Effect of Mn and Si Addition on Microstructure and Tensile Properties of Cold-rolled and Annealed Pearlite in Eutectoid Fe–C Alloys

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The microstructures and tensile properties of cold-rolled and annealed pearlite in Fe–0.8mass%C alloys with various contents of Mn and Si were investigated. With the addition of Mn and Si, the tensile strength (TS) and yield strength (YS) of cold-rolled and annealed pearlite were vastly improved, but its effect on ductility of the cold-rolled pearlite is negligible. The addition of Si is quite effective in improving the ductility of cold-rolled and annealed pearlite, especially when the strength is at a higher level, i.e., lower annealing temperature or shorter annealing period. The optimal tensile properties in the alloys with Mn or Si were obtained after annealing at 723 K for short annealing periods (30 to 120 s). The combined addition of Mn and Si is more effective in improving the tensile properties of cold-rolled and annealed pearlite.

KEY WORDS: pearlite; eutectoid steel; cold working; annealing; ultrafine-grained microstructure; mechanical property.

1. Introduction

Recently, studies on the microstructures and properties of ultra-fine-grained materials obtained by various thermomechanical processings have been actively pursued because the fine-grained structure (grain size is less than 1 μm) in alloys exhibits high strength without losing toughness.1) Pearlite, which consists of ferrite (α) and lamellar cementite (θ), is one of the most important structures in steels. For the pearlitic structures, both reduction of interlamellar spacing of pearlite (ISP) and thinning of lamellar θ occur through heavy cold rolling,2,3) and the spheroidization of α lamellae can be quite accelerated during subsequent annealing,4) leading to the formation of (α + θ) microduplex structures.5–7) The refinement of θ particles, which should result in the refinement of α grain size by pinning effects, is very important for strengthening the alloy with the (α + θ) microduplex structure. In Fe–C alloys, the spheroidization and coarsening of θ proceed rapidly. Such θ coarsening can be suppressed by the addition of a third alloying element in the tempering of martensite.8) For pearlite, the addition of alloying elements can reduce the ISP,9) but its effect on the microstructure and mechanical properties of rolled and annealed pearlite in eutectoid steels has not been clarified yet.

The present study aims to examine the microstructure and tensile properties of the cold-rolled and annealed pearlite in Fe–0.8mass%C eutectoid alloys with various contents of Mn and Si.

2. Experimental Procedure

An Fe–0.8mass%C binary alloy and Fe–X–0.8mass%C ternary alloys (X: 1 or 2 mass%Mn, 1 or 2 mass%Si) and an Fe–2mass%Mn–1mass%Si–0.8mass%C quaternary alloy were used. Their chemical compositions are listed in Table 1. The other impurities such as P and S are less than 50 ppm in those alloys. Ingots were produced by vacuum induction melting and hot-rolled to 15 mm thick plates. They were homogenized at 1 473 K for 86.4 ks. Each specimen was austenitized at 1 123 K for 1.8 ks, quenched in a salt bath and isothermally held at 873 K for 0.6 ks for pearlite transformation, and followed by air-cooling. The as-transformed specimens were cold-rolled by 40–90 %, and the specimens cold-rolled by 90 % were isothermally annealed at 723–923 K for various periods, then quenched into water. Microstructure observation for TD plane (parallel to the rolling direction and normal to the rolling plane) was made by SEM (scanning electron microscope; Hitachi S3100H) and TEM (transmission electron microscope; Hitachi H-7650).
Using the TEM micrographs on which θ lamellae interface was parallel to the incident beam. The θ particle sizes in the specimens annealed at 923 K were determined by SEM. Using the Image analysis software (AnalySIS), which digitizes an image from the photograph, the stained carbides were identified based on gray level and separated for analysis. The area (A) of a 2-dimensional section at the polished plane was measured for each particle, and converted to an equivalent circle diameter (ECD: =((4A/π)1/2) of the particle. At least, four micrographs were taken with a magnification from 3000 to 20000 for each specimen. The total number of measured particles ranged from approximately 500 to 1 300, depending on materials and annealing periods at 923 K.

The XRD (X-ray diffraction) experiment was carried out on a Philips PW1078/50 X-ray diffractometer. The tube voltage and current were 40 kV and 40 mA, respectively. The tube anode was Cu Kα (λ=0.15406 nm), and the receiving slit was 2 mm. The precise position of each peak was determined with the method "width of the curve at half".

