Delamination toughening assisted by phosphorus in medium-carbon
low-alloy steels with ultrafine elongated grain structures

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Abstract

The effect of phosphorus (P) on delamination toughening was examined for 0.4%C-1%Cr-0.7%Mn-0.2%Mo steels (mass%) comprised of ultrafine elongated grain (UFEG) structures with strong $\langle 110 \rangle$ /RD fiber textures. The UFEG structures evolved through the plastic deformation of tempered martensitic structures by multi-pass caliber rolling at a temperature of 773 K (warm tempforming, WTF). The addition of P, up to 0.093% (mass%), had little influence on the evolution of the UFEG structure and the strength of the steels. Although the tensile ductility and upper-shelf energy showed a slight tendency to decrease as the P concentration increased from 0.001% to 0.093%, the delamination perpendicular to the notch orientation of the impact specimens was pronounced over a wider temperature range. As a result of delamination, the 0.093% P-doped steel exhibited a significant inverse temperature dependence of toughness at temperatures from 250 K to 350 K. The delamination toughening was dominated by the UFEG structure, and further assisted by the phosphorus segregation. It was considered that the formation of distinct P segregation bands, which presented a structure consisting of brittle and ductile layers, may be especially effective in accelerating delamination and improving toughness in P-doped steel with an UFEG structure.

Keywords: steel; thermomechanical treatment; ultrafine grained microstructure; phosphorus segregation; delamination, toughness

1. Introduction

Impurity reduction[1-3]and grain refinement[4-8]areboth recognized as effective methods for enhancing the notch toughness of high-strength steels. The former is considered to inhibit intergranular fracture,which is often owed tograin boundary segregation due to impurities such as phosphorus (P), and the consequentloss of grain boundary cohesion[1,3].The latter is considered to increase the grain boundary area per unit volume,whichreduces the stress concentration at the grain boundaries, especially at triple junctions, and it is also considered to decrease the grain boundary segregation due to the concentration of impuritiesatthe grain boundaries.It is well known that these methods improve the intrinsic fracture resistance of high-strength steels. In addition, owing to the relaxation of the stress concentration at the crack tips,delamination perpendicular to the plane of the notchis also recognized asan effective method to improve the notch toughness at low temperatures[9-12].

Recently, Kimura et al.[13-18]have developed a thermomechanical treatment in which tempered martensitic steel is plastically deformed using multi-pass caliber rolling at an elevated temperature (i.e., warm tempforming, WTF).This treatment enhancesthe notch toughness of ultra-high-strength steel,resulting in a yield strength (σ_y) of 1.4GPa or greater. Forexample,a 0.4%C-2%Si-1%Cr-1%Mo steel (all chemical compositions are expressed in mass%) exhibited a σ_y of 1.84 GPa and a Charpy V-notch absorbed energy (vE) of 226 J at room temperature owing to the evolution of an ultrafine elongated grain (UFEG) structure with a strong $\langle 110 \rangle$ //rolling direction (RD) fiber texture during the WTF[13].Furthermore, this steel with a UFEG structuredemonstrated significant inverse temperature dependence of toughness overthe temperature range of 213 K to 333 K [13].This enhancement of the notch toughness was due to the delaminationthat occurred perpendicular to the notch orientation of the impact specimens[13-18].It was determined that the dominant factors responsible for the delamination

toughening were the transverse grain size, grain shape, $\langle 110 \rangle // RD$ fiber texture, and nanometer-sized carbide particle distribution in the UFEG structure [17].

Jafari et al. [19-22] also investigated the delamination toughening of a 0.4%C-1%Cr-0.7%Mn-0.2%Mo steel with an addition of 0.053% P. They reported that the steel sample with an UFEG structure that was processed by the WTF demonstrated a high vE due to the occurrence of delamination at a temperature of 123 K, at which P embrittlement occurred for the conventionally quenched and tempered sample. Here, two possible reasons were considered for the improvement in the notch toughness of the 0.053% P-doped steel with an UFEG structure. One reason is that the intergranular fracture along the prior-austenite grain boundaries, which results from the P grain boundary segregation, is suppressed through the formation of the UFEG structure [19]. The other reason is that the delamination is accelerated through the reduction of the interface cohesion due to the P segregation in the UFEG structure [20].

