Phosphorus and Boron Segregation at Prior Austenite Grain Boundaries in Low-alloyed Steel

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Grain boundary segregation of metalloid impurity elements such as phosphorus and antimony is known to induce temper embrittlement of low-alloyed steels. Fracture in temper embrittlement takes place mainly along prior austenite grain boundaries, which are formed in austenite at high temperatures and remain in the martensite or ferrite/pearlite microstructure after phase transformation. Numerous studies on segregation at prior austenite grain boundaries have been performed,1)–5) and these results suggest that metalloid impurity elements are segregated at prior austenite grain boundaries in low-alloyed steels. In order to reveal grain boundary segregation of impurity elements, segregation at grain boundaries in ferritic iron and steel has also been characterized.6)–9)

Besides temper embrittlement of low-alloyed steels, the microstructure formed by austenite decomposition during cooling in carbon steels and low-alloyed steels may also be influenced by grain boundary segregation. Typically, addition of a small amount of boron, which is segregated at grain boundaries, enhances phase transformation from austenite to martensite in steels, that is the hardenability.10) Since most of steel plates and sheets are produced through continuous cooling, it is of great importance to make clear the role of metalloid elements segregated at grain boundaries relevant to nucleation and growth of ferrite at grain boundaries and sub-boundaries on cooling. This prompts us to study segregation of metalloid elements at grain boundaries in austenite, and its influence on the microstructure of steels. In this work, Auger electron spectroscopy (AES) is used for investigating segregation of phosphorus and boron at prior austenite grain boundaries in manganese steels. Moreover, the microstructure of the samples, which underwent austenite decomposition, is observed. The roles of grain boundary segregation in heterogeneous evolution processes in the microstructure are discussed coupled with experimental results.

Ingots of 0.2% C–0.2% Si–2% Mn steels were produced by vacuum-induction melting. The chemical composition of these ingots is listed in Table 1. They were hot-rolled to plates of about 12 mm in thickness. Samples for AES analysis were quenched into water of 273 K after annealing at 1473 K for 1200 s, since these samples are relatively easily fractured along at prior austenite grain boundaries. Samples for the microstructure observation were stepwise cooled; they were annealed at 1173 K for 600 s after annealing at 1473 K for 1200 s, subsequently annealed at 873 K for 3600 s and finally quenched into water of 273 K. During annealing at 873 K, austenite in samples was decomposed to ferrite and pearlite.

Charpy-type impact tests of samples were performed at 77 K, and the fractured surface of samples was observed by scanning electron microscope (SEM). Samples with phosphorus containing more than 0.03 mass% were fractured along prior austenite grain boundaries. Samples for AES analysis were cut to the shape of 4×4×20 mm³ with notch from the hot-rolled plates. Auger spectra from grain boundaries were measured by selecting grain boundary planes in the fractured surface using a micro-focused electron beam of 5 keV. The segregated amount of phosphorus and boron at grain boundaries was evaluated using the Auger peak height ratio of P LVV (120 eV) and B KVV (185 ev) to Fe LMM (703 eV) in first derivative Auger spectra, respectively. The carbon Auger peak detected is considered to arise from fine carbides and carbon segregated at grain boundaries, since the bulk concentration of carbon in this sample is sufficiently high to form carbides or to be segregated at grain boundaries during annealing at 873 K and the diffusivity of carbon in steel is relatively fast. Segregation of alloying elements such as silicon and manganese with relatively small free energy of segregation was found to be negligible in these alloys. Thus, grain boundary segregation of phosphorus and boron are focused in this work. The microstructure in the center part of samples in which austenite was decomposed was observed by a conventional optical microscope. Vickers hardness was also measured to evaluate mechanical properties of the samples.

Figure 1 summarizes the Auger peak height ratio of phosphorus and boron to iron as a function of the bulk phosphorus concentration in samples quenched from 1473 K. The averages and standard deviations of these Auger peak height ratios are plotted. The results show that the average amount of segregated phosphorus increases with increasing bulk phosphorus concentration. In addition, it is noted that boron segregation, which occurs in samples added with 15 mass ppm boron, decreases the amount of segregated phosphorus.

These characteristic features of phosphorus and boron

Table 1. Chemical composition of low-alloyed steels presently investigated (mass%).

