Effect of Solute Copper on Yield Strength in Dislocation-strengthened Steels

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The effect of copper atoms in solid solution (solute Cu) on yield strength was investigated in dislocation-strengthened steels such as a martensitic steel and a work-hardened steel, which have high dislocation density. The yield strength of the martensitic steel increases with increasing content of the solute Cu. However, the increment of the yield strength by the solute Cu is smaller in the martensitic steel than in the ferritic steel. Dislocation density of the martensitic steel increases with increasing Cu content and the yield strength is also enhanced depending on the dislocation density. The increment of the yield strength can be reasonably explained by the dislocation strengthening mechanism based on the Bailey–Hirsch relationship. In the work-hardened ferritic steel, the solid solution strengthening by Cu is significant when the dislocation density is low, but it tends to disappear with increasing the dislocation density through cold-rolling. These are indicative of the facts that the yield strength of the dislocation-strengthened steel is determined by the dislocation strengthening and the contribution of the solute Cu on the yield strength disappears owing to high dislocation density.

KEY WORDS: Cu bearing steel; yield strength; solid solution strengthening; dislocation strengthening; strengthening mechanism; addition rule.

1. Introduction

In terms of the promotion of recycling steel scraps, one of tramp elements, *i.e.* Cu, has been tried to be utilized as an effective alloying element for steel in recent years. The Cu has ability to strengthen the steel through precipitation of fine Cu particles when the Cu bearing steel is air-cooled from austenitic phase after solution treatment¹⁾ or aged at dual-phase region after quenching.^{2,3)} A lot of studies in the Cu bearing steels have been concentrated on the precipitation behavior and strengthening,^{1–7)} and more over a Cu bearing steel strengthened by Cu-precipitation has been developed.^{8–10)} On the other hand, it is found that the solute Cu can improve mechanical properties of a ferritic steel. For example, authors have clarified the effect of the solute Cu on the mechanical properties of the ferritic steel, and reported that 1) the hardness has a linear square root relationship with Cu content and 2) the proportional constant of the hardness is Hv26.¹¹⁾ Hence, it could be expected that combination of the solid solution strengthening by Cu and the dislocation strengthening, obtained by cold-rolling, could be effective for further strengthening the steel.

However, an addition rule of the solid solution strengthening by Cu and the dislocation strengthening has not been clarified yet in the dislocation-strengthened steels such as the work-hardened ferritic steel or the martensitic steel. Since the steel contains high dislocation density, lattice

strain due to the solute Cu should be offset by lattice strain of the dislocations. Thus, it is thought that the solid solution strengthening by Cu could not be simply added to the dislocation strengthening in the steel because of its high dislocation density. In this study, the effect of the solute Cu on the yield strength was investigated in martensitic Fe–8mass%Ni–Cu alloys and ferritic Fe–Cu alloys. Then, the effect of the dislocation density on the solid solution strengthening by Cu was also clarified in the ferritic Fe–Cu alloys having various dislocation densities through cold-rolling.

2. Experimental Procedures

Ferritic Fe–Cu binary alloys and martensitic Fe–8mass% (%) Ni–Cu ternary alloys were used in this study. Chemical compositions of the steels are listed in **Table 1**. The ingots were produced with an induction furnace in a vacuum and then hot-rolled at 1 223 K. The martensitic Fe–8%Ni–Cu alloys were solution-treated at 1 273 K or 1 473 K for 1.8 to 3.6 ks, followed by water quenching and then subzero treated at 77 K for 1.8 ks in liquid nitrogen. The ferritic Fe–Cu alloys were cold-rolled at a reduction of 56%, annealed at 1 073 K or 1 123 K in a ferrite single-phase region for 1.8 ks in order to control the grain size through recrystallization to be about 100 μm . Furthermore, the recrystallized ferritic Fe–Cu alloys were cold-rolled at various reductions to introduce dislocations into the ferritic matrix. Mi-

Table 1. Chemical compositions of the steels used in this study (mass%).

		Ni	Cu	C	Si	Mn	Fe
Fe-8%Ni-Cu	8%Ni	8.02	<0.01	0.004	<0.01	0.15	bal.
	8%Ni-0.5%Cu	7.94	0.48	0.003	<0.01	0.15	bal.
	8%Ni-1%Cu	8.01	0.92	0.003	<0.01	0.21	bal.
	8%Ni-2%Cu	8.00	1.86	0.003	<0.01	0.13	bal.
	8%Ni-3%Cu	7.92	2.86	0.003	<0.01	0.14	bal.
Fe-Cu	pure iron	-	<0.01	0.008	<0.01	0.005	bal.
	0.5%Cu	-	0.49	0.009	<0.01	0.007	bal.
	1%Cu	-	1.00	0.007	<0.01	0.006	bal.
	1.5%Cu	-	1.40	0.003	0.02	0.17	bal.

