THE DESIGN OF THE LOW-CARBON MARTENSITIC STRUCTURAL STEEL FOR HIGH STRENGTH AND TOUGHNESS AND ITS STRUCTURE-PROPERTY RELATIONS

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Abstract.—Some design guidelines and technological processes for improving strength-toughness combinations are discussed and compared for medium and low-carbon martensitic structural steels. The structure-property relations for low-carbon martensitic structural steels based on Fe-Si-Mn-Mo-V with Cr and Ni additions have been investigated systematically by means of the statistical regression analysis techniques. The regression equations were obtained, related the composition of these steels to their properties. The contributing factors of carbon and alloy elements on strength and toughness were studied quantitatively and the optimization of the range of compositions for these steels was suggested.

In the quenched condition, the microstructures of steel consist of dislocated lath martensite, thin interlath retained austenite films and γ-carbides. The effects of various microstructural parameters on strength and toughness are discussed. The investigation shows that when one of the experimental steels is quenched from 950°C and tempered at 300-350°C, an optimum combination of strength and toughness can be obtained. The tensile strength will be greater than 1765 MPa (180 kg/mm²), the yield strength greater than 1422 MPa (145 kg/mm²) and the fracture toughness greater than 127.7 MN/m (420 kg/mm²). This shows that for developing an ultra-high strength steel, further strengthening a low-carbon martensitic steel with high toughness has an advantage over improving the toughness of a medium carbon martensitic steel. Furthermore, for the same combination of strength and toughness, the suggested steel only contains about 7% of cheap alloy elements, while the maraging steel contains around 30% of more expensive elements.

Introduction.

Fig. 1 depicts the strength-toughness relations for some typical ultra-high strength steels [1,2]. As shown in this figure, very low-carbon maraging steel exhibits superior strength-toughness combinations, whereas medium-carbon martensitic steels, such as AISI 4340 show strengths similar to maraging steel, but the latter has better toughness. In order further to strengthen and toughen ultra-high strength martensitic steel, generally there are two methods: (1) toughening the hard and brittle alloy, (2) strengthening the tough and low strength alloy. The design and research on ultra-high strength steel are usually by means of the first method. Among these, some of the methods will increase the complexity of the technological process (such as increasing austenitizing temperature) and some of the others require the addition of Si for eliminating the onset of the tempered martensite embrittlement. This latter technique is employed in 300-M steel but the value of fracture toughness can not be increased to the level of maraging steel (Fig.1).

On the other hand even though the maraging steel has superior strength-toughness combinations, it contains expensive elements Ni and Co, so that its applications are limited. Based on above consideration, the second method i.e. strengthening the tough low-carbon martensite to develop ultra-high strength steel, was chosen. This paper emphasizes two aspects of the investigation. (1) Based on the strengthening mechanisms in martensite and the alloying theory in steel, we applied the statistical regression analysis technique to clarify the relations between the compositions and properties of a series of Si-Mn-Cr-Ni-Mo-V low-carbon martensitic ultra-high...
The relations of the microstructures and mechanical properties of a typical ultra-high strength low-carbon martensitic steel were studied.

Conception and method of alloy design.

1. The strengthening of low-carbon martensite.

Generally, increasing the carbon content and utilizing heat treatment to obtain martensite are the most economic and beneficial methods for strengthening steel, carbon being the major element to obtain solid solution hardening. However, when the carbon contents in the steel is more than 0.3%, twinned martensite will be unavoidably present, and will be detrimental to the toughness, increasing the tendency for quenching cracks. Therefore, in the regression analysis, we have changed the carbon contents in four stages in order to find the optimum carbon contents of the steels. With carbon contents below 0.2%, Speich [3] has calculated that nearly 90% of the carbon is segregated to lattice defects during quenching. Above 0.2% C such sites become nearly saturated and carbon atoms are held in the "defect free" lattice. Therefore, it would appear that by increasing carbon contents suitably, it would be expected that some of the carbon atoms would occupy the octahedral interstitial sites and increase solid solution hardening and precipitation hardening by \( \varepsilon \)-carbides. Furthermore, the alloy elements such as Si, Mn, Ni and Mo in solid solutions of \( f \) and \( \alpha \)-iron are very effective strengtheners [4.5]. Making use of the above three strengthening mechanisms, it was expected that the strength of the steel would be increased to the level of ultra-high strength steels.

