Effect of Phosphorus on Hall-Petch Coefficient in Ferritic Steel

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The effect of phosphorus on the Hall-Petch coefficient (k_y) of polycrystalline ferritic steel was investigated by using interstitial free steel (IF steel) and an ultralow carbon (60 ppm C) steel containing different amount of phosphorus. The k_y of IF steel was around $100 \text{ MPa} \cdot \mu\text{m}^{1/2}$ regardless of the amount of phosphorus. On the other hand, the k_y of ultralow carbon steel containing phosphorus was higher than that of the IF steels, but significantly lower than that of the ultralow carbon steel without phosphorus. The analysis by Auger electron spectroscopy revealed that carbon segregates at ferrite grain boundary, and the amount of segregated carbon tended to be reduced by the addition of phosphorus. From these results, it can be concluded that phosphorus does not directly influence the k_y of polycrystalline ferritic iron, but indirectly decreases the k_y by reducing the amount of carbon segregated at grain boundary.

KEY WORDS: Hall-Petch coefficient; ferritic steel; phosphorus; carbon; grain boundary segregation.

1. Introduction

The relation between yield strength, σ_y , and grain size, d , in polycrystalline metals is experimentally described by Hall-Petch equation ($\sigma = \sigma_0 + k_y \cdot d^{-1/2}$), and it is known that the Hall-Petch coefficient, k_y , is about $600 \text{ MPa} \cdot \mu\text{m}^{1/2}$ in conventional low carbon steels.¹⁾ Author *et al.* has already reported that IF steel without solute interstitial elements has a low k_y value of around $150 \text{ MPa} \cdot \mu\text{m}^{1/2}$,²⁾ but it is significantly increased by the existence of a small amount of solute carbon.^{3,4)} Moreover, Author *et al.* has suggested that the increase in k_y is related with the grain boundary segregation of solute carbon atoms.^{4,5)} On the other hand, it is well known that phosphorus has a strong tendency to segregate at ferrite grain boundary. If the k_y of ferritic iron is influenced by grain boundary segregation of solute elements, segregated phosphorus also might cause a change of k_y similarly to carbon. In fact, W. A. Spitzig⁶⁾ and Sakata *et al.*⁷⁾ evaluated the k_y of ferritic steels containing different amount of phosphorus and reported that the k_y is increased with increasing the amount of phosphorus and, after reaching the maximum value, it decreases again by the further addition of phosphorus. However, the reason for the change in k_y has not been well understood. In addition, the effect of carbon has not been evaluated in their works, although the steels used contains a certain amount of carbon as well as phosphorus. In this study, only the effect of phosphorus on k_y was evaluated by using phosphorus bearing IF steels without solute interstitial elements, and then the effect of solute carbon on the k_y was also examined in the steel containing both of carbon (60 ppm) and phosphorus (1 000 ppm).

2. Experimental Procedure

The chemical compositions of the steels used in this study are listed in **Table 1**. A conventional Ti-added IF steel, in which carbon and nitrogen are completely fixed as Ti(C, N), was used as the base material (P0 steel). By adding 300, 600 and 1 000 ppm of phosphorus to the base material, phosphorus bearing specimens (P300, P600, P1000 steels) were produced. In addition, an ultra low carbon steel containing 60 ppm carbon and 1 000 ppm phosphorus was prepared to investigate the effect of both of carbon and phosphorus (C60-P1000 steel). **Figure 1** displays the heat treatment route applied to the specimens. Ingots of 30 kg with 120^t mm were solution treated at 1 473 K for 3.6 ks, and then hot-rolled to 12^t mm. After the surface grinding for de-scaling, the steel plates were cold-rolled by 90% in thickness reduction. In order to control grain size, the cold-rolled steel sheets were annealed for 1.8 ks at a selected temperature in 1 023 K through 1 123 K of ferrite single phase region. Finally, the steels with different ferrite grain size were subjected to 973 K –3.6 ks annealing followed by water-cooling, which aims to keep at a same condition for grain

Table 1. Chemical composition of steels used in this study (mass ppm).

	C	P	Ti	O	N	Fe
P0	4	<20	240	23	10	bal.
P300	8	270	290	14	16	bal.
P600	5	610	240	25	16	bal.
P1000	3	970	260	14	13	bal.
C60-P1000	64	1 100	30	43	48	bal.

[†]: The k_y of IF steel seems to be slightly different among specimens but the averaged value for a lot of data is estimated at $150 \text{ MPa} \cdot \mu\text{m}^{1/2}$.

Fig. 1. Heat treatment route and Fe-P binary equilibrium phase diagram.

