who suggested that the existing thermodynamic description of the Fe–Mn–C system underestimates the solubility of Mn in ferrite. If the thermodynamic description is modified, in accordance with existing experimental data, the above decarburization kinetics falls close to the LENP limit.

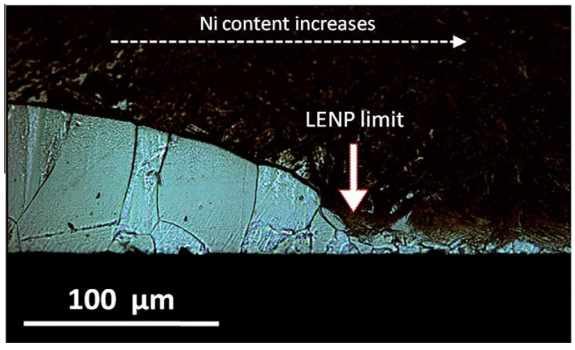

Fig. 2. Decarburization profiles in Fe–Ni–C diffusion couple after 16 min at 775 °C. Phillion et al. concluded that the ferrite layer terminates at the LE-NP limit [8].

The aim of this contribution is to provide a self-consistent explanation of the precipitation and decarburization observations in both the Fe–Ni–C and Fe–Mn–C systems. In particular, we wish to predict the temperature at which non-partitioned ferrite growth stops in both systems and explain the apparent discrepancy between the Fe–Ni–C and Fe–Mn–C systems under decarburization conditions.

2. Experimental methods

Experiments were performed in order to assess the extent of ferrite growth during decarburization above the LENP limit and deduce the operating interfacial conditions. Two alloys were prepared by arc-melting high-purity raw materials. The first alloy contained 1.64 ± 0.03Ni and 0.48C (wt.%) while the second contained 0.885 ± 0.025Mn and 0.55C (wt.%). The as-cast materials were cold-rolled to a reduction of 50% and homogenized in sealed vitreous-silica ampules for a period of 72 h at 1373 K (1100 °C).

Specimens of size $10 \times 4 \times 4$ mm^3 were sectioned from the ingot and the surfaces of the specimens were polished using SiC paper down to 4000 grit. In the case of the Fe–Ni–C alloy, decarburization experiments were carried out at 1073 K (800 °C) $\pm$ 2 K. For the present alloy, this temperature is slightly above the LENP limit. The specimens were decarburized using wet hydrogen for various times up to 900 min.

In the case of the Fe–Mn–C alloy, the specimens were decarburized for 30 and 120 min at 1123 K (850 °C) $\pm$ 2 K, 1136 K (863 °C) $\pm$ 2 K and 1143 K (870 °C) $\pm$ 2 K. Multiple temperatures were selected due to the uncertainty