Effect of Partial Solution Treatment on Toughness of 12%Cr–0.3%C Steels

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In 12%Cr–0.3%C martensitic steels, the effect of partial solution (PS) treatment in the (γ + carbide) two phase region was investigated in terms of the relation between microstructure and impact toughness. PS treatment is very effective for refining γ grains, because insoluble carbide particles works as obstacles to grain growth. The γ grain refining results in a significant lowering of Ductile–Brittle Transition Temperature (DBTT). This is mainly due to the reduction of grain boundary stress concentration which is caused by pile-up of dislocations to grain boundary. Besides, PS treatment contributes to homogeneous dispersion of carbide particles: In specimens with full solution (FS) treatment, carbide particles precipitate along lath boundary of martensite during tempering, and this causes early crack initiation in impact testing. On the other hand, in specimens with PS treatment, carbides preferentially precipitate on insoluble carbide particles which have homogeneously dispersed within the martensite matrix. This results in an increase of upper shelf energy in impact testing. It was also found that PS treatment suppresses precipitation of grain boundary carbide which occurs during slow cooling from γ phase region, because the insoluble carbide particles provide preferential precipitation site within γ grains. As a result, DBTT is not dependent on cooling rate in PS treated specimens, although it is greatly raised in FS treated specimens with slow cooling because of the grain boundary precipitation of carbide.

KEY WORDS: martensitic stainless steel; partial solution treatment; toughness; grain size; insoluble carbide; intergranular fracture; segregation.

1. Introduction

Authors^{1–3)} have investigated the effect of Partial Solution (PS) treatment on the microstructure of 12%Cr–C steels for improving toughness of martensitic stainless steel. PS treatment means the solution treatment in the two-phase region of austenite (γ) and carbide. In this treatment, key is in making carbides disperse finely within γ through the pre-treatment of quench-and-tempering^{1,2)} or isothermal eutectoid transformation.³⁾ So far, it was found that PS treatment in 12%Cr–0.3%C steel results in refining of γ grain size to about 10 μ m due to the grain boundary pinning effect by uniformly dispersed carbide particles,¹⁾ and also in the formation of very fine lath-martensitic structure in the matrix.²⁾

The packet or block is a basic microstructural unit controlling the strength and fracture of lath-martensite, because the boundaries of them act as barriers to deformation and fracture.⁴⁾ The sizes of packet and block depend on prior- γ grain size.⁴⁾ Thus γ grain refining is generally believed to be effective for lowering Ductile–Brittle Transition Temperature (DBTT), through the refining of packets and blocks. In martensitic stainless steels with hypereutectoid composition, however, the toughness might be more affected by the morphology and dispersion of carbides which retain at the solution

treatment temperature,⁵⁾ and also by the precipitation behavior of carbide on cooling from the solution treatment temperature.⁶⁾ In addition, grain boundary segregation of impurities such as phosphorus is known to be promoted with the addition of chromium,⁷⁾ hence brittle intergranular fracture becomes easy to occur in high chromium steels. In martensitic stainless steels containing a large amount of chromium, therefore, toughness should be discussed by taking both of the effect of carbide dispersion and the behavior of grain boundary segregation of impurities into consideration as well as the above mentioned microstructural factors.

In this study, the ductile–brittle transition behavior of 12%Cr–0.3%C steels was investigated in terms of the difference in solution treatment; PS treatment or Full Solution (FS) treatment in γ single phase region. And then the mechanism of toughening by PS treatment was discussed in connection with the microstructures and the behavior of grain boundary segregation of impurities.

2. Experimental Procedure

Two kinds of 12%Cr–0.3%C steel with different phosphorus content were used. One is a commercial steel with 0.02 % P (steel A), and the other is a high purity steel of 0.001 % P (steel B). Chemical compositions of

Table 1. Chemical compositions of steels used. (mass%)

steels	C	Si	Mn	P	S	Cr	Fe
A	0.28	0.24	0.47	0.023	0.005	12.30	bal.
B	0.30	0.11	0.82	0.001	0.009	12.21	bal.

others : Ni<0.01, Al<0.01, N<0.011

these steels are listed in **Table 1**. Ingots of 30 kg were produced by vacuum melting, homogenized at 1523 K for 18 ks, and then deformed to 12 mm thick plates through forging and hot-rolling at 1473 K. The steel plates obtained were once subjected to the FS treatment of 1473 K–1.8 ks followed by oil-quenching and sub-zero treatment at 77 K (in liquid N₂). After this treatment, the steels with full martensitic structure were tempered at 1073 K for 10.8 ks to make carbide particles precipitate within the martensite matrix. Finally, the steels were subjected to the FS treatment at 1473 K or the PS treatment at 1173 K for 1.8 ks, and then cooled to room temperature at various cooling rate. The cooling rate at around the nose temperature of carbide precipitation (950 K) was about 60 K/s in oil-quenching, 0.4 K/s in air-cooling, and 0.15 K/s in furnace-cooling. Specimens for mechanical tests were tempered at 923 K for a given time.

