The Effects of Cr, Mn and Ni on the Substructure and the Toughness of Tempered Martensite and Bainite in the Low C–0.5%Mo Steels

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Synopsis

The substructure and the toughness of tempered martensite and isothermally formed bainite were compared among 0.15 or 0.3% C–0.5% Mo steels containing any one of Cr, Mn, or Ni by 1.5 or 2.5%.

Even though the difference in the substructure and in the strength-toughness relationship were not large among their tempered martensites, it became marked among their bainites as the formation temperature rose. The hardness of bainite was dependent on the formation temperature rather more than on the alloying elements, but it was just the opposite for the toughness. The bainite in the Ni steels was obtained in a relatively wide temperature range with the best strength-toughness properties in spite of its very coarse substructure and also of the very coarse carbides in it. The bainite of the Mn steels showed the similar characteristics to that of the Ni steels. In the Cr steels the bainite reaction was so sluggish that it was in a very narrow temperature range that a completely bainitic structure was obtainable, the bainite being of a very poor toughness in spite of its extremely fine substructure and carbides.

These results were considered to indicate that the intrinsic toughness of the matrix endowed by the alloying elements played for the higher temperature transformation products a role more important than such microstructural factors as the effective grain size and carbide distribution.

I. Introduction

In the previous report the authors studied the effects of the austenite grain size and the C content on the substructure and the toughness of the tempered martensite and the bainite using the 5% Ni–0.5% Mo steels. It was most interesting to find in these steels that coarsening of the parent austenite grain did not cause coarsening of the substructure, and that despite the coarsened austenite the toughness of bainite was not impaired, even though that of tempered martensite got deteriorated. It was also found that increase in the C content generally brought about refinement of substructure in both structures, and that this deteriorated the toughness of bainite greatly, but that of the tempered martensite only slightly. This fact was considered to suggest that the unfavourable effect of the increased coarse carbides surpassed the favourable effect of the substructure refinement on the toughness of the bainite. Thus the toughness behaviour was closely correlated to the microstructural factors, at least, in one alloy system.

It was then thought interesting to investigate whether this relationship would be still valid when different alloying elements were employed. While the effects of the alloying elements on the toughness of steels have been investigated systematically for the equiaxed ferrite and ferrite-pearlite structures, it is only recently that investigations have started on effects of alloying elements for such transformation products as martensite and bainite. In these structures the effects of alloying elements will be exerted on the toughness of transformation products in the forms of changing the transformation characteristics, the morphology of the transformation substructure, and the intrinsic toughness of the matrix after the transformation. These effects should be discussed separately although the quantitative estimation of individual factors seems to be extremely difficult.

In this investigation three alloying elements, Cr, Mn, and Ni, were selected to compare these effects for low C high strength steels. Furthermore, the effects of austenite grain size and the C content on the substructure and the toughness of the transformation products were also investigated for each alloy steel. Procedures the same as employed in the previous report, the results of which will be quoted whenever necessary for comparison, were followed.

II. Experimental Procedure

The alloying elements Cr, Mn, and Ni were separately added by 1.5 or 2.5% to 0.5% Mo steels with two C levels of 0.15 and 0.3%. The chemical analyses of these steels are listed in Table I. The specimen preparation and heat-treatment were carried out in the same manner as in the previous paper. The 50 kg ingots were forged to 15 mm thick bars, which were cut into 12×12×55 mm for heat-treatment. Two austenitizing conditions, 1200 and 950°C, for 15 min each, were selected to obtain the coarse- or fine-grained austenite, respectively. The isothermal treatment to produce bainite was carried out in a salt bath. The completion of bainite reaction was confirmed by optical and electron microscopies. These heat-treated specimens were machined to 7×7×55 mm subsize Charpy specimens for impact tests. Vickers hardness determination was also made on these specimens.

III. Experimental Results

1. Comparison of the Substructure

1. Bainite

The temperature range in which fully bainitic structure was produced was slightly different among those alloy steels when compared at the same alloy and C content, as shown in Fig. 1. It is to be noted that the temperature range was about the same for the Ni and the Mn steels with 0.15%C, whereas for 0.3%C it was a little lower for the Mn steel than

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The Ni steel, and that for the Cr steels it was very narrow as the transformation reaction was too sluggish to complete within a reasonable time.