If this is the case, further weakening of the grain boundary with a higher concentration of P may further facilitate the delamination toughening. This is a great development regarding the conventional metallurgical concepts of P embrittlement; P grain boundary/interface segregation is considered to be a factor that increases the impact toughness of the steel. Therefore, we need to determine whether the enhancement of the delamination toughening is greater in the steel with the higher P concentration, and we also need to clarify the combined influence of the UFEG structure and P segregation on the delamination toughening.

The purpose of this study is to effectively utilize the detrimental effect of P segregation to enhance the impact toughness of high-strength steels. Thus, the effects of various concentrations of P, from 0.001% to 0.093%, on the UFEG structure, tensile properties, and impact toughness of 0.4%C-1%Cr-0.7%Mn-0.2%Mo steels will be systematically investigated. For a comparison, P-doped steels with conventionally quenched and tempered structures will also be used. The

delamination toughening mechanism will be discussed on the basis of the UFEG structure in combination with the P segregation.

2. Experimental procedures

2.1. Materials preparation

Five ingots with different P concentrations, each approximately 100 kg in mass, were prepared by vacuum melting. Following solidification, the ingots with a thickness of about 20 × 10 mm were homogenized at 1473 K for 3.6 ks, and subsequently hot-rolled into plates with a thickness of 4 × 10 mm. The reduction in area owed to the multi-pass hot rolling was about 80%. Table 1 lists the chemical compositions of the steels, namely 0.018%P steel, 0.068%P steel, and 0.093%P steel, as analyzed after hot-rolling, along with those of the 0.001%P [19, 21-23] and 0.053%P [19-22] steels as a reference. The chemical compositions are similar to those of the high-strength JIS SCM 440 (AISI 4140) steel, with the exception of the high P concentration.

The plates were cut into blocks with dimensions of 120 mm (*l*) × 40 mm (*w*) × 40 mm (*t*). The blocks were homogenized at a temperature of 1473 K for 1.8 ks, and hot-rolled using a caliber roll into square bars with a cross-section of $9 \times 10^2 \text{ mm}^2$, followed by air cooling. The hot-rolled bars were solution treated at a temperature of 1193 K for 3.6 ks, followed by oil quenching to obtain a martensitic structure. The quenched bars were tempered at 773 K for 3.6 ks, and subsequently subjected to multi-pass caliber rolling (WTF) into square bars with a cross-section of $2 \times 10^2 \text{ mm}^2$, followed by air cooling to produce the UFEG structure. The reduction in area owed to the multi-pass caliber rolling was 78% over 9 passes, which corresponds to an equivalent strain of 1.75. Note that during rolling, following three passes, the bars were held in a furnace at a temperature of 773 K for 0.3 ks and they were passed through the final groove twice to control the cross-sectional shape of the bars. The tempformed bars were annealed at

823 K for 3.6 ks, followed by water quenching; these were denoted as TF samples. For a comparison, some of tempformed bars were normalized at 1153 K for 0.6 ks, followed by air-cooling, and subsequently austenitized at 1193 K for 3.6 ks, followed by oil quenching to obtain a conventional quenched and tempered martensitic structure. The quenched bars were tempered at 823 K for 3.6 ks, followed by water quenching, (i.e., the same conditions as those of the TF samples); these were denoted as QT samples. The principal axes of the squared bar in this study were defined as illustrated in Fig.1. The axis coincident with the rolling direction is defined as the RD, the axis coincident with the direction of the main working force at the final pass is defined as the ND, and the axis normal to the RD and ND is defined as the TD. The pole figures in Fig.1 demonstrate that the $\langle 110 \rangle$ //RD fiber deformation texture provides lots of cleavage $\{100\}$ orientations parallel to the RD and on the planes with the angle of $\sim 45^\circ$ to the RD, while it provides lots of $\{110\}$ orientations on the planes normal to the RD.

2.2. Mechanical testing

Round tensile specimens (JIS-14A) with a parallel length of 42 mm and a diameter of 6 mm were cut from the squared bars along the RD. Tensile tests were conducted with a crosshead speed of 0.85 mm/min. A non-contacting video extensometer was used to measure the tensile strain over the 30 mm gauge length. Small plate specimens with a parallel length of 4 mm, a width of 3 mm, and a thickness of 1 mm were machined from the squared bars at two different angles (0° and 90°) to the RD. They were subsequently used for tensile testing at a crosshead speed of 0.11 mm/min to investigate the tensile anisotropy. The 0.2% offset yield strength was recorded. The true fracture strength (σ_F) was calculated by dividing the load at fracture by the cross-sectional area of the ruptured tensile specimens [15, 17]. The specimens (dimensions: 55 mm (l) $\times$ 10 mm (w) $\times$ 10 mm (t)) cut from the squared bars along the RD were used for Charpy

impact tests with a full-size 2 mm V-notch over the temperature range of 77 K to 623 K. Note that during the Charpy impact tests, the striking direction (SD) was set at an angle of approximately 45° to the ND and TD of the squared bars (Fig. 1).

