



Super long-range diffusion of carbon during proeutectoid ferrite transformation

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Abstract: In order to explore the possible diffusion distance of carbon during proeutectoid ferrite transformation, a slow cooling test of low carbon steel was carried out under vacuum of the thermal simulator. The microstructure and thermal expansion curve were discussed and the carbon concentration inside the sample was measured. The ferrite layer of about 450 μm thickness was obtained without pearlite on the surface of the sample in the microstructure. The thermal expansion curve shows that the ferrite layer without pearlite is formed during the local phase transformation, which is followed by the global transformation. The carbon concentration in the core of the sample (0.061%) is significantly higher than that of the bulk material (0.054%). All results show that carbon has long-range diffusion from the outer layer to the inner layer of the sample. The transformation is predominantly interface-controlled mode during local transformation, and the interface migration rate is about 2.25 $\mu\text{m/s}$.

Key words: low carbon steel; local transformation; super long-rang diffusion; interface-controlled mode

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1 Introduction

During the proeutectoid ferrite transformation from austenite, two kinds of diffusion will occur. The first one is the carbon diffusion in ferrite and austenite, which is highly temperature-dependent [1–5]. The solubility of carbon in ferrite is about two orders of magnitude smaller than that in austenite, therefore the carbon atoms will segregate to the interphase boundaries in austenite if they can't diffuse into austenite matrix in time. The exact magnitude of accumulation depends on the

diffusion velocity of carbon in austenite [6]. Carbon can diffuse through one or more austenite grains, and thus it is called long-range diffusion. The other one is the diffusion of matrix atoms, and this diffusion realizes the phase transformation from a face-centered cubic (fcc) symmetry (austenite) into a body-centered cubic (bcc) symmetry (ferrite). This process also causes the movement of the $\gamma \rightarrow \alpha$ interface into the austenite matrix. In this case, the Fe atoms move only to the adjacent positions, which is called short-range diffusion. The above-mentioned two kinds of diffusion occur between the newly formed ferrite and the adjacent austenite

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grains.

Over the past several decades, there have been a number of models describing the kinetics of proeutectoid ferrite transformation. In many of them, the proeutectoid ferrite transformation is assumed to develop under local equilibrium conditions. In this case, the carbon concentration at interface is equal to the γ - α equilibrium concentration; the rate of transformation from fcc lattice to bcc lattice is extremely fast; and the kinetics of proeutectoid ferrite transformation is considered to be diffusion-controlled [7–12]. Another extreme is called interface-controlled. In this situation, there is no carbon concentration gradient in austenite. The kinetics is reflected by interface mobility, which was defined by CHRISTIAN [13]. Actually, both the interface mobility and the diffusivity of carbon in austenite are finite, and thus the mixed-mode character was adopted to describe the proeutectoid ferrite transformation. NOLFI et al [14] investigated the mixed-mode character when they described the dissolution and growth of spherical precipitates. Extensive studies on mixed-mode models have been performed [15–22]. KOP et al [17] also modeled the transformation in terms of interface mobility. Using hot stage transmission electron microscopy, an in-situ study of austenite decomposition was realized by ONINK et al [23]; this experiment showed the phenomena occurring near the transformation interface during the austenite to ferrite transformation, and directly measured the interface migration rates. In the studies above, the ferrite nucleation is considered to occur homogeneously in all parts of the specimen, both on the surface and in the core. The diffusion of carbon only occurs between the newly-formed ferrite and adjacent austenite. Super long-range diffusion of carbon during proeutectoid ferrite transformation has not been mentioned.

The novelty of this work lies in realizing the super long-range carbon diffusion. The proeutectoid ferrite layer of about 450 μm thickness was obtained in this study due to the carbon diffusion from the surface into the interior of the specimen. Based on the results, a new process has been developed, which can achieve varying microstructure for the surface and interior of specimen. For example, ferrite microstructure with good plasticity was obtained on the surface, and the microstructure of ferrite plus bainite with high

strength was obtained in the core part of the specimen. In this way, a better combination of formability and strength was obtained for some bending or twisting workpieces. This work will be introduced in a following paper. This study just focuses on the realization of the super long-range diffusion of carbon.