As shown in Photo. 1, optical microscopy examination revealed that all the steels of the 0.15% C-1.5% X series were able to produce the fully bainitic structure. At higher magnifications by an electron microscope, these structures were found to consist of thick lath or cells, the width of which was about 0.8 µm in the Mn and the Ni steels and 0.5 µm in the Cr steel. Along the lath boundaries coarse carbides or ferrite-carbide aggregates of irregular shape (which will be called ‘degenerated pearlite’[18]) were present in the Mn and the Ni steels, whereas finely dispersed globular carbides were dominant in the Cr steel. It was thought likely that during the growth of bainitic ferrites the C enrichment took place in the retained austenite until finally precipitated as carbides.

In Photo. 2 different growth characteristics due to difference in alloying elements are shown; in the Ni and the Mn steels massive untransformed austenites are distributed sparsely corresponding to the coarse precipitation of carbides (Photo. 2(b) and (c)), whereas in the Cr steel the retained austenites are distributed finely corresponding to the fine carbides precipitation making the worm-eaten structure. The essential features did not change by the increase in the alloying elements up to 2.5% as seen from the comparison between Photos. 2 and 3, though the structure tended to become more lath-like with the increase in the content of the alloying element.

The increase in the C content from 0.15 to 0.3%, which shifted the bainite transformation temperature range to the lower side, caused the refinement of both lath-like structure and the carbides as shown in Photo. 4. In the Ni steel the lath width decreased to 0.2~0.3 µm, and the carbides became fine and abundant without giving any sign of forming degenerated pearlites, although the transformation temperature was the same as that of the 0.15% C steels. While the upper bainites in the 0.3% C-5% Ni steel was predominantly granular as described in the previous report,1) the lath-like structure occupied more than 50% in the range of transformation temperature from 400° to 450°C in the 0.3% C-1.5% Ni steel. The carbides lay elongated along the lath boundaries or in flake shape inside the granular bainite. While the bainite of the Mn steel showed features similar to that of the Ni steel, the bainite of the Cr steel exhibited much finer lath-like structure with much finer carbides. These substructural features due to the alloying element were similar to the case of the 0.15% C steel.

In the 0.3%C-2.5% X steels, where the transformation temperatures were further lowered, the lower bainite appeared partially or almost fully in the bainitic structure obtained at 330° to 400°C in each steel. In these structures the difference in alloying element did not cause great difference in the lower bainite morphology in that globular carbides lay parallel in the direction 50° to 60° from the lengthwise direction of laths[11] in the dominantly lath-like structure. The upper bainites in this series exhibited features due to the alloying elements similar to those in the 0.3% C-1.5% X series.

In the 5%Ni steels dealt with in the previous report1) it was found that the bainite substructure did not coarsen even though the parent austenite grain was coarsened in both 0.15 and 0.3% C steels. In the present experiment the effect of austenite grain size was also investigated on the bainite substructure obtained from the coarse-grained austenite for the 0.15 or 0.3% C-1.5% X series as well as for 0.15 and 0.3%
C-2.5Ni steels. In the case of the 2.5% Ni steels the well-developed bainite needles partitioned the parent austenite grains inhibiting the coarsening of the substructure as shown in Photo. 5. However, this effect was not remarkable in the 1.5% X series steels irrespective of the C content as shown in Photo. 6. The only exception was the case of the Cr steel, in which the bainite substructure remained very fine regardless of the C content and austenite grain size.

2. Martensite

All the martensites obtained in the range investigated were of packet martensite\(^1\) without any detectable particular features due to the alloying element. Nor was found any difference due to the alloying element for the processes of precipitation of carbides and cancellation of dislocations during the tempering. Coarsening of martensite substructure with coarsening of parent austenite grains was found.
in agreement with the previous report, but no detectable difference due to the alloying elements could be recognized in this behaviour, although at higher C content the coarsening became less noticeable.