2.3. Microstructural characterization

The samples were subjected to mechanical polishing to obtain a smooth surface. Following etching, they were observed by field emission scanning electron microscopy (FE-SEM) (JEOL JSM-7001F). The planes normal to the ND (ND Planes) were observed. Following mechanical polishing, the samples were subjected to electron backscattered diffraction (EBSD) analysis and electron probe micro-analysis (EPMA). The ND plane and the plane normal to the RD (RD plane) were analyzed. The EBSD analysis was performed using a FE-SEM (JEOL JSM-6500F) equipped with an orientation imaging microscope. The EBSD measurements were conducted on a hexagonal grid with a step size of 0.05 μm in an area of 25 $\mu\text{m} \times 25 \mu\text{m}$. All the raw data were subjected to clear-up by procedures including confidence index standardization and grain dilation single iteration. The inverse pole figure was calculated using the harmonic series expansion method with a series rank of 16, and orthotropic sample symmetry was enforced. Following the Charpy impact testing, the elemental distributions of the samples were mapped by EPMA (JXA-8500F) with a specific resolution of 2 μm near the fractured region. The fractured surfaces of the tested samples were observed by FE-SEM.

3. Results

3.1. Microstructure

Fig. 2 shows the matrix microstructures for the QT and TF steel samples with an addition of 0.093% P. The QT sample exhibits a typical tempered martensitic structure with equiaxed

prior-austenite grains that are subdivided by the packet and block boundaries (Fig. 2(a)). The average prior-austenite grain size was measured to be approximately 30 μm . The average linear intercept length (Fig. 2(d)) for the block was 0.60 μm ; the block boundaries were defined as grain boundaries with a misorientation angle of 10° or greater. As for the TF sample, the prior-austenite grain boundaries could no longer be recognized, and an UFEG structure with a strong $\langle 110 \rangle // \text{RD}$ fiber texture had evolved (Fig. 2(b) and (e)). The UFEG structure consists of ribbon-like and rod-like grains that are aligned to the RD (Fig. 2(c) and (f)). For the UFEG structure, the average linear intercept length of the grain boundaries with a misorientation angle of 10° or greater was measured to be 0.40 μm in the transverse direction, and 1.19 μm in the longitudinal direction ($// \text{RD}$). In addition, the carbide microstructures of both the QT and TF samples are characterized by spheroidal particles, as shown in Fig. 3. The carbide particles of the TF sample appear to be more spherical than those of the QT sample, and their long axes were observed to be almost aligned to the RD of the TF sample. It was confirmed that the microstructural features of the TF samples with an addition of 0.093% P, including the transverse grain size, grain shape, $\langle 110 \rangle // \text{RD}$ fiber texture, and carbide particle distribution were almost comparable to those of the 0.001% P and 0.053% P steels [19-23]. Hence, the addition of 0.093% P has little influence on the evolution of the UFEG structure during the WTF. Similarly, irrespective of the P concentration, the QT samples were confirmed to exhibit almost identical microstructural features, including the block size, the prior-austenite grain size, and the carbide particle distribution.

3.2. Tensile properties

Fig. 4 shows the variation in the tensile properties at room temperature as a function of P concentration. As previously reported for the 0.001% and 0.053% P steels [19-21, 23], it was