Tensile tests were performed at the initial strain rate of 2×10−3/s for the specimens of which gage size was 2.5 mm×8.5 mm×0.5 mm and longitudinal direction was parallel to the rolling direction (RD).

3. Results

3.1. Microstructure and Tensile Properties of the As-transformed Pearlite

After austenitization at 1 123 K for 1.8 ks and subsequent isothermal transformation at 873 K for 0.6 ks, fully pearlitic structures contained mostly of lamellar cementite were obtained. The effect of Mn and Si addition on ISPs and tensile properties in eutectoid alloys is shown in Fig. 1. The ISP of the 0.8C alloy is 260 nm in Fig. 1(a). By adding Mn and Si, the ISP was reduced to approximately 100 nm, less than half of the ISP in the 0.8C alloy. As seen in Figs. 1(b) and 1(c), YS (0.2% proof strength) and TS are both remarkably increased by the addition of Mn or Si. The more Mn and Si contents in the alloys, the higher the strength. The increase of TS is larger than that of YS. Mn addition results in a slight decrease of Eu (total elongation) and Ea (uniform elongation), but the ductility remains almost the same as that of the 0.8C alloy when Si is added. Thus, it is concluded that Si is effective for improving the strength-ductility balance of as-transformed pearlite.

3.2. Microstructure and Tensile Properties of Cold-rolled Pearlite

Figure 2 shows the SEM micrographs of the 0.8 C alloy cold-rolled by various amounts of reduction. The microstructures of cold-rolled pearlite are not uniform. After 40%C.R., the lamellar θ is often irregularly bent (Fig. 2(a)). By further rolling, the θ lamellae are aligned to be nearly parallel to the rolling direction as seen in Fig. 2(b). It is clear that, as rolling reduction increases, the proportion of fine lamellae (FL) region increases in the comparison of Figs. 2(b) and 2(c). The TEM micrograph of Fig. 2(d) shows that the ISP in the FL area (the upper portion of the micrograph) reaches 30–60 nm in the 0.8C alloy after 90% C.R. The ISPs in the FL region for the Mn or Si alloys reached the scale of 10 nm after 90% C.R. because of the finer initial ISPs.

The tensile properties of pearlite cold-rolled by 40–90% in the 0.8 C, 1 Mn and 1 Si alloys as a function of rolling reduction are shown in Fig. 3. The results of as-transformed specimens and 90% cold-rolled specimens of the 2Mn, 2Si and 2Mn1Si alloys are plotted in Figs. 3. Both TS and YS increase with rolling reduction. In Fig. 3(c) and 3(d), ductility (Ea and Eu) drastically decreases by 60% cold rolling, but remains nearly the same (about 3–4%) after further rolling. As the necking of the specimen takes place just before the tensile failure, the Ea and Eu are nearly the same for all of the cold-rolled specimens. When the rolling reduction is less than 75%, Si addition results in the increase in strength, especially in YS. Mn addition does not affect TS and YS so much when the rolling reduction is less than 60%. However, by further rolling, the strength (TS and YS) was sharply increased to the same levels as Si added alloys (see Figs. 3 (a) and 3(b)). Moreover, it can be concluded from Figs. 3(c) and 3(d) that the effect of the addition of Mn or Si on the ductility is negligible when the rolling re-
ductions are more than 60%.

