1. Introduction

Pearlite steel is characterized by its high strength, large work hardening rate and excellent deformability owing to fine lamellar eutectoid structure of ferrite and cementite. Therefore, ultra high strength can be achieved by cold drawing and the drawn pearlite steel wire is applied to steel code, sawing wire, bridge cable etc. in which a high specific strength is required. Recently, further strengthening is expected for the steel code in terms of global environment conservation. Since yield strength and work hardening rate are enhanced with reducing the lamellar spacing, some methods to reduce the lamellar spacing have been adopted to obtain higher strength wires: (1) increasing carbon content, (2) lowering pearlite transformation temperature and (3) addition of alloy elements such as Cr.

On the other hand, it is known in Cu bearing steels that precipitation hardening can take place by aging treatment at around 800 K. In addition, Cu particles precipitate independently from cementite particles, hence this results in an effective strengthening of low carbon steel. If the Cu particles precipitate within the ferrite phase of pearlite structure, an additional strengthening should be expected in pearlite steel.

In this study, the effect of Cu addition on phase transformation, microstructure and mechanical properties in the eutectoid steel were investigated, and then the strengthening mechanism was discussed in connection with the strengthening of ferrite phase by Cu precipitation.

2. Experimental Procedure

Fe–0.8% C–Cu alloys containing Cu up to 2 mass% Cu were used in this study: Base-steel (free Cu), 1% Cu-steel and 2% Cu-steel. The ingots of 1.5 kg were produced by melting commercial eutectoid steel (SK5) and pure Cu in Ar gas, followed by casting into a metallic mold of 100 mm×50 mm×28 mm. Chemical compositions of the cast materials are listed in Table 1. These steels were hot-rolled to 10 mm thick plates at 1 273 K. Specimens cut from the hot-rolled plates were solution-treated at 1 123 K for 1.8 ks, directly put into another furnace controlled at a given temperature of 723 to 923 K to perform isothermal pearlite transformation, and then water-quenched after holding at the temperature for 0.005 to 1.8 ks.

| Cu | C | N | O | Si | Mn | P | S | Fe |
|----|---|---|---|----|----|---|---|----|
| Base-steel | 0.06 | 0.814 | 0.0026 | 0.0011 | 0.27 | 0.35 | 0.009 | 0.002 | bal. |
| 1% Cu-steel | 1.06 | 0.831 | 0.0043 | 0.0008 | 0.26 | 0.35 | 0.009 | 0.001 | bal. |
| 2% Cu-steel | 2.06 | 0.823 | 0.0041 | 0.0018 | 0.26 | 0.35 | 0.008 | 0.001 | bal. |
Microstructure was observed with an optical microscope, a scanning electron microscope (SEM) and a transmission electron microscope (TEM). Crystallographic characterization was also carried out by means of the electron back scattering diffraction (EBSD) method using a SEM. The data obtained by EBSD method was analyzed by the orientation imaging microscopy (OIM™) system. Tensile testing was carried out by using Instron type testing machine at an initial strain rate of $10^{-3}$/s for round-bar test pieces with the gauge dimension of $3 \text{ mm} \times 10 \text{ mm}$.

3. Results and Discussion

3.1. Behavior of Isothermal Phase Transformation in Cu Bearing Eutectoid Steel

Figure 1 represents optical micrographs showing the behavior of isothermal phase transformation at 923 K in Base-steel, 1% Cu-steel and 2% Cu-steel. The dark-etched region corresponds to pearlite formed through the decomposition of austenite. The volume fraction of pearlite gradually increases during the isothermal heat treatment, and then the phase transformation finally completes in all specimens. However, the rate of the transformation tends to be retarded by Cu addition. After the investigations at different treatment temperatures, T. T. T. diagrams were drawn as Fig. 2 for each steel. These diagrams clearly indicate that Cu addition retards isothermal pearlite transformation. The similar tendency was reported in previous studies on low carbon steels. For example, Ohtsuka et al.\(^7\) reported the retardation of ferritic transformation by Cu addition in 1.5%Mn–0.5%Si–0.15%C–1.5%Cu steel, and explained the mechanism on the basis of the dragging effect by Cu at the transformation interface between austenite and ferrite.

On the other hand, Fig. 3 shows the changes in hardness of specimens during the isothermal heat treatment after the completion of pearlite transformation at 823 K and 923 K in the Base-steel and 2% Cu-steel. In the Base steel, slight softening occurs after the completion of pearlite transformation. In the 2% Cu steel, the hardness gradually lowers during the 923 K heat treatment but, in contrast, age hard-
enning occurs at 823 K. This means that the precipitation of Cu has completed during pearlite transformation when the isothermal transformation temperature is high enough, but super-saturated ferrite could be formed through isothermal pearlite transformation when the temperature is lower than 900 K. At the temperature below 800 K, it was confirmed that bainitic transformation becomes dominant. In this study, the nose temperature of 823 and a higher temperature 923 K were applied for investigating the effect of Cu addition on pearlite structure.