2 Experimental

2.1 Experimental material

The composition of the studied steel is listed in Table 1. To ensure easy diffusion of carbon, a low carbon steel with high Ar3 (austenite-ferrite transformation start temperature during cooling process) was selected. Cylindrical ingot was cast in a vacuum induction furnace in laboratory. After forging and hot rolling, a plate with thickness of 30 mm was quenched to room temperature to ensure a more homogeneous distribution of carbon. Cylindrical specimens with a diameter of 8 mm and a height of 12 mm were machined from the quenched plate.

Table 1 Chemical composition of studied steel (mass fraction, %)

C	Si	Mn	P	S	Fe
0.05400	0.26338	0.51176	0.00540	0.00228	Bal.

2.2 Experimental method

The slow cooling test was realized on the thermal simulated test machine (DSI MAXSTRAIN-20). Under the vacuum condition of less than pressure of 16 Pa the sample was heated to 950 °C at a heating rate of 10 °C/s. Austenitization took place at this temperature for 600 s, after which the sample was slowly cooled down to 200 °C at a cooling rate of 0.05 °C/s, and subsequently cooled down to room temperature at a cooling rate of 25 °C/s. The cooling rate was rather low to ensure that carbon has adequate time to diffuse when temperature is slightly lower than Ar3. The time, temperature and thermal expansion curves were automatically recorded by the thermal simulator. Figure 1 illustrates the process of the slow cooling test.

The sample after cooling test was evenly divided into two parts along the center of the height. One of the new surfaces was polished and etched with 4% nital solution (volume fraction). The microstructure of the sample was observed under

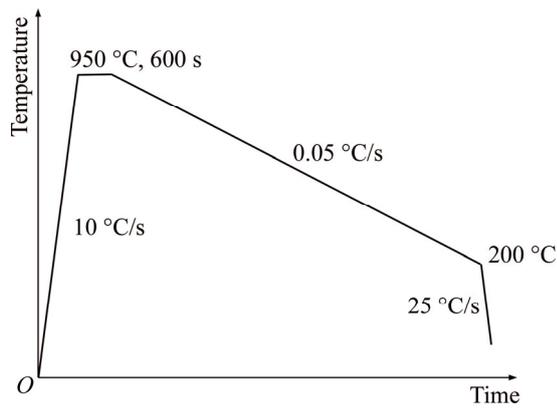


Figure 1 Schematic drawing of slow cooling test

optical microscope.

To prove the carbon diffusion from the outer layer of the specimen into the interior of specimen, the carbon concentration inside the sample was measured. The material from the outer layer of the cylindrical sample was removed with a reduction in the diameter from 8 mm to 6.8 mm, and the height was changed from 12 mm to 8 mm, as shown in Figure 2. The material of the smaller cylindrical specimen was machined into drillings, and then the carbon concentration was measured with the carbon sulfur analyzer (Leco CS-444LS USA).

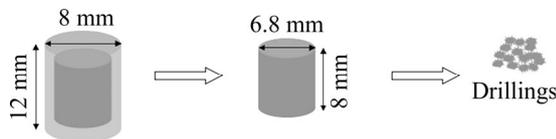


Figure 2 Schematic drawing of drillings preparation

3 Results and discussion

3.1 Experiment results

Figure 3 shows the microstructure of the investigated specimen. It can be seen that the microstructure can be divided into two different regions by the highlighted red circle in Figure 3(a). The outer white bright layer has an unevenly distributed thickness varying from 400 to 550 μm , in which only proeutectoid ferrite can be observed. Figure 3(b) shows the magnified surface region with the transition from ferrite near the surface to a mixed phase of ferrite and pearlite in the interior. Figure 3(c) shows the homogeneously mixed phase of ferrite and pearlite in the interior of the specimen.