others; P: 0.010, S: 0.010, N: 0.004

microstructures were observed with an optical microscope (OM) and a 200 kV transmission electron microscope (TEM). The ferritic Fe-Cu alloys and the martensitic Fe-8%Ni-Cu alloys were chemically etched for the OM observation with 3% nital and 3% picric acid solutions, respectively. For TEM observation, film materials were prepared by the twin-jet polishing method using a mixture of 10% perchloric acid and 90% acetic acid solutions. Grain size was determined by comparing the optical micrographs with the ASTM grain size standard. Tensile tests were carried out with an Instron-type testing machine at an initial strain rate of 10^{-3} s^{-1} . The martensitic Fe-8%Ni-Cu alloys and the as-annealed ferritic Fe-Cu alloys were machined to cylindrical test pieces of $\phi 3 \times 10 \text{ mm}$ gauge dimension, while the cold-rolled Fe-Cu alloys were done to plate test pieces with gauge length of 6 mm. Since the yield points can not apparently be obtained in all of the steels, the 0.2% proof stress is defined as the yield strength. Ms and Mf temperatures were measured using a dilatometer. The steels were machined to cylindrical test pieces of $\phi 3 \times 10 \text{ mm}$ gauge dimension. Then, the steels were heated at 2 K/s, followed by holding at 1273 K for 100 s and then cooled at 20 K/s. The temperatures of phase-transformation start and finish were measured and designated as Ms and Mf, respectively. Dislocation density and lattice parameter of matrix were evaluated by means of X-ray diffractometry. For measurement of the dislocation density, the X-ray diffraction peaks were separated into $K\alpha_1$ and $K\alpha_2$ components by the method of Rachinger,¹²⁾ and the crystallite size; D and the local strain; ϵ were estimated on the basis of the Hall method¹³⁾ as shown in Eq. (1).

$$\beta_t \left(\frac{\cos \theta}{\lambda} \right) = \frac{K}{D} + 2\epsilon \left(\frac{\sin \theta}{\lambda} \right) \quad \text{.....(1)}$$

where K is the Scherrer constant; 0.89, and β_t is the true Full Width at the Half Maximum height; FWHM of $K\alpha_1$ lines. At initial stage, the FWHM value obtained from the three planes (110), (211) and (220) of the bcc phase was used. The spread of the diffracted beams due to the instrument used was measured as the FWHM value; β_0 of $K\alpha_1$ lines of annealed pure iron samples as standard samples, and then corrected from the FWHM value; β_m of $K\alpha_1$ lines of the Fe-8%Ni-Cu alloys and the cold-rolled Fe-Cu alloys by using the following Eq. (2).¹⁴⁾

$$\beta_t^2 = \beta_m^2 - \beta_0^2 \quad \text{.....(2)}$$

Fig. 1. Change in Ms and Mf temperatures of Fe-8%Ni-Cu alloys as a function of Cu content.

Finally, the dislocation density; ρ calculated from strain broadening; ϵ is thus defined as the following Eq. (3).¹⁵⁾

$$\rho = \frac{14.4 \times \epsilon^2}{b^2} \quad \text{.....(3)}$$

where b is the Burgers vector; 0.25 nm.

3. Results and Discussion

3.1. Microstructure of As-quenched Fe-8%Ni-Cu Alloys

Figure 1 shows change in Ms and Mf temperatures of the Fe-8%Ni-Cu alloys, plotted as a function of Cu content. The steels were subjected to solution treatment at 1273 K for 100 s and cooling at 20 K/s. The Ms and Mf temperatures decrease with increasing Cu content and decrement of the temperatures is around 10 K/mass%. Since the Mf temperatures are sufficiently higher than ambient temperature in all of the steels, no austenitic phase should retain within the martensitic matrix in the Fe-8%Ni-Cu alloys used in this study. **Figure 2** represents OM and TEM images of as-quenched specimens of Fe-8%Ni alloy (a) (d), Fe-8%Ni-1%Cu alloy (b) (e) and Fe-8%Ni-3%Cu alloy (c) (f). The as-quenched Fe-8%Ni-Cu alloys exhibit a typical lath-martensitic single structure composed of martensite-packet, -block and -lath structures. There is no significant difference in the morphology of the lath-martensitic structure, because prior-austenite grain sizes were controlled to be around $200 \mu\text{m}$ in all of the steels. Moreover, TEM observation and measurement of lattice parameter of martensite using X-ray diffractometry suggest that alloying elements such as C, Cu and Ni were in super-saturated solid solution. **Figure 3** shows relation between Cu content and the dislocation density in the Fe-8%Ni-Cu alloys (hereafter simply described as “martensitic Cu steel”). The dislocation densities of the martensitic Cu steels are around $3 \times 10^{15} \text{ m}^{-2}$. The dislocation density increases with increasing Cu content, and no noticeable difference was found in the increase in the dislocation density. The increase in the dislocation density of the martensitic Cu steels is almost the same as that of martensitic Fe-9%Cr-Cu alloys,¹⁶⁾ and thought to be due to the decrement

Fig. 2. Optical and TEM micrographs of as-quenched specimens of Fe-8%Ni alloy (a) (d), Fe-8%Ni-1%Cu alloy (b) (e) and Fe-8%Ni-3%Cu alloy (c) (f).