Microstructures were observed with optical microscope and scanning electron microscope (SEM). Specimens were chemically etched with an aqueous solution of hydrofluoric acid, nitric acid and glycerin for optical microstructure observation and with an alcohol solution of picric acid for SEM observation. Impact testing was performed for the sub-sized Charpy V-notch test pieces (5 mm × 10 mm × 55 mm). Fracture surfaces of the tested pieces were examined with SEM. Three point bending tests were carried out for the similar V-notch test pieces with an Instron type testing machine at the cross head speed of 0.02 mm/s. The value of surface stress σ (Pa) and strain ε in bending tests were approximately given by the following formulas⁸⁾ from the measured load P (N) and bending displacement δ (m).

$$\sigma = 3PL/2bh^2$$

$$\varepsilon = 4h\delta/L^2$$

where L , b and h denote the distance between fulcrums, width and thickness of test pieces, respectively.

3. Results and Discussion

3.1. Microstructure of Steels with FS or PS Treatment

Figure 1 shows micrographs of the steel A with FS treatment at 1423 K (a) or PS treatment at 1173 K ((b) and (c)). Both specimens were oil-quenched from each solution treatment temperature. Mean austenite grain size was 120 and 12 μm in (a) and (b), respectively. Microstructure of the photograph (a) is characterized by the typical lath-martensitic structure constructed with martensite-blocks and -packets.⁴⁾ On the other hand, in the photograph (b), the microstructure is so small that the sub-structure of blocks and packets is hard to be distinguished. The SEM image (c) reveals that fine insoluble carbide particles (approximately 0.4 μm in

Fig. 1. Optical micrographs of the steel A (commercial steel) with FS treatment at 1423 K for 1.8 ks (a) or PS treatment at 1173 K for 1.8 ks (b), and a scanning electron micrograph of the PS treated steel (c).

diameter) present in the PS treated steel. This kind of carbide particles was identified as M₂₃C₆ type by X-ray diffractometry, and its volume fraction was calculated at about 4 vol% from the carbon solubility in γ at the solution treatment temperature.⁹⁾ Hardness is much higher in the steel with FS treatment, because all of carbon dissolves into γ and can contribute to hardening of martensite.

Figure 2 shows change in hardness of these oil-quenched specimens with tempering at 973 K. Hardness abruptly decreases at the early stage and levels off at the later stage in both specimens. The level-off hardness is HV230 for the FS treated specimen, and HV200 or less for the PS treated specimen. This result indicates difference in the behavior of precipitation and growth of carbide between the both specimens. Tempering time giving the same hardness of HV230 is 12.6 and 0.9 ks in the FS treated specimen and PS treated specimen, respectively. SEM images in **Fig. 3** show the dispersion of carbides in the steels tempered under the above mentioned conditions. In the FS treated specimen (a), carbide particles precipitate in line along prior γ grain boundaries, block boundaries and lath boundaries. The morphology of carbide is substantially sphere, but fine carbide particles connect with each other in line to form a rod-like carbide.¹⁰⁾ On the other hand, in the PS treated

Fig. 2. Change in hardness with tempering at 973 K for the commercial steel which was FS treated at 1423 K for 1.8 ks or PS treated at 1173 K for 1.8 ks.

Fig. 3. Scanning electron micrographs showing the dispersion of carbides in the commercial steel with the treatment; FS treatment (1423 K-1.8 ks)→tempering (973 K-12.6 ks) (a) or PS treatment (1173 K-1.8 ks)→tempering (973 K-0.9 ks) (b).

specimen, carbides precipitate onto the insoluble carbide particles which have been there before the tempering treatment. Thus, no large change can be observed in the carbide dispersion in the specimen (b) comparing with that in Fig. 1(c).

