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Analysis of ferrite growth retardation induced by local Mn enrichment in austenite created by prior interface passages

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Abstract

A series of new cyclic phase transformation dilatometric experiments has been designed to investigate systematically and in detail the newly discovered “growth retardation stage” during the final austenite–ferrite transformation, and to provide further evidence for the existence of residual Mn spikes in austenite created during prior cyclic phase transformations. The magnitude of growth retardation increases with increasing Mn concentration, and is absent in the binary Fe–C alloy. New experiments also prove that growth retardation does not occur at a particular temperature but when the moving austenite–ferrite interface hits the residual Mn spike. The magnitude of growth retardation is proportional to the number of prior temperature cycles in the cyclic phase transformations, and there is no growth retardation in experiments with only one temperature cycle. The fact that the growth retardation can be observed by dilatometry implies that the interface moved back and forth in a retraceable manner. The classical local equilibrium model can still qualitatively predict the newly observed features of growth retardation, while the paraequilibrium model does not work.

Keywords: Local equilibrium; Austenite; Ferrite; Interface migration; Transformation kinetics

1. Introduction

The growth kinetics of the austenite (γ) to ferrite (α) transformation in the intercritical region is of great interest in steel production, as the austenite/ferrite condition after intercritical annealing is a key factor for the kinetics of the phase transformations during further cooling. Over the past decades, the austenite to ferrite transformation has been widely studied both experimentally and theoretically [1–12]. Despite abundant effort, the effect of alloying elements on the austenite to ferrite phase transformation kinetics in Fe–C–M (M is substitutional alloying element, M = Mn, Ni, Cr, Mo, etc.) alloys is still much debated [13–26]. The uncertainty about the precise nature of the alloying element redistribution (partitioning) at the moving interface ultimately stems from the large difference between diffusion coefficient of substitutional alloying element M and the interstitial element C, which can differ by as much as 6 orders of magnitude.

Based on different assumptions for the partitioning mode of substitutional elements, two classical concepts have been proposed to describe the phase transformation kinetics in ternary Fe–C–M alloys. (i) The paraequilibrium model (PE) [27,28] relies on constrained equilibrium: the chemical potential of carbon should be the same in both phases, and the substitutional components are assumed to be immobile. Hence, the transformation rate is only determined by carbon diffusion. (ii) The local equilibrium (LE) model [29–31], in which the interface is assumed to migrate under full local equilibrium with the partitioning of both C and M. Depending on the alloy composition and temperature, the transformation rate is determined either by diffusion of either C or M. Due to the large difference in the diffusivities of C and M, there are two different partitioning modes of M during the phase transformations in the LE model. In the first mode, the carbon concentration gradient in the parent phase is almost negligible while

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that of M is large. Hence the transformation kinetics is slow and controlled by diffusion of M. This mode has been termed "local equilibrium with partitioning" (LEP). In the second mode, the transformation kinetics is fast and controlled by carbon diffusion, and a sharp "spike" of M is predicted to move ahead of the interface. This mode has been termed "local equilibrium with negligible partitioning" (LENP). However, until now, no direct experimental evidence has been obtained to prove the existence of the predicted M "spike". (The term "spike" actually refers to the pointed concentration profile calculated for a one-dimensional transformation model. In reality, the "spike" is a curved plane of negligible thickness located at the austenite side of the moving austenite–ferrite interface.) Determination of the predicted Mn spike experimentally presents two difficulties. (i) The Mn spike exists in front of the moving austenite–ferrite interface at high temperature, while modern chemical analysis techniques such as atom probe tomography [32–34] can only work well at room temperature. This means that the sample has to be quenched to room temperature, and then only the indirect chemical analysis at the stationary martensite–ferrite interface can be measured. Furthermore, it is impossible to locate exactly the position of the interface by atom probe tomography [32]. (ii) The predicted Mn spike is extremely thin, and is therefore very difficult to detect accurately by atom probe tomography [32]. In the last decades, both the LE and PE model have been widely applied to describe the growth kinetics of partitioning phase transformations in Fe–C–M alloys, and their respective relevance has been discussed at length [15,35–38]. Although much effort has been paid to addressing this issue, there are still many uncertainties about the growth mode of partitioning phase transformations in Fe–C–M alloys.