The thermal expansion curve was recorded in real time by the thermal simulator, as shown in Figure 4. From the holding temperature to 893 $^{\circ}\text{C}$, the diameter of the sample decreased linearly with the decrease of temperature due to no transformation occurring at this stage. Then the temperature continued to decrease, and the expansion curve began to deviate, which means that ferrite transformation started at 893 $^{\circ}\text{C}$. Then, the thermal expansion curve deviated from the dashed line more and more, indicating that more austenite transformed into ferrite. Finally, the thermal expansion curve rose noticeably when the temperature was lower than 844 $^{\circ}\text{C}$, which

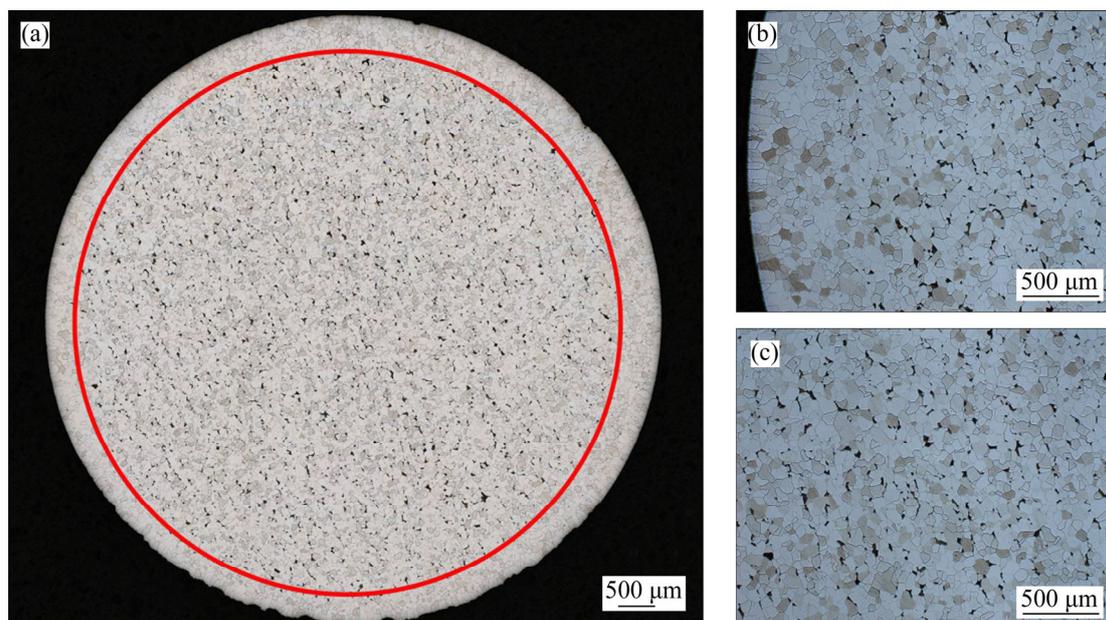


Figure 3 Microstructures after slow cooling test: (a) Whole section; (b) Specimen surface; (c) Interior

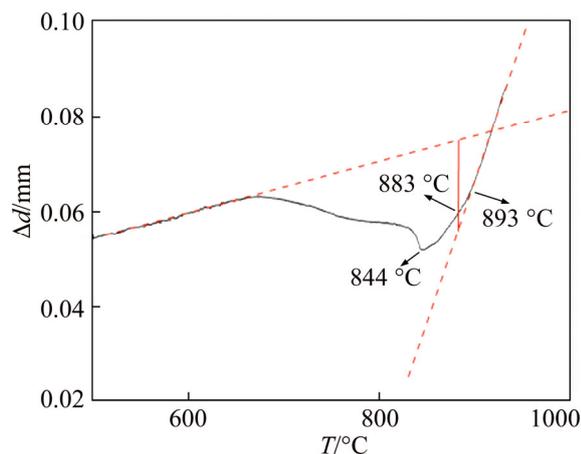


Figure 4 Thermal expansion curve of slow cooling process (Ferrite transformation started at 893 °C, diameter of specimen increased at 844 °C and local transformation ended at 883 °C, which was calculated on the base of microstructures and lever rule)

demonstrated that the effect of phase transformation expansion surpassed the effect of cooling shrinkage.

It is assumed that the carbon concentration of the proeutectoid ferrite (with tertiary cementite at room temperature) in the outer layer of the sample is 0.02%, which is the highest solubility of the proeutectoid ferrite at 723 °C. The average thickness of the outer layer is 0.45 mm. If the spare carbon atoms diffused from the outer layer into the inside of cylindrical specimen, the calculated average carbon concentration of the inside of cylindrical specimen should be 0.063%. The actual measured result of the carbon concentration of drillings is 0.061%, which is lower than the calculated carbon concentration, but is significantly higher than that of the bulk material (0.054%). This is the direct evidence of the diffusion of carbon from the outer layer to the interior.

