Direct measurement of carbon enrichment in the incomplete bainite transformation in Mo added low carbon steels

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Abstract—The overall kinetics and carbon enrichment in austenite during the incomplete isothermal bainite transformation in Fe–0.1C–1.5Mn–(0, 0.03, 0.3, 0.5, 1)Mo (mass%) alloys were investigated with quantitative metallography and Electron Probe Microanalysis in the transformation temperature range of 773–873 K. The incomplete transformation appears at 823–873 K when Mo addition exceeds 0.3 mass%; at 773 K substantial carbide precipitation accompanies bainite transformation and no transformation stasis is observed. Transformed fractions in the stasis stage are hardly affected by prior austenite grain size. Carbon concentrations in austenite in the stasis stage are lower than T_0 line and decrease with the increase of Mo addition and temperature. T_0' limit, solute drag and WB_s limit theories are used to examine the experimentally measured carbon concentration limits in austenite, and their respective flaws are pointed out.
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1. Introduction

Low carbon bainitic steels have found a wide application in many industries, e.g. shipbuilding, automobile, architecture, etc., due to their good combination of high strength and high toughness. In order to achieve enough hardenability to obtain bainite microstructures during continuous cooling in industrial production, several alloying elements like B, Mo and Nb are usually added into steels in appropriate amounts. However, such microalloying also increases the fraction of untransformed austenite, most of which finally transforms into martensite/austenite constituent (M/A) when cooled to room temperature, leading to a decrease in toughness [1]. Similar effects are also responsible for degradation of toughness in heat affected zones (HAZ) after welding, causing failure at welding joints of structural steels [2]. Since the amount of M/A is mainly determined by the degree to which bainite transformation proceeds, this might relate to a phenomenon called "incomplete transformation" (ICT) [3], in which bainite formation stops prematurely before the equilibrium amount is attained. However, despite intensive studies [3–9] over decades, the nature of ICT remains in dispute, with three

main hypotheses being the T_0' limit, solute drag and WB_s limit theories.

When Zener [10] first clearly defined the diffusionless mechanism of bainite, he believed that unlike martensite, there is no strain energy attending the growth of bainite. Thus Zener predicted that the upper temperature limit of bainite formation, B_s, should coincide with T_0 temperature, where austenite and ferrite of the same composition have the same Gibbs free energy. The ICT phenomenon is also readily accounted for in a way that during the growth of bainite, untransformed austenite continuously absorbs carbon rejected from supersaturated bainitic ferrite and its actual T_0 temperature is decreasing, thus eventually a certain point would be reached, beyond which diffusionless formation of bainite is thermodynamically impossible. Bhadeshia and Edmonds [11] inherited the diffusionless view of bainite formation and demonstrated Zener's theory in an Fe–C–Mn–Si alloy, showing that the carbon concentration limits in austenite measured by X-ray diffraction were in good agreement with T_0 line, although some data exceeded T_0 by 0.2–0.4 mass% below 623 K. In a subsequent article, after carefully examining experimental data in an Fe–C–Ni–Si alloy, Bhadeshia [12] estimated that there is a strain energy of ~400 J/mol associated with diffusionless growth of bainite, thus proposed a new limit T_0' that is in essence similar to T_0 but takes into account the strain energy. Recently Caballero et al. [13] studied the ICT phenomenon in a series of sophisticated alloy steels. The

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measured carbon concentrations in austenite in the stasis stage were again proved to be close to T_0 or T_0' limits thus were taken as new experimental evidence that ICT is a manifestation of diffusionless formation of bainite.

In contrast, Aaronson proposes that bainite forms in a reconstructive way, as allotriomorphic ferrite or pearlite does [5], and ICT results from the solute drag effect (SDE) [14] which shifts the upper limit for unpartitioned growth of bainite to much lower than Para-A_{e3} [15] line. In this mechanism, substitutional solute atoms that have slow diffusion rates would segregate at migrating interfaces due to negative interaction energy with these interfaces, exerting a drag force on them thus causing free energy dissipation, a concept originally developed for grain boundary motion [16]. When this drag force is powerful enough, the migration of interfaces could be entirely stopped, leading to the ICT phenomenon. Subsequently, after realizing that the solute diffusion is too sluggish at temperatures of interest to exert a substantial drag force, Bradley and Aaronson [17] modified the original SDE and put forward the solute drag-like effect (SDLE), which states that substitutional alloying elements that have a strong attractive interaction with carbon, when absorbed at migrating interfaces, may decrease the activity of carbon in the austenite in immediate contact with the interfaces, which in turn decrease the activity gradient of carbon in front of the interface and cause sluggish kinetics. This SDLE theory was adopted by Reynolds et al. [7] and Goldenstein and Aaronson [18] to explain the ICT phenomena observed in several high-purity ternary alloys, e.g. Fe–C–Mo, Fe–C–Mn and Fe–C–Cr. Later, Aaronson et al. [19] integrated SDE and SDLE and developed the term coupled solute drag effect (CSDE) to describe these drag forces. When the chemical potential of carbon in austenite at mobile areas of interfaces is decreased to the same level as that in regions remote from these interfaces, growth of bainite would stop. Although Aaronson's opinion experienced the gradual evolution from SDE to CSDE, hereafter this theory is still referred to as the solute drag theory for conciseness.