Recently, a growth retardation [39] stage has been discovered during the final austenite to ferrite transformation after several cyclic partial phase transformations [40] in the intercritical region of a low-Mn and low-C alloy (Fe–0.023 wt.% C–0.17 wt.% Mn). The LE model was able to describe the phenomena accurately, while the PE could not. The LE model theoretically predicted that a Mn spike (called a residual Mn spike) is trapped in the austenite due to the large difference between the diffusion rate of Mn in austenite and the interface migration rate, and it was deduced that the growth retardation stage is caused by the interaction between the moving interface and the residual Mn spike left behind by the previous transformation cycle. Ref. [39] provided the first report of growth retardation in a specific low-Mn alloy subjected to a standard type I cyclic experiment [39]; however, no systematic study of growth retardation phenomenon as a function of steel composition and thermal history has yet been performed. Furthermore, novel dedicated experiments are required to support the hypothesis that growth retardation is caused by the residual Mn spike.

In this work, a series of new experiments has been designed and performed to study systematically and in more detail the newly discovered growth retardation phenomenon, and to link it to the existence of the residual Mn spike in the austenite at high temperature. The effect of Mn concentration, number of cycles, cycling temperature and final cooling rate on the growth retardation is studied and discussed in detail.

2. Experimental

The materials investigated here are a set of pure Fe–Mn–C model alloys and a reference pure Fe–C alloy. The compositions of the alloys are presented in Table 1. A carefully tuned Bähr 805A dilatometer is used to measure the dilation of the specimen (10 mm in length and 5 mm in diameter) during the cyclic experiments. Two thermocouples, spaced 4 mm apart, were spot welded to the sample to produce an accurate temperature measurement and to check for the absence of a significant temperature gradient along the sample. The measured temperature gradient along the sample was typically of the order of 2–3 °C. In this work, standard type I cyclic experiments [26] are performed, and the heat-treatment procedure is indicated in Fig. 1. The as-received material was first fully austenized at 1000 °C for 5 min and then cooled down to T_1 for 20 min isothermal holding to create a mixed ferrite–austenite microstructure. The temperature is then cycled between T_1 and T_2 without any isothermal holding at the two heating–cooling inversion temperatures. Typically, three temperature cycles are used, but the number of cycles will be varied here to study the effect of this on the magnitude of growth retardation. Both T_1 and T_2 are located in the $\alpha + \gamma$ two-phase field in the phase diagram. After the cycling, the sample is finally cooled down from T_2 to room temperature. It is the final austenite to ferrite transformation during the final cooling which is of interest here. The kinetics of the previous cyclic transformations has been described in detail elsewhere [26]. The cooling and heating rate during the experiments were each always 10 °C min^{-1}. In some experiments, the standard type I cyclic experiment was modified to prove the assumed features of the relevant processes taking place at the moving austenite–ferrite interface. In this work, based on the ThermoCalc calculations [41], the cycling temperatures T_1 and T_2 were selected appropriately to ensure that both austenite-to-ferrite and ferrite-to-austenite transformations can take place in the fast LENP mode. Unlike the case of normal isothermal experiments, we found that in the cyclic phase transforma-

Table 1
Chemical compositions and cycling temperatures of the investigated alloys (compositions in wt.% and temperature in °C).

Alloy	C	Mn	Fe	T_1	T_2	T_3
A	0.1	0	Balance	815	855	None
B	0.1	0.49	Balance	785	842	810
C	0.1	1.0	Balance	765	822	None
D	0.023	0.17	Balance	860	885	None