characteristic that all the QT samples exhibited typical continuous yielding behavior. However, irrespective of the P addition, the sharp yield point phenomenon was observed for all the TF samples, and the σ_y approximately corresponded to the upper yield stress of the TF samples. The σ_y and tensile strength (σ_B) of the QT and TF samples do not significantly change as the P concentration increases. Hence, the strengthening effect of the P addition [24] was not observed in the macroscopic tensile test results for the QT and TF samples. The average σ_B of the TF samples (1.13 GPa) is almost comparable to that of the QT samples (1.14 GPa), while the average σ_y of the TF samples (1.06 GPa) tends to be slightly higher than that of the QT samples (1.00 GPa). Furthermore, regardless of the P concentration, the uniform elongation (ϵ_u) of the TF samples (7–8%), as well as that of the QT samples (5–6%) is almost identical. Moreover, the reduction of area (RA) of the TF sample is comparable to that of the QT sample at a P content of 0.001%, and tends to decrease as the P concentration increases. However, the TF samples exhibit slightly higher ductility than that of the QT samples at room temperature. In addition, for both the TF and QT samples, the σ_y increases as the tensile testing temperature decreases from room temperature to 77 K, irrespective of the P concentration, as shown in Fig. 5. As the P concentration is increased from 0.001% to 0.093%, the total elongation (EL) and RA of the TF samples do not significantly decrease at a temperature of 77 K; in contrast, the EL and RA of the QT samples markedly decrease as the P concentration increases from 0.053% to 0.093%. These results indicate that there is a more pronounced difference in the ductility of the TF and QT samples at lower temperatures.

3.3. Charpy impact properties

Fig. 6 shows the changes in the vE as a function of P concentration at room temperature (a), and the representative fracture appearances of the tested samples (b). For the QT samples, the

vE decreases considerably as the P concentration increases, for example, the vE decreases by 93 J and 7 J on average for the 0.001% and 0.093% P steels, respectively. Conversely, for the TF samples, the vE maintains an almost constant average value of 147 J for the 0.001% P steel and 143 J for 0.053% P steel, and increases up to 196 J for the 0.093% P steel. For the QT samples, the crack propagates across the central portion of the bar regardless of the P concentration, and develops shear lips around the edges of the 0.018% P steel specimen (Fig. 6(b)). A similar fracture appearance is exhibited by the TF 0.018% P steel samples. However, for the 0.068% P and 0.093% P steels, the TF samples exhibit an erratic crack path with a component in the longitudinal direction of the bar, indicating the occurrence of crack-arrester type delamination fracture. The delamination fracture becomes more pronounced in the 0.093% P steel, and the TF samples did not separate into two pieces during the impact test, as indicated by the arrows in Fig. 6(a) and (b).

In the geometry of the crack-arrester [9-11], delamination is thought to relax the triaxial stress conditions and blunt the crack tip. To fracture a material, crack re-initiation is necessary and this occurs under conditions of almost uniaxial tension; the impact specimen virtually behaves as an un-notched specimen. Additionally, it can be expected that the stress fielding effect from the formation of microcracks along the RD will reduce the driving force for fracture [25]. As a result, a high vE can be achieved through this type of delamination [26, 27].

Fig. 7 shows the change in the vE as a function of testing temperature for the TF and QT samples. Here, the upper-shelf energy for the TF samples was defined as the vE at 623 K for 0.093% P, at which none of the samples exhibited delamination fracture. The upper-shelf energy of the TF 0.093% P steel sample (134 J) is slightly lower than that of the TF 0.053% P (142 J) and 0.001% P steel (149 J) samples; however, it is still higher than that of the QT 0.001% P steel sample (98 J). In addition, it should be noted that the TF samples show a high vE owing to the

delamination at lower temperatures, whereas the QT samples exhibit a considerably low νE as a result of brittle rupture at lower temperatures. Furthermore, for the 0.001% P steel, the delamination was confined to a narrow temperature range in the vicinity of 123 K [23]. As the P concentration increases, the delamination occurs over a wide temperature range from 123 K to higher temperatures; the delamination commences at 423 K for the 0.053% P steel [20, 21], and at 523 K for the 0.093% P steel. The νE of the 0.093% P steel TF sample exhibits a significant inverse temperature dependence at temperatures in the range of 250 K to 350 K. The TF samples that did not separate into two pieces because of the delamination are indicated by the data points with arrows in the temperature range of 123 K to 348 K, as shown in Fig. 7(a). Furthermore, compared to the QT 0.001% P steel sample, the TF 0.093% P steel sample has superior impact properties. Therefore, the addition of P was also demonstrated to effectively control the delamination toughening of the steels with an UFEG structure, especially for those with a P concentration range of 0.05 % to 0.09%.