3.2. Effect of PS Treatment on Toughness

3.2.1. Charpy Impact Energy Transition

Figure 4 shows Charpy impact energy transition in the steels with FS treatment at 1473 K or PS treatment at 1173 K. Specimens were cooled at various cooling rates of oil-quenching, air-cooling and furnace-cooling from the each solution treatment temperature. Hardness of test pieces was controlled to be around HV230 by varying tempering time at 973 K. When PS treated specimens are furnace-cooled, most of carbon precipitates as carbide on slow cooling, and the shortage of carbon in γ leads to the occurrence of $\gamma \rightarrow \alpha$ ferritic transformation.¹¹⁾ The specimen with such a ferritic structure is so soft (below HV230) that the data of

Fig. 4. Effect of PS treatment and cooling rate from the solution temperatures on Charpy impact transition behavior in the commercial steel; FS treatment (1423 K-1.8 ks)→tempering (973 K-12.6 ks) or PS treatment (1173 K-1.8 ks)→tempering (973 K-0.9 ks).

Fig. 5. Scanning electron micrographs of fracture surface in the commercial steel tested at 200 K after the treatment; FS treatment (1423 K-1.8 ks)→tempering (973 K-12.6 ks) (a) or PS treatment (1173 K-1.8 ks)→tempering (973 K-0.9 ks) (b).

furnace-cooled specimens were not shown for PS treated steel. The important findings in Fig. 4 are as follows: Through the PS treatment,

- (1) DBTT* is lowered.
- (2) Upper shelf energy is increased.
- (3) There is no cooling rate dependence of DBTT in PS treated specimens, while the DBTT of FS treated specimens rises with lowering cooling rate.

These favorable effects by PS treatment will be discussed below in terms of microstructural factors such as prior γ grain size, carbide dispersion, and so on.

3.2.2. Effect of PS Treatment on Ductile-Brittle Transition

After Charpy impact testing at 200 K, the fracture surface of test pieces were observed by SEM to discuss fracture mechanism of the test pieces. Figure 5 shows fracture surface of the FS (a) and PS (b) treated specimens which were air-cooled from the solution treatment temperatures. The SEM images show brittle in-

* In this study, DBTT means 50% fracture surface transition temperature.

Fig. 6. Charpy impact energy transition of the high purity steel with the treatment; FS treatment (1423 K–1.8 ks)→tempering (973 K–12.6 ks) or PS treatment (1173 K–1.8 ks)→tempering (973 K–0.9 ks). Fracture surface was observed for the test pieces fractured at 200 K.

tergranular fracture surface in the FS treated specimen, and quasi-cleavage fracture surface in the PS treated specimen. The behavior of brittle fracture was same in the specimens treated at other cooling rates. Fracture mechanism might be dependent on two factors; the difference in γ grain size, and the behavior of grain boundary segregation of impurity. First, the effect of γ grain size was investigated by using a high purity steel in which the phosphorus content is reduced as low as possible. Figure 6 shows Charpy impact energy transition and SEM images of fracture surface of the steel B (0.001% P) with FS treatment at 1473 K or PS treatment at 1173 K. Austenite grain size of PS treated specimens was refined to the almost same size as the steel A, and hardness is also controlled to be around HV240 in both steels. There is no difference in DBTT between both specimens, though the upper shelf energy is surely increased through PS treatment just similar as in the steel A. It should be noted here that even the FS treated specimens do not undergo intergranular fracture, but do quasi-cleavage fracture at low temperature. This suggests that intergranular fracture is caused by phosphorus which segregates at grain boundary, and that the high purity steel has sufficient grain boundary strength to suppress intergranular fracture even if the γ grain size is as large as 100 μm .

The suppression of intergranular fracture in commercial steels is likely related to two phenomena as follows in terms of refining of γ grains:

- (I) Dilution of impurity segregated at grain boundary due to an increase of total grain boundary area.¹²⁾
- (II) Reduction of stress concentration at grain boundary.¹³⁾

The impurity dilution effect (I) can be explained on basis of McLean's theory¹⁴⁾ by taking the effect of γ grain size into consideration. Equilibrium impurity concentration at grain boundary X_b is given by the McLean's Eq. (1) in relation to the bulk concentration X_m and temperature T .