3.2. Effect of Cu on Pearlite Structure

Pearlite in Fe–C alloys is characterized by lamellar structure composed of ferrite and cementite as schematically shown in Fig. 4. It is well known that the strength and work hardening rate of pearlite increases with reducing the lamellar spacing.8) On the other hand, Takahashi et al.9) reported that the ductility and toughness of pearlite are enhanced by refining blocks which were composed of several colonies that have the same crystallographic orientation for ferrite matrix. These two kinds of structural factors are important for discussing mechanical properties of pearlite steel. Figure 5 represents TEM images of the Base-steel and 2% Cu-steel isothermally heat-treated at 823 K and 923 K. Typical lamellar structure is observed in both steels. There is no significant effect of Cu addition on the morphology and thickness of the cementite plates. Figure 6 shows the lamellar spacing measured in specimens isothermally heat-treated at 823 K, 873 K and 923 K. The lamellar spacing tends to increase with rising isothermal heat treatment temperature, but does not depend on Cu content. On the other hand, block structure can be clearly observed by EBSP method in pearlite steel. Figure 7 represents orientation imaging micrographs showing the crystallographic orientation of ferrite. The grain boundaries with misorientation angle more than 15° are drawn by black lines. Each region surrounded by the black line roughly corresponds to a eutectoid block. It is also clear that Cu addition does not give a significant influence on the block size. Since both of

Fig. 3. Changes in hardness of Base-steel and 2% Cu-steel during isothermal heat treatment after pearlite transformation at 823 and 923 K.

Fig. 4. Schematic illustration showing pearlite structure.

Fig. 5. TEM images showing the lamellar structure of Base-steel and 2% Cu-steel just after pearlite transformation at 823 and 923 K.

Fig. 6. Effect of Cu addition on lamellar spacing of pearlite structure in Base-steel, 1% Cu-steel and 2% Cu-steel just after pearlite transformation at 823, 873 and 923 K.
lamellar spacing and block size generally become finer with an increase of the driving force for pearlite transformation, the above results suggest that Cu addition up to 2% does not affect the driving force too much.

In order to clarify the redistribution of Cu during pearlite transformation, Cu content in pearlite and in untransformed region was measured by means of EPMA analysis (Fig. 8). The EPMA line profile reveals that no long range redistribution has occurred between untransformed austenite and pearlite. On the other hand, short distance redistribution between ferrite and cementite was indirectly estimated from the chemical composition analysis of cementite extracted by iodine methanol method. The result of Table 2 demonstrates that most of Cu has been ejected from cementite phase. Since the volume fraction of cementite is 12 vol% for 0.8% C steel, the concentration of Cu in ferrite phase are calculated at approximately 2.3 mass% in the 2% Cu-steel. The solubility of Cu in ferrite phase is smaller than 0.4 mass% below 923 K, the excess Cu (1.9 mass% Cu) should precipitate within the ferrite phase. Figure 9 represents magnified TEM image and its trace showing a microstructure near (pearlite/austenite) interface in 2% Cu-steel isothermally heat-treated at 923 K. It should be noted that Cu particles can be observed in the ferrite area adjacent to the transformation interface. Chairungsri et al. has also reported that ε-Cu (fcc-Cu) particle precipitates on (pearlite/austenite) interface in hypereutectoid steel. These results indicate that Cu particles precipitate during pearlite transformation and not after the transformation. In this

![Table 2. Chemical analysis for cementite within eutectoid structure of 2% Cu-steel isothermally heat-treated at 823, 873 and 923 K.](image)

| Temperature (K) | Cu content (mass%) |
|----------------|--------------------|
| 923            | 0.003              |
| 873            | 0.003              |
| 823            | 0.004              |

**Table 2.**

Fig. 7. Crystallographic orientation imaging maps of Base-steel (a), 1% Cu-steel (b) and 2% Cu-steel (c) just after pearlitic transformation at 923 K.

Fig. 8. EPMA line analysis between untransformed austenite and pearlite in 2% Cu-steel isothermally heat-treated at 923 K. Solid triangles indicate (austenite/pearlite) interfaces.

Fig. 9. TEM image (a) and its trace (b) showing a microstructure near (pearlite/austenite) interface in 2% Cu steel isothermally heat-treated at 923 K.
case, the redistribution of Cu between ferrite and cementite should be realized by the interfacial diffusion along the transformation interface and this might be one of the reasons why pearlite transformation of the eutectoid steel has been retarded by Cu addition.