3.4. Fractographs

Fig. 8 shows the representative fracture surfaces of the QT and TF samples with a 0.093% P concentration that were subjected to testing at room temperature. Intergranular fracture occurred along the boundaries of the prior-austenite grains of the QT sample (Fig. 8(a)). Furthermore, in the TF sample (Fig. 8(b) and (c)), the fracture mode of the delamination planes is characterized as a mixture of quasi-cleavage and intergranular fracture. The quasi-cleavage fracture region is roughly aligned along the longitudinal direction parallel to the RD, similar to those of the low P samples that exhibited delamination [23]. As indicated by the arrows in Fig. 8(c), it can be observed that cracks tend to propagate along the grain boundaries of the UFEG structure. Similar intergranular fracture was observed on the delamination planes as a result of the slow strain rate

tensile testing of the pre-hydrogen-charged notched specimens; as the hydrogen content increased, the intergranular fracture was facilitated and the delamination cracking was enhanced[28]. Hence, it is demonstrated that the delamination fracture in the P-doped steel becomes more brittle and pronounced because of the intergranular fracture, leading to the acceleration of the delamination crack propagation along the RD.

4. Discussion

This study further confirmed that the 0.4%C-1%Cr-0.7%Mn-0.2%Mo steels, even with a high P concentration of 0.093%, exhibited excellent impact properties through the introduction of an UFEG structure with a strong $\langle 110 \rangle // \text{RD}$ fiber texture. For the sample with the UFEG structure, the addition of 0.093% P resulted in delamination over a wide temperature range of 123 K to 523 K (Figs. 6 and 7). In addition, owing to the delamination, a significant inverse temperature dependence of toughness was observed between temperatures of 250 K to 350 K. In this study, the delamination toughening of the P-doped steels with an UFEG structure was discussed in relation to the P segregation.

Fig. 9 shows the delamination crack of the TF 0.093% P steel sample that underwent Charpy impact testing at 253 K, in which a significant inverse temperature dependence of toughness was observed. The corresponding crack regions, indicated by the labels in Fig. 9(a), were mapped using EPMA, as shown in Fig. 9(b-e). Along the RD, the bands with high (red color) and low (blue and green color) P concentrations are co-existent. These mapping results indicate that delamination cracks preferentially initiate and propagate along the P segregation bands with high P concentration regions, as shown in Fig. 9(b-d). The arrow in Fig. 9(e) shows a step that formed between the delamination cracks along the P segregation bands. Fig. 10 shows brittle cracks in the QT 0.093% P steel sample that underwent Charpy impact testing at 253 K.

Interestingly, the cracks propagated along the prior-austenite grain boundaries (Fig. 10(a)) of the QT sample without being influenced by the P segregated bands, as shown in Fig. 10(b). This may be responsible for the isotropic prior-austenite grain structure of the QT samples. Once cracks initiate at the prior-austenite grain boundaries owing to the reduction of grain boundary cohesion by the P segregation, the main cracks in the SD can easily propagate along the weakened boundaries. Fig. 11 shows the SEM images and EPMA mappings of the delamination cracks of the TF 0.001% P and 0.093% P steel samples that were Charpy impact tested at 123 K. Note that both the TF samples exhibited delamination fractures at 123 K, and the delamination fracture became more prominent as the P concentration increased. For the 0.093% P steel, the delamination fracture is more pronounced along the distinct P segregation bands (Fig. 11(f)). Furthermore, for the 0.001% P steel, delamination occurs despite the lack of significant phosphorus segregation. These results indicate that the UFEG structure with a strong $\langle 110 \rangle$ //RD fiber texture in the TF samples is a key factor for delamination to occur, which is further assisted by the P segregation.

Fig. 12 shows the σ_y , σ_F , and RA of the small tensile specimens tested at a temperature of 77 K, as a function of P concentration and tensile direction. The σ_y in the RD ($\sigma_{y//RD}$) is slightly higher than that in the SD ($\sigma_{y//SD}$). Such strength anisotropy is commonly observed for steels with UFEG structures [14-17]. The addition of P has little influence on the σ_y in the tensile directions parallel to the RD and SD. When the specimens were tensioned along the RD, all the TF samples exhibited significant necking prior to failure, resulting in the large $RA_{//RD}$ and $\sigma_{F//RD}$ (Fig. 12(a)). The degradation of the tensile ductility with P addition is minor in the RD, as indicated in Fig. 5. Furthermore, the $RA_{//SD}$ and $\sigma_{F//SD}$ are low, even in the 0.001% P steel, and they markedly decrease with the addition of 0.02% P (Fig. 12(b)). The $RA_{//SD}$ is almost zero for the steels with a P concentration of 0.05% or greater, and the $\sigma_{F//SD}$ corresponds with the $\sigma_{y//SD}$. Hence, it is

demonstrated that at a temperature of 77 K, the effect of the P addition on the ductile failure is minor for the TF samples tensioned in the RD, while for the samples tensioned in the SD, brittle fracture becomes more likely as the P concentration increases.