2. Comparison of Strength and Toughness of the Tempered Martensite and the Bainite

1. Tempered Martensite

Figure 2 shows the tempering curves for hardness and for ductile-brittle transition temperature of the
martensite obtained in the steels, with Cr, Mn, and Ni all set at 1.5%, quenched from 950°C and tempered at temperatures between 400° to 600°C. The softening by tempering became greater in the order of Cr, Mn, and Ni. This order was unchanged through the increase in the C content from 0.15 to 0.3%, which merely translated the curves upwards. It will be noted from the figure that the difference in hardness between steels was small at 600°C, becoming greater as the tempering temperature was lowered. Though not shown in the figure, this trend was not changed when the austenite grain was coarsened.

As for the toughness, expressed in terms of ductile-brittle transition temperature, the difference was also small among the steels when tempered at 600°C. As the tempering temperature was lowered, the transition temperature was increased, that is, the toughness was deteriorated greatly in the Cr and the Mn steels but slightly in the Ni steels. The increase in the C content did not necessarily reduce the toughness in spite of the hardness rise. The embrittlement due to the coarsening of austenite grain was small in the Ni steels but increased in the order of the Mn and the Cr steels regardless of the C content. The embrittlement was greater when the C content was lower, in agreement with the previous report. 1)

Figure 3 shows relationships between the hardness and the transition temperature of the tempered martensite in the 1.5% X steels. When the toughness was compared at equal strength level, the Ni steels showed the best property, followed by the Cr steels, and the Mn steels were the worst, regardless of the austenite grain size and the C content. In the Cr and the Mn steels, increase in hardness caused a great deterioration of toughness in contrast to the Ni steels, which showed only a small change of toughness. The trends were the same even when the alloying content was increased to 2.5%.

The changes of the relationship between hardness and toughness with the change in the alloy content are shown in Fig. 4. In the Ni steel, increase in Ni content brought about improvements in the toughness, especially in the 0.15%C steels. Even when the austenite grain size was large, the Ni addition in the range investigated improved the toughness. In the Cr steel the toughness as well as the hardness was reduced as the Cr content increased. In the Mn steel the increase in Mn content raised the hardness, but did not change the relationship between hardness and toughness greatly.

2. Bainite

Figure 5 shows the relationship between the hardness and toughness and the formation temperature of bainite in each steel. The hardness increased as the formation temperature was lowered in each steel. When compared at the same formation temperature, the hardness tended to be higher when the C content was higher. On the other hand, hardness did not necessarily increase as the formation temperature was lowered by the increase in alloy content. While the hardness distribution against the formation temperature fell within a relatively narrow band, the toughness value in terms of the transition temperature scattered widely, though in the individual steels the
toughness of bainite was generally reduced as the formation temperature was raised. When the alloying element was the same, the formation temperature vs. the transition temperature curve shifted upwards in the bainite with higher C content.

The effects of the austenite grain size and the C content on the hardness and the transition temperature of the bainite in the 1.5%X steel are shown in Fig. 6. In the 0.15%C steels the effect of the austenite grain size on the hardness of bainite can be said to be small on the whole, though the harness was slightly lower in the bainite obtained from coarse-grained austenite than in that from fine-grained austenite. The difference in hardness due to the alloying element was also small, though becoming larger in the order of Ni, Mn, and Cr. The toughness was deteriorated more in the order of Ni, Mn, and Cr steels. Although the austenite grain size dependency of the bainite toughness had been small in the 5%Ni steel, the toughness of bainite was greatly impaired regardless of the C content in the 1.5%X steels when the austenite grain was coarsened.

Therefore, it was decided to study whether this fall of toughness would occur in the 2.5%Ni steels or not. The results are shown in Fig. 7 together with those for 5%Ni steels. The bainite in the 2.5%Ni steel showed little austenite grain size dependency both for the toughness and for the strength, similarly as in 5%Ni steels.

In Fig. 8 relationships between the hardness and
the transition temperature of various bainites are shown. Although only a few data are available for the case of the 0.15\% C steels, it may be said that the strength and the toughness of the Mn and the Ni steels were similar while the Cr steel seemed to be stronger and more brittle. The bainite of the 2.5\% Ni steel was as strong and tough as that of the 1.5\% Ni steel, while the bainite of the 5\% Ni steel had similar toughness but with a hardness some 50 Hv higher at 0.15\% C level. The bainite of the 2.5\% Mn steel was a little harder and much less tough than that of the 1.5\% Mn steel. At 0.3\% C level the bainite of the 1.5\% Ni steel was the toughest and that of the 1.5\% Mn and the 1.5\% Cr steel was far brittle. Increase in the C content from 0.15 to 0.3\% did not change the toughness of the bainites greatly while the hardness was raised somewhat. At 0.3\% C level the increase in the alloying element from 1.5 to 2.5\% generally caused a reduction in the toughness.