3.3. Microstructure and Tensile Properties of Cold-rolled and Annealed Pearlite

The SEM micrographs of cold-rolled and annealed pearlite in the 0.8C, 1Mn and 1Si alloys are shown in Fig. 4. After 90% C.R. and annealing at 923 K for 1.8 ks, the deformed $\theta$ lamellae were completely spheroidized. The average ECD of $\theta$ particles in the three alloys are 0.77 $\mu$m, 0.44 $\mu$m and 0.30 $\mu$m, respectively. Apparently, $\theta$ particles in 1Si and 1Mn alloys are much finer than those in the Fe–0.8C alloy, i.e., because of the addition of Mn and Si, the growth of $\theta$ particles is significantly retarded. The dominant ECD distribution is in the range between 0.40 $\mu$m to more than 1.10 $\mu$m for the 0.8C alloy in Fig. 4(a). The suppression of $\theta$ growth by Mn addition is more significant than that by Si addition when Figs. 4(b) and 4(c) are compared. For the 1Si and 1Mn alloys, they are in the ranges between 0.20–0.70 $\mu$m and 0.12–0.48 $\mu$m, respectively. The average ECD is plotted against the annealing time in Fig. 5. It is noted that the coarsening of $\theta$ particles gradually intensifies with increasing holding time, and the combined addition of Mn and Si is more effective in suppressing the coarsening of $\theta$ during annealing at 923 K.
The tensile property of the specimens cold-rolled and annealed at 923 K is plotted against annealing period in Fig. 6. Both the strength (TS and YS) and ductility (E_t and E_u) are improved by the addition of Mn or Si. The greater the Mn and Si content, the higher the strength and the better the ductility. For the alloys with Mn, the region in which E_t and E_u are nearly constant appeared between the annealing periods between 30 s and 120 s. This is similar to the result reported by Chen et al.\textsuperscript{11)} in an Fe–0.5mass%C–0.6mass%Mn–0.3mass%Si alloy. In the alloys with Si, both E_t and E_u are larger than those with Mn, especially when the strength is higher. Thus, it can be concluded that the addition of Si is quite effective for improving the ductility during annealing at 923 K. In addition, the combined addition of Mn and Si is effective in strengthening the alloy annealed at 923 K for short annealing periods.

The microstructure changes in the 1Mn alloy corresponding to the annealing at 723 K for 30 to 120 s are shown in Fig. 7. In the specimen annealed for 30 s (Fig. 7(a)), the majority of \( \theta \) lamellae still maintains their original alignment as in the case of cold rolling although local spheroidization or fragmentation of \( \theta \) occurs partly. After annealing for 120 s (Fig. 7(b)), spheroidization of the fragmented \( \theta \) becomes more apparent. Furthermore, the dislocation density seems to decrease and low-angle boundaries can be recognized between spheroidized \( \theta \) at the position of
original lamellar $\theta$, indicating that there are some misorientations between adjacent $\theta$ lamellae in the deformed specimen as shown previously.\textsuperscript{6)}

Figure 8 shows the relationship between the tensile properties and annealing time in the specimens cold-rolled by 90\% and annealed at 723 K. TS and YS are tardily decreased with increasing annealing time at 723 K. $E_t$ and $E_u$ are first increased with annealing time during the annealing up to 120 s but decreased by further annealing in the 0.8 C alloy. The addition of Mn or Si significantly improves the strength (TS and YS) and ductility ($E_t$ and $E_u$) although the change with annealing time exhibits the same tendency as the 0.8 C alloy except for the 2Mn1Si alloy. In the 2Mn1Si alloy, the decreases of TS and YS are the smallest and the ductility remains high even after the annealing for 1.8 ks. Superior tensile properties (YS of $\approx 1700$ MPa, TS of $\approx 1 \text{900 MPa}$ and $E_u$ of 5–7\%) are achieved by annealing at 723 K for shorter periods after 90\% C.R..

4. Discussion

4.1. The Strengthening of Pearlite by Cold Rolling

High strengths of the cold-rolled pearlite are related to the combined strengthening by fine ISP, a high density of dislocations as well as solid solution strengthening. Heavily cold-rolled pearlite structures are similar to the cold-drawn ones. It is known that the strength of drawn pearlitic wire can be described as a function of ISP. Embury and Fisher\textsuperscript{12)} demonstrated that the strength of cold-drawn pearlitic wires is increased with drawing strain. Langford\textsuperscript{13)} reported that ISP decreases as drawing strain increases. Sevillano\textsuperscript{14)} and
Nishida et al.\textsuperscript{19,20} reported that the strength of drawn wire is increased with the inverse of ISP. The strength (TS and YS) of the 1Si alloy is the highest among the three alloys of the 0.8C, 1Mn and 1Si alloys under the same cold rolling condition. The second highest is 1Mn alloy (see Fig. 3). This might be because the ISPs of 1Si and 1Mn alloy are much finer than that of 0.8C alloy (see Fig. 1(a)) and the solid solution strengthening effect of Si on α is higher than that of Mn.