Brittle fracture occurs when the tensile stress in the process zone of the notch root and/or the crack tip exceeds the critical brittle fracture stress [8]. When the weak interfaces are present along the RD for the V-notch impact specimen in Fig. 1, the interaction between the weak interface along the RD and the resolved normal tensile stress (σ_t) along the SD ($\sigma_{t//SD}$) may cause brittle delamination [9, 11]. Fig. 13 shows the Yoffe diagram for the UFEG structure with a strong $\langle 110 \rangle // RD$ fiber texture [14, 15, 17], illustrating the relationship between the σ_t and the cleavage fracture stress (σ_{cf}). For the UFEG structure with a strong $\langle 110 \rangle // RD$ fiber texture, the $\{100\}$ pole figure demonstrates that many $\{100\}$ cleavage planes are distributed on both the SD planes ($\perp SD$) and the 45° planes (which are inclined at an angle of 45° to the RD). As a result of the elongated grain shape, the coherence length of the $\{100\}$ cleavage planes along the 45° direction is shorter than that along the RD, and thus, the cleavage fracture stress along the 45° direction ($\sigma_{c//45^\circ}$) is greater than the cleavage fracture stress along the SD ($\sigma_{c//SD}$). Similarly, owing to the elongated grain shape and good grain boundary continuity along the RD, the intergranular fracture stress in the SD ($\sigma_{g//SD}$) is low [19, 28]. Hence, the weakest interfaces can be observed along the RD. Since $\{100\}$ cleavage planes scarcely exist on the RD planes normal to the RD (Fig. 2), the cleavage crack will barely propagate in the SD. If the Tresca yield criterion is assumed in the process zone within the plastically yielding region of the notch root, the maximum values of the σ_t along the RD and SD in the process zone can be approximated on the basis of σ_y as $2.6 \times \sigma_y$ and $1.6 \times \sigma_y$ [16], respectively. When the $\sigma_{t//SD}$ exceeds the $\sigma_{c//SD}$ below T_1 , cleavage cracks initiate and propagate along the RD, causing delamination to occur. As the temperature decreases, the $\sigma_{t//SD}$ increases and the delamination becomes more

pronounced, enhancing the νE . Furthermore, in addition to the delamination cracking along the RD, the cleavage crack initiation and propagation along the 45° direction is facilitated below T_2 , in which the resolved normal tensile stress along the 45° direction ($\sigma_{t//45^\circ}$) exceeds the $\sigma_{c//45^\circ}$. The delamination is subsequently suppressed, leading to a reduction of the νE .

Additionally, the macroscopic mode of the delamination fracture is characterized by a stepwise crack propagation in which “terraces” and “steps” are formed [15, 18, 26-27]. The terraces correspond to delamination planes and are approximately parallel to the RD (Fig.8 (b)). In the TF sample with an UFEG structure, the deflection of the transverse cracks and delamination was observed to occur in relation to “packet bands” that were formed through the extension of martensite packets in the RD [18]. The UFEG structure was mainly developed through the extension of martensite blocks within the packets. The crystallographic orientation and geometric arrangement of the UFEGs are relatively similar within a packet band [15, 18], and the packet band may have relatively good continuity of the $\{100\}$ cleavage planes and weak UFEG boundaries (including carbide particles). Hence, cracks can penetrate the packet band without any significant deflection, and the size of packet bands may be considered to be an effective grain size in order to control the delamination toughening in a TF steel with an UFEG structure. The reduction in the width of the packet bands can lead to the suppression of the transverse crack propagation, leading to the enhanced delamination. Since the packet band size, in addition to the packet size, correlates to the prior-austenite grain size, the refinement of the prior-austenite grain size is an effective mechanism for this. Actually, in the 0.4%C-2%Si-1%Cr-1%Mo steel, the inverse temperature dependence of toughness was demonstrated to become significant at lower temperature as the prior-austenite grain size decreases in the grain size range of 50 to 600 μm , although the UFEG structure is almost identical [18]. In the present steel samples, the average prior-austenite grain size was about 30

