Microstructure Control for Toughening a High Carbon Martensitic Stainless Steel

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A High carbon martensitic stainless steel (Fe-12%Cr-0.7%C) was subjected to isothermal aging after full solution treatment, and then solution-treated again in the two phase region of austenite and $M_{23}C_6$ carbide; partial solution (PS) treatment. Microstructural development during these heat treatment was investigated, and mechanical properties for the PS treated steel were evaluated by comparison with a referential steel without isothermal aging. During the isothermal aging at 923K, the supercooled austenite undergoes eutectoid transformation and decomposes to ferrite and $M_{23}C_6$ carbide, and the carbide particles are finely dispersed within the matrix. Insoluble carbide particles retained during the following PS treatment contribute to suppressing austenite grain growth effectively through the grain boundary pinning effect. Ductile-brittle transition in the PS treated steel is characterized by a lower transition temperature and a higher upper-shelf energy compared with the referential steel. This is due to the grain refining of prior austenite as well as the homogeneous dispersion of carbide particles through the PS treatment with isothermal aging.

KEY WORDS: high carbon martensitic steel; isothermal aging; partial solution treatment; eutectoid transformation; carbide; grain size; toughness; tensile strength

1. Introduction

High carbon martensitic stainless steels are usually solution-treated at around 1200K where two phases of austenite and carbide ($M_{23}C_6$ or M_7C_3) exist, in order to avoid coarsening of austenite grains. The insoluble carbide particles, however, are retained coarsely on grain boundaries, and they make the ductility of steels lower. For dispersing carbide particles finely and homogeneously, authors proposed the partial solution (PS) treatment¹⁾; re-solution treatment in the (austenite + carbide) two phase region after the pre-treatment of quenching from austenite single phase region (FS treatment) and tempering. Through the pre-treatment, coarse carbide particles fully dissolve into austenite during the FS treatment, and then fine carbide particles re-precipitate within martensite matrix during the following tempering. Since the dispersed carbide particles are retained at the PS treatment temperature, austenite grains are also refined through the pinning effect by these fine particles. Therefore, the PS treatment allows an increase of carbon content for strengthening without reducing ductility so much.

In the Fe-13%Cr-C (mass%) system, the maximum carbon solubility in austenite is about 0.7%C²⁾. But so far as the quenching from FS treatment temperature is applied as a pre-treatment in the PS treatment, carbon content available for strengthening is limited to about 0.3% at the maximum owing to the problems of quench-cracking and retained austenite. On the other hand, it has been already

known that high carbon stainless steels undergo eutectoid transformation (austenite $\rightarrow$ ferrite + carbide) during isothermal aging after austenitization³⁾. Through this transformation, carbide is directly formed from austenite without undergoing martensitic transformation, so that carbon content of steels can be increased to the maximum value of 0.7%C without causing such problems on the quenching. The purpose of this work is to improve mechanical properties of high carbon stainless steels by applying the PS treatment to the steels which have undergone the eutectoid transformation as the pre-treatment.

2. Experimental Procedure

An ingot of 30kg was prepared by vacuum melting, homogenized at 1523K for 18ks, and then formed to a 10mm thick plate through forging and hot-rolling at 1473K. Chemical composition of the steel used is shown in Table 1. Route of heat treatment is shown in Fig.1. The steel was once subjected to the FS treatment at 1523K for 1.8ks in Ar gas atmosphere, and then quickly dipped into salt bath kept at 923K for isothermal transformation. After this pre-treatment, the steel was subjected to the PS

Table 1. Chemical composition of the steel used (mass%).

C	Si	Mn	P	S	Cr	Fe
0.69	0.19	0.31	0.006	0.003	12.7	bal.

Fig. 1 Heat treatment route for Partial Solution treatment.

treatment for 1.8ks at a temperature between 1173K and 1403K, followed by oil-quenching. Tempering of the quenched specimens was carried out at 923K.

Microstructures were observed with optical and transmission electron microscopes (TEM). Thin foil specimens for TEM observation were prepared by jet-polishing method in the solution of 10% perchloric acid and 90% acetic acid. The prior austenite grain size of martensitic structure was determined by comparing optical micrographs with the ASTM grain size standards. The prior austenite grain boundaries were revealed clearly by using sensitization technique⁴⁾. Tensile tests were carried out for cylindric test pieces of $\phi 3\text{mm}$ and 10mm gauge length with Instron-type testing machine at the crosshead speed of 0.02mm/s. Impact tests were carried out for half size Charpy V-notch specimens.