<table>
<thead>
<tr>
<th></th>
<th>C</th>
<th>Si</th>
<th>Mn</th>
<th>P</th>
<th>S</th>
<th>B</th>
</tr>
</thead>
<tbody>
<tr>
<td>Sample A</td>
<td>0.19</td>
<td>0.21</td>
<td>2.04</td>
<td>0.005</td>
<td>0.004</td>
<td>0.0003</td>
</tr>
<tr>
<td>Sample B</td>
<td>0.19</td>
<td>0.21</td>
<td>2.01</td>
<td>0.005</td>
<td>0.004</td>
<td>0.0009</td>
</tr>
<tr>
<td>Sample C</td>
<td>0.19</td>
<td>0.20</td>
<td>2.00</td>
<td>0.031</td>
<td>0.005</td>
<td>0.0002</td>
</tr>
<tr>
<td>Sample D</td>
<td>0.19</td>
<td>0.20</td>
<td>1.98</td>
<td>0.056</td>
<td>0.006</td>
<td>0.0002</td>
</tr>
<tr>
<td>Sample E</td>
<td>0.19</td>
<td>0.20</td>
<td>1.91</td>
<td>0.079</td>
<td>0.006</td>
<td>0.0003</td>
</tr>
<tr>
<td>Sample F</td>
<td>0.19</td>
<td>0.20</td>
<td>2.03</td>
<td>0.061</td>
<td>0.005</td>
<td>0.0015</td>
</tr>
<tr>
<td>Sample G</td>
<td>0.19</td>
<td>0.21</td>
<td>1.98</td>
<td>0.095</td>
<td>0.005</td>
<td>0.0015</td>
</tr>
</tbody>
</table>
segregation at prior austenite grain boundaries may be interpreted based on a model, which was proposed for grain boundary segregation in a ternary system. This model is based on the experimental results on the mutual influence on grain boundary segregation of different metalloid elements in ferrite. By extending an expression for equilibrium segregation of solute elements at grain boundaries in a binary system, the relationship for equilibrium segregation in a ternary system may be given by

\[
X_f^I(1 - X_f^I + X_f^J) = X_f^J(1 - X_f^I + X_f^J) \exp\left(-\frac{\Delta G_{gb}^I}{kT}\right)
\]

\[
X_f^J(1 - X_f^I + X_f^J) = X_f^J(1 - X_f^I + X_f^J) \exp\left(-\frac{\Delta G_{gb}^J}{kT}\right)
\]

where \(k\) is the Boltzmann constant, \(T\) the equilibrium temperature, and \(\Delta G_{gb}^I\) and \(\Delta G_{gb}^J\) the free energy of segregation of solutes \(I\) and \(J\), respectively. \(X_f^I\) and \(X_f^J\) are the fraction occupied by segregated atoms \(I\) and \(J\), respectively. \(X_f^0\) is the fraction of the grain boundary site available for segregated atoms, \(X_f^I\) and \(X_f^J\) are the fraction occupied by segregated atoms \(I\) and \(J\), respectively. As seen in these expressions, different segregated atoms are mutually interfered at grain boundaries. Actually, such behavior is observed in phosphorus and boron segregation at austenite grain boundaries, as shown in Fig. 3. The fact that the addition of small amount of boron suppresses phosphorus segregation at austenite grain boundaries suggests that the boron with a large free energy of segregation, presumably about 100 kJ/mol, affects segregation of phosphorus with a free energy of about 50 kJ/mol. Although it may be inferred in a similar manner that carbon influences grain boundary segregation of phosphorus and boron in austenite, such carbon effect is insignificant in the present case. This is because carbon may be segregated or finely precipitated at grain boundaries of samples during cooling after annealing at high temperatures.