2. The development of high toughness in the low-carbon martensite.

The high toughness of low-carbon martensite is determined by its substructures but there may be other factors which may be increasing the toughness further. Recently, a thin interlath retained austenite film, of thickness about 100-200\( \mu \)m, has been observed and studied in Fe-C alloy [6]. Retained austenite is a ductile phase, which may have caused crack blunting and branching thus further improving the toughness. It follows that the features required to obtain a structural steel with high strength and high toughness are: (1) By means of various strengthening mechanisms to strengthen the martensite and yet maintain the substructure with retained dislocations, (2) stabilized thin interlath austenite films retained in the lath martensite boundaries. Obviously the former feature is the more important.

As a rule, the \( f \)-stabilizing elements are beneficial in producing thin interlath retained austenite films in the martensite lath boundaries. Among those Ni, Mn, are effective \( f \)-stabilizers, therefore, in alloy design. We use them to obtain retained austenite films.

An important method of increasing the toughness at a given strength is to increase the tempering temperature. In order to do this, tempered martensite embrittlement should be suppressed and caused to occur at 400°C and above. The elements such as Si, Ni, Al can effectively inhibit cementite nucleation and growth, thus stabilizing the retained austenite indirectly. One method of developing ultra-high strength steel is to use Si to modify AISI 4340 and 4330 steels. In the present work use has been made of Si and Ni in the design of the ultra-high strength steels.

3. The regression analysis.

In this paper, a statistical regression analysis technique has been employed for the design of chemical composition. The selected variables are the composition parameters i.e. C, Ni, Si, Mn, Mo and tempering temperature, which have the major effects on mechanical properties. \( V, S, P \) and quenching temperature were kept in constant. (\( V=0.14\%, \ S=0.01\% \)). The changing levels of the various elements were respectively: C-0.20%, 0.25%, 0.30%, 0.35%; Si-1.2%, 2.0%; Mn-1.5%, 2.0%; Cr-0.5%, 1.0%, 1.5%; Ni-0%, 0.5%, 1.0%, 1.5%; Mo-0.25%, 0.8%(wt.%), and the tempering temperatures are 300°C and 350°C.
Through statistical analysis of 25 batches of steels (31 states) and 9 variations of compositions and temperature conditions, the regression equations were as follows [7]:

\[
K_t = 361.7 - 9450 + 75.6Mn + 42.4Ni + 29.4Mo + 7.19Cr + 4.88Si \quad (\text{kg/mm}^2) \quad R = 0.93
\]

\[
G_t = 81.7 + 227.4C + 34.5Si + 15.18Mn + 3.81Mo + 2.8Ni + 1.63Cr \quad (\text{kg/mm}^2) \quad R = 0.94
\]

\[
G_s = 78.2 + 211.4C + 5.56Si + 1.35Ni + 1.63Mn + 0.325Mo + 1.25Cr \quad (\text{kg/mm}^2) \quad R = 0.95
\]

\[
J = 16.2 - 16.2C + 0.58Mo - 0.49Mn - 0.34Ni + 0.25Cr - 0.26Si \quad (%) \quad R = 0.89
\]

\[
\psi = 81.8 - 81.8C - 3.6Mo - 2.4Si - 1.6Mo - 0.5Mo - 0.5Ni \quad (%) \quad R = 0.92
\]

\[
\alpha_t = 12.66 - 16.3C - 0.35Ni - 0.26Cr + 0.18Mo + 0.15Ni - 0.09Si \quad (\text{kg-m/cm}^3) \quad R = 0.90
\]

In above equations the level of significance is equal to 0.01. Using two parameters 31 and 9, we can ascertain check function value $F = 3.4$ and calculate the interrelation coefficient $R$. Through the regression calculation, if the $R$ values are greater than 0.77, the regression equations are available. Where $K_t$ is the fracture toughness, $G_t$ the tensile strength, $G_s$ the yield strength, $J$ the elongation, $\psi$ the reduction of area and $\alpha_t$ the impact toughness value (Mesenager specimen).