Assuming that the precipitation of Cu would not affect the interfacial diffusion, the time required for the redistribution of Cu is roughly estimated by the Eq. (1).

\[ x = (D\tau)^{1/2} \ [m] \] ..........................(1)

Where \( x \), \( t \) and \( D \) are the diffusion distance, the time and the diffusion coefficient, respectively. The activation energy for interfacial diffusion is generally believed to be a half of that for lattice diffusion, so that the interfacial diffusion coefficient of Cu, \( D_{Cu}^{Gb} \), is calculated with Eq. (2) using an activation energy for the lattice diffusion of Cu in austenite, 280 000 J/mol.

\[ D_{Cu}^{Gb} = 4.34 \times 10^{-5} \exp(-280 \text{,}000 / 2RT) \ [m^2/s] \] ...(2)

When the diffusion distance of Cu is given at a half of lamellar spacing; (200/2) nm, the time required for redistribution of Cu is estimated at approximately 2.0 \times 10^{-2} s at 923 K. On the other hand, the growth rate of pearlite interface has been reported at 5.0 \times 10^{-7} m/s. Therefore, the migration distance of pearlite interface during the time for redistribution of a Cu atom would be around 10 nm. Considering that the diameter of Cu particle is around 20 nm, there should be some interaction between the migration of pearlite interface and the redistribution and precipitation of Cu because of their kinetically competitive relation.

From the results obtained above, the behavior of Cu precipitation accompanied with pearlite transformation in Cu bearing eutectoid steel is schematically summarized in Fig. 10. The redistribution and precipitation of Cu continuously occur at the (ferrite/austenite) interface. This retards the pearlite transformation as well as strengthens the steel. In addition, if the pearlite transformation is undergone at a lower temperature, Cu atom could not sufficiently redistribute and precipitate on the (ferrite/austenite) interface. That would result in the precipitation within ferrite phase after the passage of (pearlite/austenite) interface and the occurrence of age hardening.

3.3 Effect of Cu Addition on Mechanical Properties of Pearlite Steel

Figure 11 shows nominal stress–nominal strain curves obtained by tensile testing for the Base-steel, 1% Cu-steel and 2% Cu-steel isothermally heat-treated at 823 K for 0.3 ks. This heat treatment condition corresponds to that for the maximum hardness of 2% Cu-steel with full pearlite structure (see Fig. 3). The Change in true stress and work hardening rate are also shown in Fig. 11(b) as a function of true strain. It is found that the strength of pearlite steels is significantly increased by the addition of Cu. In particular, the 2% Cu addition raises the yield strength by 250 MPa. On the other hand, the work hardening rate is not markedly affected by the Cu addition, and therefore, the uniform elongation is also unchanged despite the strengthening. This indicates that the Cu particles dispersed in ferrite phase is effective for preventing dislocation movement as well as enhancing dislocation accumulation. As for yield strength of pearlite steels \( (\sigma_y) \), the following equation is empirically established.

\[ \sigma_y = \sigma_0 + k S^{-1} \ [MPa] \] ..........................(3)

Where \( S \) is the lamellar spacing, \( \sigma_0 \) is the friction stress of ferrite and \( k \) is a constant. Based on this relation, the 0.2% proof stress of each specimen was plotted as a function of the inverse of its lamellar spacing as shown in Fig. 12. Each specimen keeps good liner relationship with the identical slope, which implies that the effect of lamellar spacing on yield strength is essentially not changed even when Cu is precipitated within ferrite phase. However, 2% Cu-steel ex-
proximistic yielding of the ferrite phase which is softer than the cementite phase. Therefore, under the assumption that the additional rule for strength is correct; the average increment could be calculated at around 330 MPa. This value agrees roughly with the experimental value of 250 to 330 MPa (see Fig. 12). Since Cu in eutectoid steel has a feature to be concentrated into ferrite and precipitate finely there, it is concluded that Cu is highly effective alloying element to strengthen pearlite steel.

4. Conclusions

Phase transformation behavior, microstructure and mechanical property were investigated in the eutectoid steel containing Cu up to 2 mass%. The results obtained are summarized as follows:

(1) The pearlite transformation proceeds with the short range redistribution of Cu atoms between ferrite and cementite through the interfacial diffusion at (pearlite/austenite) interface, although the long range redistribution between pearlite and untransformed austenite does not take place. This seems to be one of the reasons of the retardation of pearlite transformation by the Cu addition in eutectoid steel.

(2) There is no influence of the Cu addition on the lamellar spacing and block size of pearlite structure.

(3) The Cu precipitates at the ( ferrite/austenite) interfaces during pearlite transformation as well as within the ferrite phase after the transformation when the Cu content is larger than its solubility at the transformation temperature.

(4) The yield strength and tensile strength of the pearlite in Cu bearing eutectoid steel depends on not only lamellar spacing but also the dispersion of Cu particles precipitated in the ferrite phase. The 0.2% proof stress is given by the addition of precipitation strengthening in ferrite phase to the strength of Cu-free pearlite which has a linear relationship to the inverse of lamellar spacing.

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