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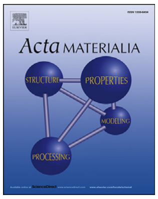

Full length article

Coupled solute drag and transformation stasis during ferrite formation in Fe-C-Mn-Mo

W.W. Sun [a], H.S. Zurob [b], C.R. Hutchinson [a, *]

[a] *Department of Materials Science and Engineering, Monash University, Clayton, 3800, Vic, Australia*
[b] *Department of Materials Science and Engineering, McMaster University, Hamilton, ON, Canada*

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ABSTRACT

Ferrite growth kinetics in a series of quaternary Fe-C-xMn-0.4Mo (wt. %) alloys ($x = 0.5, 0.8, 1.1, 1.3$) has been studied using the decarburization technique at temperatures between 755 °C and 806 °C. It is shown for the first time that the ferrite growth kinetics in the quaternary system can be well predicted using solute drag parameters (E_b and D^{trans}) tuned from experiments on model ternary Fe-C-Mn and Fe-C-Mo alloys. This should be interpreted as great encouragement for the steel phase transformations community and provides hope for extrapolation of research activities on model ternary Fe-C-X systems to real industrial steels. The important effect of carbon segregation to the migrating interface is discussed in the context of Qiu et al.'s recent unsuccessful attempt to predict the growth behaviour in the Fe-C-Mn-Si quaternary system based on parameters tuned from the Fe-C-Si and Fe-C-Mn systems.

Using the successful Fe-C-Mn-Mo growth model, traditional ferrite precipitation at lower temperatures of 550 °C and 650 °C is then described and a new explanation for transformation stasis is proposed (local carbon profile inversion) which is consistent with recent analytical transmission electron microscopy (ATEM) measurements showing negligible interfacial solute segregation at the onset of stasis in an Fe-C-Mn-Mo alloy. We propose that the onset of transformation stasis is controlled by the competition between the carbon flux in the austenite away from the interface and the decrease in the interfacial carbon content due to the interfacial dissipation processes. Critically, it is the rate of change of the interfacial dissipation with velocity that matters, $\frac{\partial \Delta G^{diss-total}}{\partial v}$, and not the absolute magnitude of the dissipation, $\Delta G^{diss-total}$ for transformation stasis.

1. Introduction

It is now well established in physical metallurgy that solute in solution may have a drastically retarding effect on the migration of solid state interfaces. The effect is most obvious during grain growth [1–3], but is also important during recrystallization [4–15] and phase transformations [16–19]. This effect is known as 'solute drag', or sometimes diffusional dissipation of free energy [20], and models have been proposed to quantitatively describe the effect as a function of solute content, temperature and interface velocity. The models due to Cahn [21] (the force approach) and Hillert [22] (the dissipation approach) have come to dominate the literature and under certain conditions the two models reduce to the same result [23].

A key feature of these solute drag models is that for their quantitative use, choices must be made for two critical parameters: E_b (the interaction energy between the solute atom and the migrating interface) and D^{trans} (the effective mass transfer coefficient of solute across the migrating boundary). Whilst some guidance for the choices of E_b may be gleaned from experimental measurements of solute segregation to interfaces [24–29], or from atomistic simulations [30], it should be admitted that D^{trans} is essentially used as a fitting parameter. Not even its temperature dependence is known with any certainty. This is a critical point because the interface velocity at which the solute drag force, or dissipated energy, passes through a maximum, is controlled by D^{trans}.

For practical metallurgy applications, the situation is more complicated because real alloys are multi-component and each solute will exhibit its own characteristic interactions with the interface, i.e. its own E_b and D^{trans}. When the solutes co-exist in an alloy, they may interact and modify the interaction of the other

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* Corresponding author.
E-mail address: christopher.hutchinson@monash.edu (C.R. Hutchinson).

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solutes with the migrating interface. It is well known in surface science that the presence of one segregating solute to a surface may significantly affect the segregation of other solutes (co-segregation or anti-segregation) [31,32]. This has also been experimentally observed at grain boundaries [33–35] and it is reasonable to expect a similar interaction to occur at phase interfaces. The multi-solute effect on migrating interfaces is known in physical metallurgy as 'coupled solute drag' [26,36–41] and was originally introduced to highlight that in Fe-C-Mo alloys, the segregation of Mo to a migrating ferrite/austenite interface may be enhanced because of segregation of carbon to the interface [36]. Mo and C have an attractive interaction and the co-segregation may manifest itself as a coupled solute drag effect that is greater than the sum of the solute drag separately expected from Mo and C in isolation. It was suggested that the coupled solute drag effect was the reason for the large effect that Mo has on ferrite formation in steels, even leading under some circumstances to complete transformation stasis [42–44].

Indeed, it is in the field of phase transformations in steels where solute drag and coupled solute drag have received the most sustained attention [18,19]. The reasons are twofold – the first is because ferrite precipitation from austenite during cooling of steels from elevated temperature is an extremely important technological problem. The size, shape and topology of ferrite are dominant factors controlling the mechanical response of many steels. The second reason is because of this technological importance of steels, the thermodynamic and kinetic properties of the important solution phases (ferrite and austenite) are now quite well established. This means quantitative models for the kinetics of phase transformations can be developed for comparison with experimental data and estimates of the (coupled) solute drag effect may be made, subject to the uncertainties regarding the interface thermodynamics and kinetics (E^b and D^{trans}).