3. Results and Discussion

3.1 Isothermal transformation of 12%Cr-0.7%C steel

Fig.2 shows the TTT diagram of 12%Cr-0.7%C steel. Solution treatment before the isothermal aging was performed at 1523K for 1.8ks, where carbide is fully dissolved into austenite. The nose temperature of this diagram is at around 960K. Since the purpose of the isothermal aging is to disperse carbide finely within matrix, a lower temperature; 923K was selected for the isothermal aging temperature. Fig.3 shows microstructural change of the steel during the isothermal aging at 923K. Dark phase on prior austenite grain boundaries is the eutectoid structure formed through the decomposition of supercooled austenite to ferrite and carbide. The eutectoid structure grows into untransformed austenite grains, and the transformation almost completes after 5.4ks aging. Fig.4 represents TEM

Fig.3 Optical micrographs of 12%Cr-0.7%C steel isothermally transformed at 923K.

Fig. 2 TTT diagram of 12%Cr-0.7%C steel. Ts and Tf denote starting and finishing points of eutectoid transformation, respectively.

images showing morphologies of carbide in the eutectoid structure. The carbide was identified as $M_{23}C_6$ type by X-ray diffraction analysis in both of specimens (a) and (b), and the volume fraction in the eutectoid structure is theoretically calculated at about 14vol% from the mass balance of carbon¹⁾. The photograph (a) shows just a front of the eutectoid structure. A lamellar eutectoid-colony is growing into the untransformed region. Observations from various direction made it clear that the morphology of carbide is not plate-like but fibrous. The diameter of carbide fibers is about 20nm and the mean spacing of them is 50nm. During isothermal aging, carbide grows and changes the morphology to sphere or ellipsoid as shown in the photograph (b), but the distribution of carbide particles is even much finer than that obtained by the quench-and-tempering method in Fe-12%Cr-(0.12~0.34)%C alloys⁴⁾. This means that isothermal transformation is an effective

method as a pre-treatment for the PS treatment in high carbon stainless steels.

Fig. 4 Transmission electron micrographs showing morphologies of carbide in the eutectoid structure. Isothermally aged at 923K for 1.8ks (a) and 16.2ks (b) after the FS treatment of 1523K-1.8ks.

3.2 Microstructure of 12%Cr-0.7%C steel with PS treatment

After the pre-treatment of isothermal aging at 923K, the steel was subjected to the PS treatment in (austenite + $M_{23}C_6$) two-phase region. **Fig.5** shows an optical (a) and transmission electron (b) micrographs of the steel which was oil-quenched from the PS treatment temperature of 1173K. The microstructure of matrix is of typical lath martensite characterized by high density of dislocations, though the martensite blocks and packets are too small to be discerned in the optical micrograph. TEM examination revealed the presence of retained $M_{23}C_6$ carbide particles of about 0.2 μ m in diameter. The volume fraction of retained carbide was evaluated to be about 8vol%. Such insoluble carbide particles contribute to suppressing austenite grain growth effectively through the grain boundary pinning effect⁴⁾, and also making the arrangement of martensite-laths irregular⁵⁾. **Fig.6** shows the relations between austenite grain size and solution treatment temperature in 12%Cr steels with various amount of carbon. Bold line is the result of 12%Cr-0.7%C steel used in this study, and the data of lower carbon steels (0.12~0.34%C)⁴⁾ are also shown in this figure. Broken lines display the lowest FS temperatures expected from carbon solubility in austenite of 12%Cr steels¹⁾. Solution treatment below the critical temperatures just means PS treatment. Austenite grain size of each steel is kept small in the temperature region of the PS treatment,

Fig. 5 Optical (a) and transmission electron (b) micrographs showing lath martensitic structure in the specimen oil-quenched after the PS treatment of 1173K-1.8ks.