It will be seen that the sequence of alloy elements which mainly act as strengtheners are C, Si, while those mainly act as tougheners are Mn, Ni, Mo. Ductility and impact value are basically depend upon the carbon contents. The results of the experiment proved the prediction of alloy design.

The relations between microstructure and mechanical properties of a typical ultrahigh strength low-carbon martensitic steel.

The microstructures and mechanical properties of a typical vacuum melted alloy will be discussed, the chemical composition being given in the following table.

<table>
<thead>
<tr>
<th>chem. comp.</th>
<th>C</th>
<th>Si</th>
<th>Mn</th>
<th>Cr</th>
<th>Ni</th>
<th>Mo</th>
<th>V</th>
<th>S</th>
<th>P</th>
</tr>
</thead>
<tbody>
<tr>
<td>wt%</td>
<td>0.25</td>
<td>1.22</td>
<td>2.05</td>
<td>1.44</td>
<td>1.51</td>
<td>0.79</td>
<td>0.14</td>
<td>0.01</td>
<td>0.01</td>
</tr>
</tbody>
</table>

Fig. 2 shows the relation between the mechanical properties and tempering temperature of the steel. As shown, the as-quenched steel gives $G_t > 150$ kg/mm$^2$. $G_s > 210$ kg/mm$^2$, its strength being similar to that of AISI 4340. However, the strengthening effects in 4340 are mainly due to solid solution hardening by carbon and precipitation-hardening by precipitated carbides during auto-tempering, whereas the experimental steel besides being strengthening by above mechanisms, also reflects the effects of the large amounts of Si and Mn. Thus the strength of the experimental steel is as great as that of as-quenched 4340 steel. Because the carbon contents of the experimental steels are relatively low, the toughness of steels is greater than that of 4340 steel. Therefore the fracture toughness of the as-quenched steel is nearly twice that of the 4340 steel. This shows that the conception of strengthening low-carbon martensite is successful.

The high toughness of the as-quenched steel depends upon its microstructure. The substructures of the specimens which were employed in fracture toughness testing were observed by transmission electron microscopy. The microstructures of steel consisted of the following features: dislocated lath martensite and precipitated carbides due to autotempering. The dark field micrographs and selected area electron diffraction pattern analysis showed the presence of retained austenite in the form of thin interlath films at the martensite lath boundaries. Therefore, the high-toughness of the experimental steel on the one hand is due to $\varepsilon$-carbides precipitation during quenching, and on the other hand due to large plastic flow in low carbon martensite prior to fracture and the action of the retained austenite films at the lath boundary which make the direction of a propagating crack deviate from the main path. The topography of the fracture surface of as-quenched 4340 steel is mainly quasi-cleavage.
fracture [8]. Prior to fracture surface of the impact tested sample observed by scanning electron microscopy showed that the topography of the fracture surface of the as-quenched experimental steel is mainly the equiaxed dimples of ductile fracture. Prior to fracture, the plastic flow in the matrix is large and consequently it expended more energy. Once the crack nucleates, plastic flow in the matrix will result in crack blunting. In a same manner, the presence of retained austenite at lath boundaries also results in crack branching [2]. As a rule, lath martensite basically does not exhibit the preexistence of microcracks, whereas medium-carbon martensite contains not only dislocated martensite but also some twinned substructure, and thus tends to show presence of preexisting microcracks; thus its toughness should be lower.