In a recent study, Qiu et al. [45] performed a systematic set of ferrite growth experiments in the Fe-C-Mn-Si system to critically test for the existence of a coupled solute drag effect. This system had previously been suggested to be one where a synergistic effect of the Mn and Si will exist because of an attractive interaction between the Mn and Si and their interaction with the migrating interface [38,40,41]. Qiu et al. used the decarburization approach [46–54] to experimentally drive ferrite formation from austenite because this approach leads to a macroscopically planar ferrite layer growing in from the surface of the sample which can be measured very accurately, yielding precise measurements of ferrite growth kinetics. The key feature of Qiu et al.'s study that differentiates it from prior work is that the E_b and D^{trans} for Si and Mn were first independently calibrated on a series of ternary Fe-C-Si [52] and Fe-C-Mn [51] alloys using the Zurob et al. model [55], before a quaternary version of the same model was used to predict the ferrite growth kinetics in the quaternary Fe-C-Mn-Si steels [45]. This really was a 'prediction' because all solute drag parameters were fixed based on calibration in the respective ternary systems. The comparisons between experiment and model were made on a range of quaternary alloy compositions and at a range of temperatures. Under all cases, the predicted solute drag far exceeded the experimentally observed effect. An example is shown in Fig. 1, comparing the measurements of ferrite growth at 755 °C in an Fe-0.68C-1.58Mn-1.33Si (wt. %) alloy under decarburization conditions, with the prediction of ferrite growth according to the Zurob et al. model using solute drag parameters tuned from the ternary systems. The experimental measurements suggest the existence of an anti-coupled solute drag effect [45]. This is a surprise because the opposite was expected from the literature [38,40,41].

Qiu et al. [45] offered several potential explanations for this surprising observation in the quaternary Fe-C-Mn-Si system:

- They suggested that the thermodynamics of the interface may be dominated by strain energy contributions and that the chemical contributions (e.g. Mn-Si interaction in the interface) are much less important. If this is the case, we should make similar observations in other quaternary systems regardless of the interaction energies between the substitutional solutes.
- They suggested that segregated carbon to the interface may play a much larger role than generally appreciated. Although Mn has an attractive interaction with C, Si has a strongly repulsive interaction with C. If segregation of Mn to the migrating interface leads to enhanced interfacial segregation of C, then perhaps this decreases the 'effective' interaction of the Si with the interface leading to a decreased solute drag from Si. This would still represent a coupled solute drag effect – but it highlights that the 'coupling' may lead either to an increased, or decreased, net solute drag effect. The potentially important role of C has been previously highlighted by Enomoto [56]. If this is the origin of the effects observed by Qiu et al. [45] (e.g. Fig. 1) then it should be much less important in a system where both substitutional solutes have an attractive interaction with C. An example is Fe-C-Mo-Mn.
- Finally, Qiu et al. suggested that there may exist only limited permissible sites within the migrating interface for segregation of Mn and Si. If the sites are quickly filled by one solute (e.g. the solute with a lower solute drag effect) then there may be no room for the other solute to segregate and exert a solute drag effect. This would represent a 'competition for sites' within the interface. In fact, Mn and Si interact with the migrating ferrite/austenite interface only moderately strongly – the levels of segregation are not expected to be very high (Fig. 9 in Ref. [45]). If a competition for sites within the interface is the reason for Qiu et al.'s observations of an anti-coupled solute drag effect, then this effect should be even worse in systems where stronger solute segregation tendencies are exhibited (e.g. Mo in steels) and should show a dependency on the concentration of solute added. For example, a series of Fe-C-Mo-Mn steels with constant Mo content and increasing Mn content would allow a critical test of the 'competition for sites' hypothesis.

The present contribution has two related objectives. The first is to present a set of systematic decarburization experiments to test the above hypotheses for the origin of the anti-coupled solute drag effect observed in the Fe-C-Mn-Si system [45]. The Fe-C-Mn-Mo system has been chosen for this purpose and a series of alloys containing 0.4Mo (wt. %) and increasing Mn contents from 0.5 to 1.3 wt. % are selected. As we shall show, the effect of C at the interface is likely the key issue.

Whilst the Fe-C-Mn-Mo system is an ideal choice to test the hypotheses listed above, it is also a system that exhibits its own unique ferrite precipitation characteristics. Certain Mo added steels are known to exhibit ferrite/bainite 'transformation stasis', also called 'incomplete transformation' [42–44]. An example is shown in Fig. 2 taken from the work of Furuhara et al. [27]. This plot shows the ferrite/bainite transformation kinetics in two alloys at 550 °C: Fe-0.15C-1.49Mn (0.15C Base) and Fe-0.15C-1.49Mn-0.49Mo (wt. %) (0.15C Mo). The addition of Mo greatly retards the transformation and a stasis in transformation occurs after approximately 60s and persists until ~10^5 s, after which transformation continues.

There exist a number of competing theories to explain the transformation stasis (recently reviewed by Hillert and Borgenstam [57]) and one of these is due to solute drag from the interaction between Mo and the migrating interface. Furuhara et al. [27] prepared samples for analytical transmission electron microscopy (ATEM) from the migrating interface in the Fe-0.15C-1.49Mn-0.49Mo (wt. %) alloy plotted in Fig. 2 using a focused ion beam.