Fig. 7. Relations between equilibrium phosphorus concentration at grain boundary and grain size at 973 K in the high purity and commercial steel. Evaluated after the McLean theory.¹⁴⁾

$$X_b/(1-X_b) = \{X_m/(1-X_m)\} \exp(\Delta G_b/RT) \quad \text{.....(1)}$$

ΔG_b : free energy of grain boundary segregation

R : gas constant

Total grain boundary area per unit volume S is given by the Eq. (2) as a function of nominal grain size D .¹⁵⁾

$$S = 4/(\pi^{1/2}D) = 2.26/D \quad \text{.....(2)}$$

And further, the relation among mean chemical composition X_o , volume fraction of grain boundary layer f , X_b and X_m is given by the Eq. (3) from the viewpoint of mass balance.

$$X_o = fX_b + (1-f)X_m \quad \text{.....(3)}$$

When X_m is presumed to be small enough, the Eq. (4) is constructed from the Eqs. (1), (2), and (3).

$$X_b/(1-X_b) = \{X_o - 2.26t(X_b/D)\} \exp \Delta G_b/RT \quad \text{....(4)}$$

t : thickness of grain boundary layer

Figure 7 shows the calculated equilibrium phosphorus concentration at grain boundary as a function of grain size in the steel A (0.02% P) and B (0.001% P) in the case of 973 K tempering. The thickness of grain boundary layer t and free energy of grain boundary segregation ΔG_b were estimated to be 1 nm¹⁶⁾ and 55.2 J/mol,⁷⁾ respectively. In the high purity steel, the phosphorus concentration at grain boundary is kept very low all over the grain size. This result agrees with the fact that intergranular fracture hardly occurred in the steel B independent of solution treatment condition. On the other hand, in the commercial low purity steel, a lot of phosphorus segregates at grain boundary and the concentration exceeds the critical amount for grain boundary fracture; 20 at%¹²⁾ in the grain size range larger than 10 μm . The segregation concentration is markedly diluted in the grain size range below 10 μm , but the grain refining from 100 to 10 μm does not give a great influence on the grain boundary segregation of phosphorus. Thus, the toughening of the commercial steel by PS treatment cannot be explained by the impurity dilution effect through grain refining.

Secondly, the stress concentration reduction effect (II)

Fig. 8. Schematic illustration showing the relation between the stress at grain boundary and grain size under the condition of a constant applied stress.

was discussed by pile-up model of dislocations at grain boundary.¹⁷⁾ When a Frank-Read source exists at the center of a grain, the number of pile-up dislocations n is given by the Eq. (5).

$$n = (\tau - \tau_f)D / Gb \quad \dots\dots\dots(5)$$

- τ : applied shear stress
- D : grain size
- G : shear modulus
- b : Burgers vector
- τ_f : stress required for activating the Frank-Read source

When τ_f is much smaller than τ , the stress concentrated at grain boundary τ_g is expressed as follows;

$$\begin{aligned} \tau_g &= n\tau \\ &= \tau^2 D / Gb \quad \dots\dots\dots(6) \end{aligned}$$

Figure 8 schematically displays the relation between τ_g and D under a constant applied stress τ . τ^* denotes the critical stress required for grain boundary fracture. When τ_g exceed τ^* , intergranular fracture occurs. τ^* is generally lowered by grain boundary segregation of impurity such as phosphorus. This figure displays that, under a constant τ , τ_g increases in proportion to the grain size, and $\tau_{g(100 \mu m)}$ is ten times as large as $\tau_{g(10 \mu m)}$. In the high purity steel, grain boundary is thought to be strong enough, hence the relationship $\tau_{g(10 \mu m)} < \tau_{g(100 \mu m)} < \tau^*$ must be realized. This means that grain boundary fracture does not occur even in the specimens with large grain size (100 μm). In the commercial steel, however, grain boundary strength is not so high as the high purity steel, hence the value of τ^* should be between $\tau_{g(10 \mu m)}$ and $\tau_{g(100 \mu m)}$; $\tau_{g(10 \mu m)} < \tau^* < \tau_{g(100 \mu m)}$. This means that grain boundary fracture occurs only in the case the steel has a large grain size (around 100 μm) and be suppressed by grain refining to 10 μm .

From the above discussions, it is concluded that the toughening by PS treatment results from the decrease of grain boundary stress concentration which is produced by grain refining.