The microstructure of samples stepwise cooled by annealing at 1473 K for 1200 s, at 1173 K for 600 s and at 873 K for 3600 s was observed by optical microscope, in order to investigate the effect of phosphorus and/or boron addition on the microstructure evolved during austenite decomposition. Figures 2(a), 2(b), 2(c) and 2(d) show micrographs of Sample A (base), B (0.0009% B), D (0.056% P), and F (0.061% P, 0.0015% B), respectively. The areas with a bright contrast are ferrite formed during decomposition of austenite, while the areas with a dark contrast are mainly the pearlitic microstructure. Different morphologies of ferrite are observed in these micrographs. Ferrite is formed along prior austenite grain boundaries, which is called grain boundary ferrite allotriomorph. This ferrite is found in all the samples stepwise cooled in the present conditions. On the other hand, plate-like ferrite formed inside prior austenite.
ite grains is referred to as Widmanstätten ferrite. The phosphorus addition is found to change the shape of Widmanstätten ferrite from plate-like to fine granular, as shown in Fig. 2(c). On the other hand, boron addition inhibits formation of Widmanstätten ferrite in steels regardless of phosphorus addition, as shown in Figs. 2(b) and 2(d).

These changes of ferrite morphology by phosphorus and/or boron addition appear to correspond to the present experimental results, suggesting that boron segregation suppresses phosphorus segregation at austenite grain boundaries. Although inside of austenite grains could not directly be analyzed in this work, Widmanstätten ferrite is likely to nucleate at sub-boundaries formed inside austenite grains during austenite decomposition. Boron is also considered to segregate at sub-boundaries, in which the density of segregation sites is lower than that in prior austenite grain boundaries. Thus, boron segregated at the sub-boundaries may suppress nucleation of Widmanstätten ferrite in a sample containing phosphorus by boron addition. Segregation of phosphorus may also occur at the sub-boundaries. However, the diffusivity and free energy of segregation of phosphorus are lower than those of boron, and therefore phosphorus may be insignificant for inhibiting ferrite nucleation. Phosphorus may rather influence growth process of Widmanstätten ferrite. This is consistent with the fact that the shape of Widmanstätten ferrite is changed by phosphorus.

Vickers hardness of the above samples after austenite decomposition was measured to evaluate the influence of phosphorus and/or boron addition on the mechanical properties. Figure 3 shows Vickers hardness of the samples stepwise cooled as a function of the bulk phosphorus concentration. The results show that hardness increases with increasing phosphorus concentration. The increase in hardness by phosphorus addition is mainly attributed to solid solution hardening by phosphorus. Although the amount of boron is very small, boron is likely to slightly increase the hardness, in spite of. This may be caused by a decrease of the fraction of Widmanstätten ferrite by boron addition.

As related to hardenability of steels, the effect of alloying elements on austenite decomposition have extensively investigated, and the mechanisms on austenite decomposition have been discussed. In these studies, austenite decomposition has mainly been explained by the changes of the phase stability of ferrite and austenite by addition of alloying elements. However, the effect of small amount of metalloid elements on austenite decomposition appears to be different from that of metallic elements, because they sometime influence interfacial phenomena in the microstructural formation through segregation. Actually, grain boundaries are considered to act as preferential sites for ferrite nucleation in austenite, and the mechanisms of nucleation and growth of ferrite have been proposed.

In addition to these earlier works, the present results indicate that microstructural features in grain boundaries can be controlled by addition of small amount of metalloid elements, and thereby it may be possible to control the microstructure formed during austenite decomposition. Although alloying elements are considered to directly change the bulk properties such as mechanical properties, it is of great interest to note that segregation of small amount of metalloid element contributes to the interface phenomena for controlling formation of the microstructure. Since the local structure of interfaces such as grain boundary and sub-boundary, being atomically distorted, is quite different from that of the matrix, such microstructures may become the nucleation site of ferrite in austenite decomposition. Segregation of elements at these interfaces is considered to modify their local structure or stability, and thereby the morphology of ferrite nucleated at the interfaces is also varied.

In conclusion, the results obtained in this study are summarized as follows:

1. Boron segregation at austenite grain boundaries was found to suppress phosphorus segregation. These results indicate that boron may preferentially occupy segregation sites at grain boundaries.
2. Phosphorus addition is likely to change the shape of Widmanstätten ferrite from plate-like to granular-like. On the other hand, the formation of Widmanstätten ferrite is inhibited by boron addition regardless of phosphorus addition. Since nucleation sites of ferrite are considered to be grain boundaries and sub-boundaries where phosphorus and boron are segregated, the microstructural changes can be attributed to the segregation of phosphorus and boron.

REFERENCES