When the experimental steel was tempered at 200-350°C, $K_I$, $\Delta K$ and CVN were all increased with increasing tempering temperature, the maximum value of fracture toughness being 428 kg/mm$^2$, after tempering below 350°C. The values of fracture toughness of the tempered steel were all more than 400 kg/mm$^2$. The experimental results on retained austenite, measured by Xray spectroscopy, showed that the retained austenite was stable below 350°C so that its amount did not change significantly. Therefore during tempering at 200-350°C, the microstructure features (dislocated martensite-interlath retained austenite) of the experimental steel did not change. The only difference between them is the quantity of the precipitated carbides during tempering which are more than that in as-quenched condition. Due to the carbides being fully precipitated and the residual stresses relieved after tempering at 300-350°C, the ductility ($\delta$ and $\psi$) and the toughness ($K_I$, $\Delta K$, CVN) were all raised to the maximum value, while $\sigma_y$ was greater than 145 kg/mm$^2$. Therefore, the experimental results showed that the effect of alloy additions not only made a great contribution to the strength of the steel, but raised the toughness of the steel by means of stabilizing the retained austenite film and deferring the onset of the tempered martensite embrittlement.

$K_I$, $\Delta K$ and CVN all decreased rapidly, after tempering at 400°C which is close to the temperature for tempered martensite embrittlement. TEM observation showed that plate-like cementite precipitated within the laths and the retained austenite decomposed into stringers of coarse carbides at these boundaries. The dark field micrographs and selected area electron diffraction patterns showed that the precipitated carbides along the lath boundary were Fe$_3$C as shown in plate 1(a)(b)(c) and (d). The fracture surface observed by SEM showed that the fracture mode had changed from ductile dimple into mainly quasi-cleavage. This shows that the stringers of coarse cementite at the lath boundaries increased, the ease of propagation and resulted in embrittlement. Thus the decomposition of interlath retained austenite into cementite films is a major cause of tempered martensite embrittlement [9].

Conclusion.

The conclusions drawn from this investigation are as follows:

1. The conception of alloy design based on strengthening low-carbon martensite is correct. It improves the toughness for a given strength and obtains the desired microstructures. A series of Si-Mn-Cr-Ni-Mo-V low-carbon martensitic ultra-high strength steels have been designed successfully. A higher toughness for a given strength can be achieved compared with medium-carbon martensite.

2. The effective methods for strengthening low-carbon martensite are increasing carbon contents adequately and using Si-Mn-Ni-Mo to form solid solution hardening. The alloy element combinations of the experimental steel not only result in strengthening low-carbon martensite, but also stabilize the interlath retained austenite film at the martensite lath boundaries and suppress the onset of the tempered martensite embrittlement. Thus the experimental steels give high toughness.

3. The microstructure of the as-quenched steels consist of dislocated lath martensite, retained austenite in thin interlath films and $\epsilon$-carbides in martensite
resulting from auto-tempering. In this condition, the steels have $\sigma_u \geq 150$ kg/mm$^2$, $\sigma_a \geq 210$ kg/mm$^2$, this strength being similar to as-quenched 4340. Nevertheless the fracture toughness, $K_I \geq 310$ kg/m$^{3/2}$ is significantly superior to 4340.

4. When the experimental steel was tempered at 300-350°C, its microstructure features did not change, but the carbides were fully precipitated and the residual stresses further relieved. In this condition, the steel showed $\sigma_T \geq 145$ kg/mm$^2$, $\sigma_a \geq 180$ kg/mm$^2$ and $K_I \geq 400$ kg/mm$^{3/2}$. An optimum combination of strength and toughness was obtained, which was even better than that of maraging steel. From the economic point of view, the experimental steel only contains about 7% of cheap alloy elements, while the maraging steel contains nearly 30% of expensive alloy elements.

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Fig. 1 Fracture toughness versus strength for high-strength steels

Fig. 2 Strength, ductility and toughness versus tempering temperatures for the experimental steel.

Plate 1 Bright-field image (a) and dark-field image (b) of the experimental steel quenched from 950°C and tempered at 400°C. SAD pattern (c) and the corresponding indexed pattern (o matrix, • cementite) (d) revealing cementite in lath boundary.