Fig. 9. Stress-strain curves obtained by three points bending tests in the commercial steel with the treatment; FS treatment (1423 K -1.8 ks)→tempering (973 K-12.6 ks) or PS treatment (1423 K-1.8 ks)→tempering (973 K-12.6 ks)

Fig. 10. Scanning electron micrograph in the area near a crack tip: Observed in a three points bending test piece of the commercial steel which was FS treated at 1423 K for 1.8 ks and then tempered at 973 K for 12.6 ks. Bending test temperature was 300 K.

3.2.3. Microstructural Factor on the Increase in Upper Shelf Energy by PS Treatment

The process of ductile fracture was investigated by means of three points bending tests to discuss the mechanism of increase in upper shelf energy by PS treatment. Figure 9 shows the surface stress-strain curves obtained by three points bending tests using Charpy impact test pieces with FS or PS treatment in the steel A. After work-hardening, a crack initiates at the maximum stress point, and then stress decreases with crack propagation. There is no difference in the maximum stress between both test pieces, but the strain giving maximum stress shifts to higher strain side in the PS treated steel. This result means that the PS treated specimen requires a larger energy for crack initiation than the FS treated specimen and this causes the difference in upper shelf energy as already shown. Figure 10 is a SEM micrograph of the FS treated specimen. The

Fig. 11. Schematic illustration showing the difference of fracture mechanism between FS and PS treated steels.

microstructure was observed at the area just near a crack tip of the three point bending test pieces. Carbide particles precipitate in line along lath boundaries, and a lot of microvoids are formed at the interface between carbide particles and matrix. These microvoids grow and coalesce to form micro-cracks. **Figure 11** schematically shows the mechanisms of ductile fracture in the PS treated and the FS treated specimens. In the FS treated specimen, microvoids formed along lath boundary carbide can easily coalesce and grow to a micro-crack. While, in the PS treated specimen, microvoids are formed in random corresponding to the dispersion of carbide particles, hence they are hard to grow to micro-cracks. This means that a large strain energy is required for the crack initiation.

3.2.4. Influence of Carbide Precipitation Behaviors on Cooling upon Toughness

Figure 12 shows SEM micrographs of steel A with FS or PS treatment followed by air-cooling or furnace-cooling. In the FS treated and air-cooled specimen (a), film-like carbide was observed at prior austenite grain boundaries. Since the full martensitic structure was obtained by oil-quenching after FS treatment in steel A (Fig. 1(a)), the grain boundary carbide is not an equilibrium phase at the solution treatment temperature but a product formed on cooling. When the cooling rate is further decreased, eutectoid transformation ($\gamma \rightarrow \alpha + M_{23}C_6$ carbide³⁾) follows the precipitation of grain boundary carbide, as shown in the specimen (b). Such precipitate on grain boundaries cause an intergranular fracture. On the other hand, in the PS treated specimen (c), carbide precipitates on cooling not at grain boundaries but preferentially on insoluble carbide particles which has already existed at PS treatment temperature. As a result, the carbide dispersion is not changed so much in any cooling rate, and this is the reason why the PS treated specimen is not embrittled by slow cooling after

Fig. 12. Scanning electron micrographs showing the effect of PS treatment on the behavior of carbide precipitation on cooling. Air-cooled (a) and furnace-cooled from FS temperature (1423 K) (b), and air-cooled from PS temperature (1173 K) (c).

PS treatment.

4. Conclusions

The effect of Partial Solution treatment on toughness of 12%Cr–0.3%C steels was discussed in connection with microstructure and grain boundary segregation of impurities. The results obtained are as follows:

(1) PS treatment results in refining of γ grain size because of the grain boundary pinning effect. The γ grain refining leads to a lowering of ductile-brittle transition temperature (DBTT). This is mainly due to the reduction of grain boundary stress concentration which is caused by pile-up of dislocations to grain boundary.

(2) In specimens with full solution (FS) treatment, carbide particles precipitate along lath boundary during tempering, and this cause an early crack initiation in impact testing. On the other hand, in specimens with PS treatment, carbides preferentially precipitate on insoluble carbide particles which have homogeneously dispersed within the martensite matrix. This produces an increase of upper shelf energy.

(3) PS treatment suppresses precipitation of grain boundary carbide which occurs during slow cooling from γ phase region, because the insoluble carbide particles provide preferential precipitation sites within γ grains.

Hence, DBTT is not dependent on cooling rate in PS treated specimens, although it is greatly raised in FS treated specimens with slow cooling because of the grain boundary precipitation of carbide.

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