Fig. 6 Relations between austenite grain size and re-solution treatment temperature in 12%Cr-C steels. Broken lines display the lowest FS temperature for each steel.

but an abrupt grain growth occurs above the critical temperature. It should be noted here that austenite grain size of the 0.7%C steel is much smaller than those of the other low carbon steels and less than 10 μ m even at high temperature of around 1400K. The refining of prior-austenite grains by PS treatment could give desirable effects on toughness because of the reduction of stress

concentration at grain boundary or the dilution of impurity segregated at grain boundary through an increase of total grain boundary area⁶⁾.

The isothermal aging as the pre-treatment significantly influences the dispersion of carbide particles. Fig.7 represents SEM images of 12%Cr-0.7%C steels showing the difference in carbide dispersion between in the steel with isothermal aging before PS treatment (developed in this work) and in a conventionally produced steel which has been directly solution-treated after hot-rolling without isothermal aging. In the developed steel (a), carbide particles are dispersed homogeneously within the matrix, while in the conventional steel (b), coarse carbide particles exist along grain boundaries. The retention of coarse carbide particles enhances crack initiation and accelerates brittle intergranular fracture at low temperature⁶⁾, so the disappearance of such carbides should improve toughness of the 12%Cr steel.

Fig.7 Scanning electron micrographs showing the difference in carbide dispersion between in the developed steel with isothermal aging before PS treatment (a) and in a conventionally produced steel without isothermal aging (b).

3.3 Mechanical properties of the developed 12%Cr-0.7%C steel

Fig.8 shows Charpy impact energy transitions of the 12%Cr-0.7%C steels with tempering at 923K. Closed circles and open circles show the results of the developed steel with isothermal aging and of the conventional steel without it, respectively. Hardness of both specimens were controlled to be around HV300 by varying tempering time. The isothermal aging before PS treatment results in the lowering ductile-brittle transition temperature (DBTT) by about 30K, and also in increasing the upper-shelf energy. The toughening in the developed steel would be due to the

Fig. 8 Effect of isothermal aging on Charpy impact energy transition in 12%Cr-0.7%C steel. The isothermal aging was performed at 923K for 16.2ks after FS treatment. Both the developed steel (closed circles) and referential steel without isothermal transformation (open circles) were subjected to PS treatment of 1173K-1.8ks, and then tempered at 973K.

grain refining of prior austenite as well as the dissolution and homogeneous re-precipitation of carbides through the pre-treatment. Fig.9 shows the relation between tensile strength and elongation of the developed steel and other commercial 12%Cr-C system martensitic stainless steels which are standardized by JIS. The developed steel is characterized by having higher strength with moderate ductility compared with any other commercial steels.

Though high carbon stainless steels have been thought to be difficult to apply for structural use because of their brittleness, we can conclude that the addition of large amount of carbon is very effective for improving mechanical properties of martensitic stainless steel if only the grain size is kept small and the carbide particles are dispersed finely.

Fig. 9 Relation between tensile strength and elongation in 12%Cr martensitic stainless steels. The numbers in this figure denote the steels standardized by JIS; 403 (12Cr-0.1C-low Si), 410 (12Cr-0.1C), 420J1 (12Cr-0.2C), and 420J2 (12Cr-0.3C).

4. Conclusions

Isothermal aging was applied to a 12%Cr-0.7%C martensitic steel as a pre-treatment of PS treatment for the purpose of dispersing carbide particles finely and homogeneously, and then the mechanical properties of the PS treated steel was examined in connection with the microstructures. The results obtained are as follows:

- (1) During the isothermal aging at 923K, the supercooled austenite undergoes eutectoid transformation and decomposes to ferrite and $M_{23}C_6$ carbide, and the carbide particles are finely dispersed within the matrix.
- (2) Insoluble carbide particles retained at a PS temperature contribute to suppressing austenite grain growth effectively through the grain boundary pinning effect. Austenite grain size was kept at 10 μ m or less even at high temperature of around 1400K.
- (3) By the pre-treatment of isothermal aging before PS treatment, the ductile-brittle transition temperature is lowered, and besides, the upper-shelf energy is increased. This is due to the grain refining of prior austenite as well as the homogeneous dispersion of carbide particles.
- (4) Tensile properties of the developed steel is characterized by higher strength with moderate ductility compared with commercial martensitic stainless steels.

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