Unlike T_0' limit and solute drag theories, WB_s limit theory proposed by Hillert [9] does not start from assuming the mechanism of bainite transformation (i.e. diffusionless or reconstructive) but takes a completely different approach. When applying Zener–Hillert equation [20] to examine experimental lengthening rates of acicular ferrite in Fe–C binary alloys, Hillert found that the extrapolation of measured growth rates to zero velocity did not yield the equilibrium carbon concentration. He directly related this effect to what was later described as the ICT phenomenon, proposing that there is a thermodynamic barrier to the growth of acicular ferrite. The experimentally determined value for this barrier indicated no sharp change between Widmanstatten ferrite at higher temperatures and bainitic ferrite at lower. Therefore, Hillert held that there is no essential difference between Widmanstatten ferrite and bainite in terms of growth mechanism, and suggested using a common WB_s to refer to the limits for carbon diffusion controlled growth of acicular ferrite [9]. Hillert tested the validity of WB_s by examining published data in some alloy steels showing a transformation stasis and found that these data could be fitted equally well with the WB_s and T_0' lines. In most alloys investigated, the shift of WB_s by addition of substitutional elements can be well explained purely by thermodynamic effect; in Mo or Cr added alloys, however,

an additional amount of energy needs to be added to the growth barrier obtained in Fe–C systems, which is suggested to originate from solute drag effect.

As can be seen from the brief review above, considerable controversies still remain upon the mechanism of ICT and further study is required. Recently, the ICT phenomena in Nb, Mo or B + Mo added low carbon steels have been preliminarily investigated by Furuhara et al. [21,22]. However, effects of alloy contents on ICT have yet to be revealed in detail. In the present study, different amounts of Mo, which is a potent hardenability enhancing element, were added into an Fe–0.1C–1.5Mn (mass%) alloy and the incomplete bainite transformation was more systematically investigated. In particular, direct measurement of carbon concentration in austenite was conducted by Electron Probe Microanalysis (EPMA) to clarify the role of carbon enrichment in the ICT phenomenon, based on which the three theories mentioned above were examined. In addition, effects of prior austenite grain size on ICT were also briefly studied.

2. Experimental procedure

A series of Fe–0.1C–1.5Mn–(0, 0.03, 0.3, 0.5, 1)Mo (mass%) alloys were used in this study. Hereafter they are referred to as 0Mo, 0.03Mo, 0.3Mo, 0.5Mo and 1Mo alloys, respectively. The alloy ingots were prepared by vacuum melting and casting, followed by hot rolling to ~15 mm. 1Mo alloy was homogenized at 1473 K in Ar atmosphere for 172.8 ks. Samples of 0Mo–0.5Mo alloys were encapsulated into Ar-filled silica tubes, first homogenized at 1423 K for 86.4 ks, cold rolled to a final thickness of ~5 mm, and then homogenized at 1423 K for another 345.6 ks. Chemical compositions of all the alloys after homogenization and their characteristic temperatures calculated by using ThermoCalc with TCFE5 database are listed in Table 1.

Specimens of ~6 × 5 × 3 mm were cut from homogenized samples and austenitized in vacuum furnace at 1373 K. The austenitization time was 1.8 ks for 0Mo, 0.3Mo, 0.5Mo and 1Mo alloys and 0.6 ks for 0.03Mo alloy, which produced similar nominal grain sizes of 183, 185, 189, 190, 178 μm in 0–1Mo alloys, respectively. The austenitized specimens were subsequently quenched into salt bath and isothermally held at 773, 823, 848 or 873 K for 10 s to 86.4 ks, and finally quenched into iced brine. To study the effect of prior austenite grain size on the ICT phenomenon, 0.5Mo alloy was used and austenite microstructures with another three different grain sizes were made: a coarser austenite grain size of 317 μm was achieved by austenitizing the specimen at 1473 K for 1.8 ks, and two finer austenite grain sizes of 43 μm and 18 μm were obtained by first austenitizing the specimen at 1373 K for 1.8 ks to make carbide dissolve and then quenching it into iced brine, followed by a second austenitization at 1173 K for 0.6 ks and 60 s, respectively. These austenized specimens of 0.5Mo alloy were then quenched into salt bath and isothermally held at 848 K for 0.3–10.8 ks.

Transformed specimens were thinned by mechanical polishing from a thickness of ~3 mm to ~1.5 mm thus cross sections close to the center of the original specimens were observed. Well-polished specimens were then etched by using 3% Nital for Optical Microscopy (OM) and Scanning Electron Microscopy (SEM; Jeol JSM-7001F