However, recent TEM or AP-FIM (atom probe field ion microscopy) studies reported that α lamellae change to nanocrystals and the dissolution of θ occurs during heavy cold drawing.\textsuperscript{16–20} Such dissolution of θ during cold drawing was also pointed out by means of Mössbauer spectroscopy.\textsuperscript{3,21–23} In fact, the present authors also observed the nanocrystalline θ formed by heavy cold rolling.\textsuperscript{21} Thus, the strain hardening of pearlite structure cannot be simply explained by the refining of ISP. In the present work, it was observed that XRD peaks of pearlitic α shift to the lower angle side by cold rolling with respect to that of the as-transformed one, i.e., the lattice parameter of α is increased due to the cold rolling (Fig. 9). As the cold rolling reduction increases, the shift of α peak gets larger, toward larger lattice parameter. For the case of 90% C.R. in the 0.8C alloy, the lattice parameter of α reached 0.28718 nm, which corresponds to 0.64 at% (0.14 mass%) of carbon in α from the relationship given by Fasiska and Wagenblast\textsuperscript{24} when it is assumed that the increase of carbon content only causes the lattice parameter change of α.

\[
\begin{align*}
\alpha_a (\text{nm}) &= (0.28664 \pm 0.00001) \\
&+ (0.84 \pm 0.08) \times 10^{-3} \text{ (at\% C).} \quad (1)
\end{align*}
\]

This result might indicate that the dissolution of θ occurs during cold rolling.

Nam et al.\textsuperscript{21} determined the change of θ fraction in pearlite versus the drawing strain in a eutectoid steel (Fe–0.81mass%C–0.4mass%Mn–0.2mass%Si) by the use of Mössbauer spectroscopy. They reported that dissolution of θ starts from the early stage of deformation when ISP is finer. According to their results, the dissolution of θ starts at the drawing strains of 1.5 for the ISP of 175 nm and its amount of dissolution increases with strain. 90% C.R. is equal to the true strain of 2.6. A quarter to a third of the θ in pearlite dissolves at such a strain in the study by Nam et al. Therefore, the solid solution strengthening by carbon in θ could be strong, especially in the heavily cold-rolled specimens. It was reported that distribution of carbon atoms in θ is non-uniform\textsuperscript{19,20} and ranges between 0.2 and 3 at% for the true strain of 4.22.\textsuperscript{19} A Mössbauer study on the alloying effect on the θ dissolution shows that the amount of dissolution changes depending on the third alloying element.\textsuperscript{21} For example, Mn favors the θ dissolution whereas Si does not influence noticeably. However, a further study is necessary to examine the dissolution of θ in the alloyed pearlite by cold deformation.

The dissolution of θ during heavy cold working should influence the mechanical properties during low temperature annealing to some extent as discussed in the next section.

4.2. The Mechanical Characteristics of Heavily Cold-rolled and Annealed Pearlite

For the strength of (α+θ) microduplex structures, the mean free slip path of dislocations in α is one of the most important parameters to be considered. Liu and Gurland\textsuperscript{25} studied the change of mechanical properties with the α grain size and the distribution of θ particles in the tempered martensite in the alloys with 0.065–1.46 mass% C. It was shown that the strength is almost proportional to the −1/2 power of the α grain sizes in low or medium carbon alloys (less than 0.3 mass% C) (i.e. Hall–Petch relationship) and the −1/2 power of the interparticle spacing of θ in high or ultra-high carbon alloys (over 0.55 mass% C). In recent years, Sherby’s group systematically investigated the relationship between strength and microstructures in ultra-high carbon alloys. Syn et al.\textsuperscript{26} concluded that in medium, high and ultra-high carbon alloys, YS is proportional to the −1/2 power of the interparticle spacing (\( \lambda_{\alpha} \)) and average size (\( d_{\alpha} \)) of α grains. The relationship derived by them is as follows:

\[
\text{YS (MPa)} = 310 \cdot \lambda_{\alpha}^{-1/2} \cdot d_{\alpha}^{-1/2} \quad (\text{MPa}) \quad ...(2)
\]

where \( \lambda_{\alpha} \) and \( d_{\alpha} \) are in μm. In the present work, after 90% C.R. and annealing at 923 K for 120 s, the \( \lambda_{\alpha} \) and \( d_{\alpha} \) in the 0.8C alloy are about 0.75 μm and 1.35 μm, respectively. According to Eq. (2), the derived YS is about 750 MPa. It is very near to the experimental result (see Fig. 6). This indicates that Eq. (2) is applicable to the case of pearlite heavily cold-rolled and annealed.