μm , irrespective of the P concentration, and the packet band size was also considered to be almost comparable. Fig. 14 shows the representative fracture surfaces of the TF samples with a 0.093% P concentration that were subjected to testing at 77 K. In addition to the quasi-cleavage fracture, intergranular fracture is observed on the delamination planes along the RD (Fig. 14(a, c)). Furthermore, it should be noted that the brittle transverse cracks are observed as indicated by the arrows in Fig. 14 (a, b). The occurrence of the transverse cracks appears to suppress the delamination crack propagation along the RD. The fracture mode of the brittle transverse cracks is quasi-cleavage (Fig. 14 (b)). Such brittle transverse cracks are suggested to be associated with the family of $\{100\}$ planes, and were commonly observed in the TF 0.001% P and 0.053% P [20] steel samples that were subjected to testing at 77 K, in which the vE showed a sharp drop (Fig. 7).

On the basis of the above Yoffee diagram (Fig. 13), it is interpreted that for the present 0.001% P sample with an UFEG structure, the $\sigma_{c//SD}$ may be relatively high (Fig. 12) and high $\sigma_{t//SD}$ is required to cause brittle fracture. The difference between the $\sigma_{c//45^\circ}$ and $\sigma_{c//SD}$ is also minor. As a result, delamination may be confined to occur within a narrow temperature region in the vicinity of 123 K (Fig. 7). Furthermore, in the P-doped steels, the P segregates to the weak interfaces, such as the grain boundaries, ferrite matrix/cementite interfaces, and $\{100\}$ planes, and consequently decreases the interface cohesion [20, 21]. However, the ductility and toughness in the RD planes are not significantly impaired by the addition of P (Fig. 12). Hence, this can provide a condition in which delamination could occur at higher temperatures as the P concentration increases. Additionally, it should be noted that distinct P segregation bands form for the 0.093% P steel sample (Figs. 9 and 11). Fig. 15 shows the P concentration line profiles in the TD for the TF samples with a different P concentration. The P segregation bands are confirmed to become markedly distinct in the 0.093% P steel sample. For example, the P

concentration in the regions of high P concentration appears to reach up to about 0.15 mass%, while it is close to 0.05 mass% in the regions of low P concentration. This is considered to be especially effective to promote delamination toughening compared to the homogeneous distribution of P. As indicated in Figs.9 and 11, it is likely that the regions of high P concentration may become both initiation sites and propagation paths for delamination. The $\sigma_{g//SD}$ is considered to especially decrease owing to the high P concentration and the intergranular fracture along the boundaries of the UFEGs (Fig. 8) becomes more significant. As shown in Fig. 16, the P segregation bands are long along the RD. This can provide a condition in which the brittle cracks propagate along the RD without any significant deflection in the regions of high P concentration. Furthermore, in the regions of low P concentration, the UFEG structure may maintain high ductility and toughness at lower temperatures, consequently suppressing the transverse crack propagation along the SD and 45° directions.

Therefore, enhanced delamination toughening over a wide temperature range of 123 K to 523 K for the TF 0.093% P steel sample is associated with the highly ductile UFEG structure combined with the brittle P segregated bands inherited from the solidification process of the ingot. Our strategy to enhance the toughness of high-strength steel is to arrest the propagation of the main cracks along the transverse directions in the hierarchical, anisotropic, and ultrafine grain structure [18, 29-30], in addition to suppressing the crack initiation. These findings further indicate that the use of the solidification structure is effective to enhance the toughness of high-strength steel with an UFEG structure.