3.2 Discussion

Based on the theory of mixed-controlled mode [15, 18], the transformation changes from interface-controlled mode to diffusion-controlled mode due to the variation of carbon concentration distribution in austenite, as shown in Figure 5.

In the slow cooling test, the specimen was gradually cooled from the outer layer to the interior [24]. The thermal conductivity of the steel is the lowest at the temperature of Ar₃. It is more beneficial to form a temperature gradient. When both the surface temperature and the interior

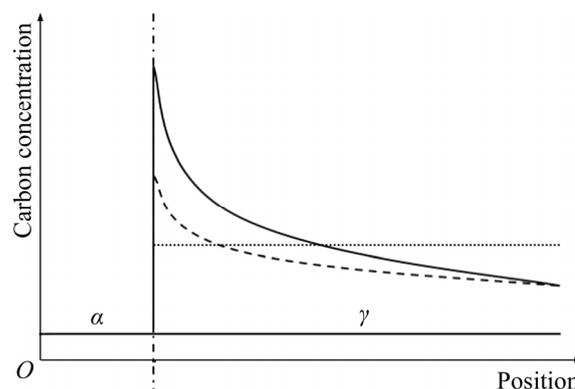


Figure 5 Schematic carbon concentration profiles at ferrite-austenite interface (The dotted line gives the profile for interface-controlled mode, the dashed line for mixed-mode, and the solid line for diffusion-controlled mode, according to KRIELAART et al [16])

temperature are higher than Ar₃, the microstructure remains austenite, as shown in Figure 6(b). At this stage, the austenite volume shrinks with the decreasing temperature without phase transformation. Thus, the thermal expansion curve decreases linearly with the decrease of temperature.

At a moment of slow cooling, the surface temperature of the specimen becomes lower than Ar₃ and ferrite will nucleate on the surface of specimen, while the internal structure remains austenite due to the higher temperature, as shown in Figure 6(c). Because of the low solubility of carbon in ferrite, the carbon atoms will diffuse from ferrite into austenite with the growth of ferrite, which means the carbon atoms will migrate from surface of the specimen to the interior. Since carbon diffusion is heavily temperature dependent, it is assumed that the concentration of carbon inside the austenite phase remains homogeneous at this stage when the temperature is high enough, as shown by the dotted line in Figure 5. The increased carbon concentration of austenite inside the specimen further reduced the transformation driving force, which makes the internal austenite more stable. At this stage, the phase transformation is interface-controlled mode. Phase transformation takes place only on the surface and does not occur in the interior of the sample, therefore it is defined as “local transformation”. With the growth of ferrite close to the surface, the thickness of ferrite layer increases gradually. Figure 3 shows that about 11.25% of the austenite in diameter direction has

transformed into ferrite, based on the lever rule, the ending temperature for local transformation should be 883 °C, as indicated by the arrows in Figure 4.

Since the transformation mode here is interface-controlled, the interface migration rate depends on the corresponding driving force and the interface mobility. The driving force for interface migration is a function of carbon concentration and temperature, and the interface mobility is determined by the coherency of interface, solute drag, pinning effects, etc., thus the interface migration rate varies during the local transformation. According to the thermal expansion curve, the cooling rate of this experiment was 0.05 °C/s, and the local transformation last from 893 to 883 °C, resulting in a time interval of 200 s. With the migration path of about 450 μm measured from Figure 1, the average interface migration rate can be estimated to be 2.25 μm/s.

When the temperature of the central specimen is lower than Ar3, as indicated by the dashed line in Figure 6(a), ferrite nucleation will occur at the grain boundary of austenite in the interior, as the microstructure in Figure 6(d). From this time on, the ferrite transformation begins in the whole sample. The transformation is thus defined as

“global transformation” at this stage. At the beginning of global transformation, the carbon concentration at the interface is close to the average value of the specimen and almost keeps homogeneous in austenite, so the transformation is also interface-controlled. Because of lower temperature and higher ferrite volume ratio than those of local transformation, the diffusion of carbon in austenite becomes more difficult, and carbon will accumulate at the interface. The corresponding carbon concentration profile is given by the dashed line in Figure 5. The transformation becomes mixed-mode, and the interface migration becomes slower. When the carbon concentration at the interface reaches equilibrium, as shown by the solid line in Figure 5, the interface stops migrating, and the ferrite grains stop growing until the carbon concentration at the interface becomes lower than the equilibrium value again.