A generalized conclusion may be deduced from above results that, for the estimation of the alloying elements on the strength and toughness of bainite, Ni is the best and Mn and Cr are less effective by approximately the same extent.

**IV. Discussion**

The result of the microstructural investigation of the transformation products can be summarized as follows. The difference in the microstructure among the steels due to alloying elements was not detectable in the tempered martensite and the lower bainite, but became large in the upper bainite. On the other hand, the difference in the strength and the toughness among the steels were small for martensites tempered at high temperatures, but the toughness of the bainite differed greatly among the steels, although the difference in the strength was small among them. In this respect it should be of an interest to relate the microstructure to its strength and toughness.

In the previous report, even though only one alloy series, that of the 5\% Ni steels, was dealt with, correspondence between the microstructure and the strength–toughness property was explainable to some extent in terms of the effective grain size and the morphology of carbides. For individual steels used in this investigation also the relationships between the microstructure and the strength and toughness seem readily explainable by these two factors.

As for the tempered martensite, the toughness, compared at the same strength level, was better in the 0.3\% C steel than in the 0.15\% C steel in each alloy series as shown in Fig. 3. This fact can be explained to be due to the reduction in the effective grain size brought about by the substructure refinement with the increase in the C content. On the other hand, the increase in the austenite grain size resulted in the deterioration of toughness. A similar deterioration of toughness due to coarsening of austenite grain was found in the bainite of the 1.5\% Mn and the 1.5\% Ni steels (Fig. 6), but not in the 2.5 and 5\% Ni steels (Fig. 7) because the coarsening of the austenite grain did not accompany coarsening of substructure.

It was also noted that the drop in hardness and in toughness of bainite due to the austenite grain coarsening was larger in the 0.3\% C steels than in the 0.15\% C steels (Fig. 6). The carbides were found to grow with coarsening of austenite grain. The fact that the drop in the hardness and in the toughness was larger in the 0.3\% C steels where the carbides were abundant suggests that the effects of the carbides are important both on the strength and on the toughness.

In an alloy with a given austenite grain size the increase in the C content may certainly increase the number of carbides and reduce the transformation temperature to cause the substructure refinement together with the carbide refinement. Therefore it is thought that the toughness was not impaired but the hardness alone was increased as shown in Fig. 8.
However, the situation must have been changed when the alloying element was changed. Large differences were found in the toughness of the bainites based on different alloying element even if they were formed at the same temperature. This fact could not be explained by the two factors alone.

In Table 2 the size of the unit fracture facet determined on the fracture surface of the bainite of the 0.3% C-1.5% X steels are listed together with the austenite grain size. They do not seem different among each other considering the relatively large error incident to such a determination. If fracture facet size is to increase from 4 to 5 μm it will be only some 20°C rise in the transition temperature as expected from the facet size vs. transition temperature curve derived by Kunitake, et al. The bainite of the Ni steel contained very coarse carbides, the coarsest among the three steels, as shown in Photo. 4. From these substructural considerations, the toughness of the bainite of the Ni steel should be inferior to those of the Mn and the Cr steels. However the result was just the opposite. Among the 0.15% C-1.5% X steels, the substructure and carbides in the Ni steel are also the coarsest, and those in the Cr steel bainite are by far the finer. The brittle fracture facet size was again not greatly different among these steels. The toughness, however, was the best for the Ni steels, followed by the Mn steel, and the worst for the Cr steel. When the martensites tempered at 600°C were compared, the toughness was not different so much among them; the Ni steel was, if anything, the best, although the agglomeration of carbides was rapid in the Ni steel.

Thus, it is difficult to explain the toughness behaviour only by the microstructural factors of the transformation products, especially of the higher transformation products, for steels with different alloying element. Therefore it is essential to take the effect of alloying on the intrinsic toughness of the matrix into consideration. Although this effect was not so marked in the tempered martensite, it became apparent as the bainite substructure was coarsened to resemble the equi-axed ferrite structure with the increase in transformation temperature.