Fig. 2. Optical micrograph, high-angle grain boundary map and inverse pole figure of P600 steel recrystallized at 1023 K (a), (c), (e) and 1173 K (b), (d), (f).

boundary segregation of carbon and phosphorus. Microstructure was observed with an optical microscope and a scanning electron microscope (SEM). Crystallographic orientation was identified by means of electron backscatter diffraction (EBSD) method using the SEM. Tensile testing was carried out at initial strain rate of $3.3 \times 10^{-3} \text{ s}^{-1}$ for plate test pieces standardized by JIS13B. Grain boundary segregation behavior was analyzed by means of Auger electron spectroscopy for some intergranular fracture surfaces of a sample which was cooled to liquid nitrogen temperature and then fractured by impact in the SEM equipment. In this article, the grain size was evaluated by the nominal grain size obtained by the quadrature method.

3. Results and Discussions

3.1. Microstructure and Tensile Property

Figure 2 represents optical micrographs ((a), (b)), high-angle grain boundary maps ((c), (d)) and inverse pole figures to normal direction ((e), (f)) of P600 steel recrystallized at 1023 and 1173 K, respectively. Both specimens have an

Fig. 3. Nominal stress – strain curves of P600 steel with different grain size.

equiaxial-grained ferritic structure bounded by high-angle grain boundaries and no strong texture. The ferrite grain size was increased from 12 to 145 μm with rising temperature due to normal grain growth after recrystallization. Figure 3 shows nominal stress-strain curves of P600 steel with three

different grain sizes. In this figure, only the low strain region was displayed to emphasize the yielding behavior. Since a clear yield point cannot be detected in most specimens, 0.2% proof stress was adopted as the yield strength in this paper.

3.2. Effect of Solute Phosphorus on Hall-Petch Coefficient

Figure 4 shows the changes in 0.2% proof stress as a function of inverse of square root of ferrite grain size. In all steels, Hall-Petch relationship is realized in the grain size range of 10 through 100 μm . For the IF steel without phosphorus (P0 steel), 150 $\text{MPa}\cdot\mu\text{m}^{1/2}$ has been reported as a reasonable value of the k_y .²⁾ The stress at $d^{-1/2}=0$ (open marks) is the friction stress which is required to move dislocations in matrix. It is estimated at 50 MPa for P0 steel and this value is almost same as the value reported for single crystal of pure iron.⁸⁾ This result supports the reasonability of the value 150 $\text{MPa}\cdot\mu\text{m}^{1/2}$ for the k_y in pure ferritic iron. On the other hand, it is obvious that the k_y is almost same in all P-series steels and lower than that of P0 steel, although the friction stress increases with an increase of phosphorus content. This means that phosphorus makes the matrix strength increase greatly but does not affect or slightly lowers the k_y of ferritic iron. However, it should be noted here that the k_y in C60-P1000 steel is fairly higher than that of P1000 steel. The difference between both steels is just whether solute carbon exists or not. This makes it clear that, in the previous researches,^{6,7)} the change in k_y reported as the effect of phosphorus is not due to phosphorus but due to the small amount of solute carbon contained as impurity. The k_y obtained from Fig. 4 is plotted against phosphorus content as shown in **Fig. 5**. In addition, the data of C60 steel,⁴⁾ in which only carbon is added by 60 ppm, is plotted in this figure. The k_y of P-series steels exhibit a constant value of 100 $\text{MPa}\cdot\mu\text{m}^{1/2}$ regardless of the phosphorus content. The k_y of C60-P1000 steel is 270 $\text{MPa}\cdot\mu\text{m}^{1/2}$. This value is obviously higher than those of P-series steels but lower than that of C60 steel (around 550 $\text{MPa}\cdot\mu\text{m}^{1/2}$). This means that small amount of carbon gives a large influence to the k_y of ferritic iron but the effect of carbon is reduced by the coexistence with phosphorus.

3.3. Effect of Solute Phosphorus on the Friction Stress

The yield strength of polycrystalline steels is affected by both of grain refinement strengthening and solid solution strengthening by alloying elements. In order to evaluate the solid solution strengthening by alloying elements, it is recommended to adopt the friction stress, because it just reflects the strength of matrix itself. **Figure 6** shows the relation between phosphorus content and the friction stress obtained in the Fig. 4. The increment of friction stress can be expressed as follows: $\Delta\sigma_0 \text{ (MPa)} = 250 \times [\text{mass}\%P]^{1/2}$. In previous papers, the change of yield strength has been discussed as a function of the change of phosphorus content. If the contribution by phosphorus was evaluated by the same way, the increment of friction stress is expressed as 500 $\text{MPa}/[\text{mass}\%P]$. This agrees well with the results reported by Bolling & Richman⁹⁾ or Hopkins & Tipler.¹⁰⁾ Anyway, it is sure that phosphorus is one of the elements which cause large solid solution strengthening in ferrite phase.

Fig. 4. Hall-Petch relationship in P0, P300, P600, P1000 and C60-P1000 steels.

Fig. 5. Relation between Hall-Petch coefficient and phosphorus content.

Fig. 6. Relation between friction stress and phosphorus content.