Finally, a further cooling below Ar1 (austenite-pearlite transformation start temperature during cooling process) leads to a transformation from the remaining austenite inside the specimen to pearlite, and the temperature profile is given by the solid line in Figure 6(a). Figure 6(e) shows the schematic of the resulting microstructure.

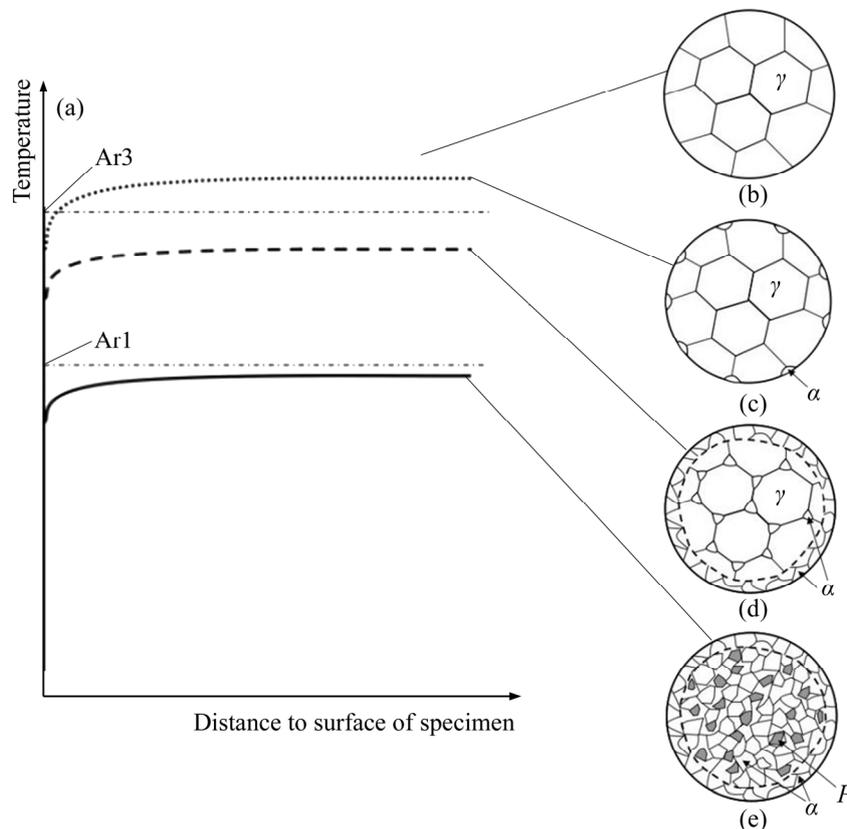


Figure 6 Schematic of temperature profile (a) and microstructure development (b–e) during slow cooling test

4 Conclusions

1) In the slow cooling test of a low carbon steel, two stages of transformation including local transformation and global transformation took place. The ferrite layer of 450 μm thickness was obtained on the surface of the sample during the local transformation.

2) The measured carbon concentration in the interior specimen shows that carbon on the surface of a sample has a super long-range diffusion, and the diffusion distance should be greater than the thickness of the ferrite layer.

3) In the local transformation, the phase transformation mode is interface-controlled, and the interface migration rate is about 2.25 $\mu\text{m/s}$.

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中文导读

先共析铁素体相变过程中碳的超长程扩散

摘要：为研究先共析铁素体相变过程中碳原子可能的扩散距离，在热模拟的真空环境下进行了低碳钢的缓冷试验，分析了金相组织和热膨胀曲线，并测量了试样芯部的碳含量。观察金相组织发现试样的表面获得了 450 μm 厚的铁素体层，该铁素体层中不含珠光体。热膨胀曲线显示不含珠光体的铁素体层形成于全局相变之前的局部相变过程中。试样芯部的碳含量(0.061%)显著高于基体材料的碳含量(0.054%)。结果表明，碳从试样表层到试样芯部发生了超长程扩散。局部相变主要为界面控制模式，界面迁移速率大约为 2.25 $\mu\text{m/s}$ 。

关键词：低碳钢；局部相变；超长程扩散；界面控制模式