It is generally known that the addition of Ni to steels improves the low temperature toughness. The reason of this has been thought to be due to its effect of facilitating the cross-slip, which should be especially effective in the present case where the coarse carbides are abundantly scattered in the bainite matrix. Although the addition of Mn to the steels has been said to refine the carbides in steels, it seems necessary to investigate further its effect on the deformation characteristics in order to clarify the reason why the Mn steels are not so inferior to the Ni steel in the toughness. As for the Cr steel an interesting research subject might exist in the interfaces between matrix and carbides which should have some peculiarity because Cr was a carbide-forming element and retarded the bainite reaction greatly.

It was found that when tempering the martensite at a low temperatures, say, 300°C, the toughness was reduced greatly for the Mn and the Cr steels but much less so for the Ni steels. As the frequent occurrence of the intergranular fracture was found under this tempering condition in all the steels prepared from coarse-grained austenite, not only the point that the alloying element affects the sensitivity to the intergranular brittleness, but also the intrinsic toughness of the matrix to accomodate the coherency strain of the carbides precipitated at lower temperature should be considered.

V. Conclusion

The substructure and the toughness of the transformation products were compared among the 0.5% Mo steels containing 1.5 or 2.5% of Cr, Mn or Ni with two levels of the C content, 0.15 and 0.3%, austenitized at 950°C or 1200°C. The following is the summary of the results.

(1) The isothermal transformation characteristics were different in accordance with the alloying element: the Mn steels tended to have the lower transformation temperature range. The Ni steels had a wide temperature range to produce the bainite, whereas in the Cr steels the transformation reaction was so sluggish that the temperature range where complete bainite structure could be obtained within a reasonable period of time was very narrow.

(2) Each steel exhibited a characteristic growth behaviour of bainite and a characteristic carbide morphology in it. Among the 0.15% C-1.5% X steels, for instance, the bainitic ferrite of the Mn and the Ni steels grew extensively enclosing degenerated pearlite colonies in themselves, whereas in the Cr steel the extremely sluggish formation of carbides resulted in the worm-eaten morphology during the growth of bainite and the substructure and carbides of final products were extremely fine.

(3) The increase in the C content caused the refinement of bainite substructure and carbide in any one of those steels. The coarsening of austenite grain caused coarsening of the bainite substructure regardless of the C content in the 1.5%Mn and the 1.5%Ni steels, whereas the substructure coarsening did not occur in the 1.5%Cr steel and the Ni steels with more than 2.5%Ni.

(4) The hardness and the toughness of the martensites tempered at 600°C was not different among the steels regardless of the species and content of alloying elements. At lower tempering temperatures, the Ni steels were softened rapidly with the toughness maintained, whereas for the Cr and the Mn steels the softening was small and the toughness was greatly

Table 2. Austenite grain size and unit facet size of bainite formed at 425°C in the 0.3% C-1.5% X-0.5% Mo steels

<table>
<thead>
<tr>
<th></th>
<th>Austenite grain diameter (μm)</th>
<th>Unit facet size (μm)</th>
</tr>
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<tbody>
<tr>
<td>Cr steel</td>
<td>17</td>
<td>4.6</td>
</tr>
<tr>
<td>Mn steel</td>
<td>14</td>
<td>4.4</td>
</tr>
<tr>
<td>Ni steel</td>
<td>15</td>
<td>3.2</td>
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impaired. The embrittlement due to the coarsening of austenite grain was larger in any 0.15% C steel than in the 0.3% C steel. This embrittlement was the smallest in the Ni steel.

(5) While the hardness of the bainite was not dependent on the alloying elements but dependent on its formation temperature, the toughness was strongly influenced by the species and the content of alloying elements in such a way that Ni was the best, followed by Mn and then by Cr. The increase in the alloy content generally reduced the toughness of bainite. The increase in the C content caused the refinement of the bainite substructure to result in the increase in hardness with little change in the toughness. When the substructure of bainite was coarsened with the increase in the austenite grain size, its toughness was also deteriorated.

(6) These results are considered to mean that the intrinsic toughness of the matrix endowed by the alloying elements plays for the higher temperature transformation products a role more important than such microstructural factors as the effective grain size and the carbide distribution.

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