In the alloyed cases, however, the coefficient \( k \) in the Hall–Petch relationship for α of binary alloys changes largely in grain boundary strengthening with alloy content.\textsuperscript{27,28} Thus the coefficients in Eq. (2) need corrected properly in the alloyed steels. For example, in the present work, the coefficients of \( \lambda_{\alpha} \) and \( d_{\alpha} \) in Eq. (2) would be about 340 and 140 for the 1Mn steel, respectively. \( \alpha \) was strengthened due to solid solution strengthening with the addition of Si or Mn, as well as the refinement of θ particles and α grains. Consequently, the strength of the alloys with added Si or Mn is much higher than that of the 0.8C alloy, especially when the annealing temperature is high.

Recently, it was found that the dispersed θ is also important for improving the ductility (the uniform elongation) in ultrafine-grained ferrite alloys.\textsuperscript{29} The finer the particle, the larger the work hardening exponent and, thus, the better the \( E_a \). The refinement of θ particles by the addition of Mn or Si results in the significant increase in \( E_a \) at 923 K, com-
pared with the 0.8C alloy. The present result is in accordance with the above-mentioned result well (see Fig. 6).

For the case of cold rolling by 90% and annealing at 723 K for relatively shorter periods, the specimens showed a marked improvement in $E_u$ (5 to 7%) without a decrease in TS (1 900 to 1 700 MPa) and YS (1 750 to 1 450 MPa) in all the alloys with Mn or Si. Because such annealing at 723 K is in the initial stage of the spheroidization of $\theta$, the density of dislocations which are presumably piling up on the $\theta/\alpha$ interface should decrease causing a fair reduction of the remaining internal stress in the cold-rolled pearlite. When stress concentration is relaxed, it is expected that ductility is improved with respect to the as-cold-rolled case.

On the other hand, the heavy cold working could cause the dissolution of $\theta$. As a consequence, carbon concentration in $\alpha$ increases. During the annealing at 723 K, the carbon concentration in ferrite changes accompanied with the strain aging. Figure 10 shows the corresponding change of XRD peak positions of ferrite during annealing at 723 K. It is evident that the peaks are shifted to the right after annealing for 30 s with respect to the as-cold-rolled case, indicating that the C content in $\alpha$ decreases during annealing presumably by some carbide precipitation. The longer the holding time, the more apparent peak shift to right, and the more precipitation of carbide and perhaps stress relaxation in $\alpha$. After 120 s holding, further peak shift cannot be seen, implying that the carbon content in $\alpha$ reaches to the equilibrium one and internal stress is almost relaxed. As the interaction energy between interstitials and dislocations in $\alpha$ is larger than the binding energy between carbon and $\theta$, the heterogeneously distributed carbon atoms would be segregated to dislocations (or other defects) in $\alpha$. Thus, Cottrell atmospheres around dislocation lines are formed by carbon and $\theta$. Strain aging causes the C content in $\alpha$ to decrease, while its effects on the ductility is negligible.

(3) During the annealing at 923 K after cold rolling, the growth of $\theta$ is remarkably retarded and the strength is raised by the addition of Mn or Si. The addition of Si is effective for improving the ductility especially for higher strength. The combined addition of Mn and Si is more effective for improving the tensile properties of pearlitic alloys heavily cold-rolled and annealed at 923 K.

(4) For the low temperature (723 K)–short time annealing, TS and YS of alloys with added Mn and Si are little changed in comparison with the cold-rolled specimens, but the ductility is obviously improved. The optimal tensile properties in the alloys with Mn or Si are obtained after annealing at 723 K for 30 or 120 s.

5. Conclusions

Fully pearlitic Fe–0.8mass%C binary alloy, Fe–X–0.8mass%C ternary alloys (X: 1 or 2mass%Mn, 1 or 2 mass%Si) and an Fe–2mass%Mn–1mass%Si–0.8mass%C quaternary alloy were cold-rolled by various reductions between 40 and 90% and annealed at 723–923 K for different periods of time. By examining the microstructure and tensile properties, the following results were obtained:

(1) For the as-transformed specimens, the TS and YS are increased although the $E_u$ and $E_y$ hardly change with the addition of Mn or Si.

(2) As the rolling reduction increases, the strength of the cold-rolled specimens increases although the ductility remains nearly the same after the drastic decrease by 60% cold rolling. The addition of Mn and Si results in the increase in strength whereas its effects on the ductility is negligible.

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