3.4. Relation between Hall-Petch Coefficient and Grain Boundary Segregation Behavior

According to the dislocation pile-up model, polycrystalline metals yields when the stress concentration at grain boundary exceeds a critical grain boundary shear stress which is required for the generation of secondary dislocations at grain boundary. In this model, the critical grain boundary shear stress is included in the k_y . Author *et al.* have already reported that small amount of solute carbon enhances the k_y of ferritic iron and that carbon atoms segre-

Fig. 7. SEM images showing intergranular fracture and Auger electron spectroscopy spectrum in P1000 (a) and C60-P1000 (b).

gated at grain boundary might increase the critical grain boundary shear stress. From this point of view, there should be strong relationship between the change in the k_y and the grain boundary segregation behaviors of carbon and phosphorus.

Figure 7 shows intergranular fracture surface and Auger electron spectra obtained from each point indicated by the arrows in P1000 (a) and C60-P1000 steels (b). A clear peak of phosphorus appears in P1000 steel (a) and the phosphorus concentration was estimated at 8.9 at.% (5.0 mass%). On the other hand, in C60-P1000 steel (b), both peaks of carbon and phosphorus appear simultaneously. This means the co-segregation of both elements at grain boundary. Thus, the concentration of segregated phosphorus is lowered to 4.6 at.% (2.6 mass%) due to the co-segregation with carbon. Some researchers have reported the similar phenomenon.¹¹⁻¹³⁾ Suzuki *et al.* have proposed that the grain boundary coverage of carbon θ_c and phosphorus θ_p in Fe-C-P alloy is given by the following equations under the site-competition between both elements.¹³⁾

$$\frac{\theta_c}{1-\theta_c-\theta_p} = \frac{C_c}{1-C_c} \exp\left(\frac{F_c}{RT}\right) \quad \text{..... (1)}$$

$$\frac{\theta_p}{1-\theta_c-\theta_p} = \frac{C_p}{1-C_p} \exp\left(\frac{F_p}{RT}\right) \quad \text{..... (2)}$$

Where C_c , C_p , F_c , F_p and R are the bulk concentrations of carbon, phosphorus, the segregation energies of carbon, phosphorus and gas constant, respectively. When the F_c and F_p are given at 80 and 50 kJ/mol,^{12,14,15)} respectively, the relation between θ_c and θ_p in P1000, C60-P1000 and C60 steels is calculated as shown in Fig. 8. This calculation demonstrates that carbon and phosphorus are concurrently segregated at grain boundary (co-segregation), and the both amounts of segregated elements are lowered in comparison with the case of single segregation. It has not been cleared yet how the interstitial carbon atoms compete with the substitutional phosphorus atoms at grain boundary, but carbon

Fig. 8. Relation between carbon and phosphorus in the segregation behavior at 973 K calculated with the site competition model.

seems to have some repulsive interaction against phosphorus. As a result, a part of carbon atoms might be rejected from grain boundary by segregated phosphorus. Accordingly, it is possible that the change in k_y by phosphorus addition, which has been reported by W. A. Spitzig and Sakata *et al.*, is reasonably explained in terms of grain boundary segregation behavior of carbon as illustrated in Fig. 9. When the solute carbon is completely fixed by carbide-former such as Ti and Nb, the steel has a very low k_y (a). However, if a small amount of carbon exists in solid solution, the k_y is significantly increased by the segregation of solute carbon (b). While, in the steels containing both of phosphorus and carbon, some carbon atoms are rejected from grain boundary owing to the repulsive interaction with phosphorus, and the k_y lowers continuously with increasing the amount of phosphorus ((c) and (d)).

From the above discussions, it is concluded that the k_y of ferritic steel strongly depends on the carbon concentration at grain boundary, but it has not been known exactly why segregated phosphorus does not change the k_y . However, it

Fig. 9. Schematic illustration showing the relationship between Hall-Petch coefficient and grain boundary segregation behaviors of carbon and phosphorus.

is likely that the effect of alloy element on the critical grain boundary shear stress is substantially difference between interstitial elements and substitutional elements. In order to obtain clear answer, further systematical researches will be required for many alloying systems.

4. Conclusions

The effect of phosphorus on the Hall-Petch coefficient of ferritic steel was investigated in Ti-added IF steel and an ultralow carbon steel containing different amount of phosphorus. The results obtained are summarized as follows:

- (1) Phosphorus greatly increases the yield strength

owing to the solid solution strengthening, but does not affect or slightly lower the Hall-Petch coefficient of polycrystalline ferritic steel.

- (2) The Hall-Petch coefficient of ferritic steel seems to depend on the carbon concentration at grain boundary. In ferritic steels containing both carbon and phosphorus, grain boundary segregation of carbon is prevented by co-segregated phosphorus and, as a result, the Hall-Petch coefficient of ferritic steel is lowered with increasing phosphorus content.

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