5. Conclusions

The effect of the P concentration on the delamination toughening of 0.4%C-1%Cr-0.7%Mn-0.2%Mo steels processed by WTF at a temperature of 773 K was evaluated by microstructural observation, tensile tests, and Charpy V-notch impact tests. The main results are summarized as follows:

- (1) The addition of 0.001–0.093% P had little influence on the evolution of the UFEG structure during the warm tempforming; the transverse grain size, grain shape, $\langle 110 \rangle // RD$ fiber texture, and the distribution and morphology of the carbide particles of the UFEG structures were almost comparable, regardless of the P concentration.
- (2) The tensile properties including σ_y , σ_B , and ϵ_u did not significantly change as the P concentration increased from 0.001% to 0.093%, while the RA tended to decrease. However, at lower temperatures in particular, the RA did not tend to significantly decrease for the UFEG structure compared with the conventional quenched and tempered structure.
- (3) Although the upper-shelf energy of the TF sample tended to slightly decrease from 149 J to 134 J as the P concentration increased from 0.001 to 0.093%, the P addition assisted delamination to occur over a wider temperature range. The TF 0.093% P steel sample exhibited a significant inverse temperature dependence of toughness at temperatures of 250 K to 350 K.
- (4) The UFEG structure is a key factor for delamination toughening, and it is further assisted by P segregation at weak interfaces, such as grain boundaries, ferrite matrix/cementite interfaces, and $\{100\}$ planes. The formation of distinct P segregation bands in the highly P-doped steel may be especially effective to promote P-assisted delamination toughening, resulting in the significant inverse temperature dependence of toughness at temperatures of 250 K to 350 K in the TF 0.093% P steel sample.

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List of Captions:

Table 1. Chemical compositions of 0.018% P steel, 0.068% P steel, and 0.093% P steel along with those of 0.001% P [19, 21-23] and 0.053% P [19-22] steels (mass%).

Figure 1. Schematic drawing of a pair of caliber rolls and the relationship between the position of a rolled bar and an impact bar. $\{110\}$ and $\{100\}$ pole figures are also shown for the TF sample of the 0.093% P steel.

Figure 2. EBSD maps of the QT and TF 0.093% P steel samples. Inverse pole figure maps for the RD combined with image quality maps (a, b, c), and corresponding grain boundary maps with a misorientation angle above 10° (d, e, f). Inverse pole figure for the RD is also shown for the TF sample.

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Figure 4. Changes in the yield strength (σ_y), tensile strength (σ_B), uniform elongation (ε_u), total elongation (EL), and reduction of area (RA) at room temperature, as a function of P concentration of the QT and TF samples.

Figure 5. Changes in the yield strength (σ_y), total elongation (EL), and reduction of area (RA) as a function of tensile testing temperature for the 0.001% P [23], 0.053% P [20], and 0.093% P steels.

Figure 6. Changes in the Charpy V-notch absorbed energy (vE) at room temperature as a function of P concentration of the QT and TF samples (a), and the fracture appearance of the impact samples after testing (b). Data points with arrows indicate that the samples did not separate into two pieces during the impact test.

Figure 7. Changes in the Charpy V-notch absorbed energy (vE) with testing temperature for TF and QT samples of (a) 0.093% P steel, as well as the (b) 0.053% P [20-21], and (c) 0.001% P

[21, 23] steels for comparison. Data points with arrows in (a) indicate that the samples did not separate into two pieces during the impact test.

Figure 8. SEM fractographs of the QT sample (a) and TF sample (b, c) of the 0.093% P steel following Charpy V-notch impact testing at room temperature. The observed position of (c) is marked in (b). The arrows in (b) and (c) indicate the steps between the delamination planes and the cracks along the grain boundaries of the UFEG structure, respectively.

Figure 9. SEM image (a) and EPMA mappings (b, c, d, e) for P distribution along the crack propagation paths in following Charpy impact tests at 253 K. The observed positions of (b, c, d, e) are marked in (a).

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Figure 11. SEM images and EPMA mappings along the crack propagation paths for the TF 0.001% P steel and 0.093% P steel samples following Charpy impact tests at 123 K. SEI images (a, d), BEI images (b, e) and EPMA mappings (c, f) for P distribution. The observed local positions for BEI and EPMA are marked in (a, d).

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Steels	C	Si	Mn	Cr	Mo	Al	P	S	O	N
0.001%P	0.40	0.24	0.73	1.04	0.22	0.022	0.001	<0.001	<0.004	0.003
0.018%P	0.40	0.24	0.70	0.99	0.20	0.022	0.018	<0.0005	0.001	0.002
0.053%P	0.42	0.25	0.72	0.98	0.20	0.003	0.053	0.001	0.001	0.004
0.068%P	0.40	0.25	0.71	1.01	0.20	0.022	0.068	<0.0005	0.001	0.002
0.093%P	0.41	0.24	0.71	1.00	0.20	0.022	0.093	0.0005	0.001	0.001

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