Fig. 3. Relation between Cu content and dislocation density in Fe-8%Ni-Cu alloys.

of the Ms temperature caused by Cu addition. The decrement of the Ms temperature leads to the increase in volume expansion on the martensitic transformation and the retardation of self tempering after the phase transformation.

3.2. Yield Strength of the Martensitic Cu Steels

It is known that the strengthening mechanism in the martensitic steel is very complicated and the yield strength has a strong dependence on some strengthening factors such as the solid solution strengthening by alloying elements, the dislocation strengthening and the grain refinement strengthening. Norström *et al.* have proposed that the yield strength of the martensitic steel; σ_y is derived from

the summation of the strengthening mechanisms, as shown in the following equation.^{17,18)}

$$\sigma_y = \sigma_0 + \sigma_i + K_y D^{-1/2} + K_s d^{-1/2} + \beta G b [\rho_0 + k(\%C)]^{1/2} \quad (4)$$

where σ_0 , K_y , K_s , β and k are constants, σ_i is the solid solution strengthening of alloying elements, D is the size of packet, d is the lath width, G is the shear modulus and $[\%C]$ is the amount of carbon (C). Since all of the steels have very small amount of C, *i.e.* around 0.004%, and besides, there is no noticeable difference in size of lath and packet of martensite, the yield strength could be explained by the summation of the dislocation strengthening and the solid solution strengthening by Cu as shown in the following equation^{†1};

$$\sigma_y = \sigma'_0 + \sigma_i + \beta G b \rho^{1/2} \quad (5)$$

where σ'_0 is a constant containing packet size (D) and lath width (d). The authors have reported that the solid solution strengthening is in proportion to square root of concentration of atomic solution in the ferritic Fe-Cu alloy, thus the 0.2% proof stress in the martensitic Cu steel can be plotted as a function of square root of atomic percentage of alloying element (solid circle) as shown in **Fig. 4**. The 0.2% proof stress of the ferritic Fe-Cu alloys (hereafter simply described as “ferritic Cu steels”) are also plotted in this figure to show the influence of the solid solution strengthening by Cu (open square).¹⁹⁾ The 0.2% proof stresses of both steels increase linearly with square root of atomic percentage of Cu ($[Cu]^{1/2}$). However, there is a marked difference

^{†1} Since the solid solution strengthening by Cu in Fe-Cu alloy is around 10% or more of the dislocation strengthening, the contribution of the solid solution strengthening by Cu is not negligibly small in discussing the addition rule of both strengthening mechanisms.

Fig. 4. Relation between Cu content and the 0.2% proof stress in the martensitic Cu steels and the ferritic Cu steels.

Fig. 5. Relation between Cu content and the measured increment of 0.2% proof stress in martensitic Cu steels (solid circle). The contributions of the dislocation strengthening (grey square) and the solid solution strengthening (dashed line), and besides, the summation of both strengthening mechanisms (open square) are also shown in the figure.

in the increment of the 0.2% proof stress between the steels: the yield stress of the martensitic Cu steel is gradually increased with increasing Cu content at a rate of 17 MPa/(at%)^{1/2}, although that of the ferritic Cu steel is done at a much larger rate of 57 MPa/(at%)^{1/2}. This means that the addition rule, Eq. (4), is not suited to the case of the martensitic Cu steel and the influence of the solid solution strengthening by Cu remarkably decreases. **Figure 5** shows comparison among the experimentally measured increment of the 0.2% proof stress of the martensitic Cu steel (solid circle), the contribution of the solid solution strengthening by Cu to the 0.2% proof stress (data of the ferritic Cu steel as shown in Fig. 4; dashed line), the contribution of the dislocation strengthening (grey square) and the summation of both strengthening mechanisms (open square). The contribution of the dislocation strengthening is estimated by put-

Fig. 6. Relation between the measured 0.2% proof stress and the calculated 0.2% proof stress in the martensitic Cu steels.

ting the dislocation densities of the martensitic Cu steels (Fig. 3) into the Bailey–Hirsch equation²⁰⁾ shown below;

$$\Delta\sigma_y = \beta G b (\rho^{1/2} - \rho_0^{1/2}) \dots \dots \dots (6)$$

where β is a constant; 0.5,²¹⁾ ρ and ρ_0 are the dislocation density of the martensitic Cu steels and the dislocation density of the martensitic 0% Cu steel, respectively. The increment of the measured 0.2% proof stress is extremely smaller than the summation of both strengthening mechanisms. Moreover, the increment of the measured 0.2% proof stress can not reach the value of the contribution of the solid solution strengthening. Conversely, it should be stated that the increment of the measured 0.2% proof stress is close to the contribution of the dislocation strengthening, although the contribution of the dislocation strengthening has some errors. **Figure 6** shows relation between the measured 0.2% proof stress and the calculated 0.2% proof stress by only considering the dislocation strengthening. The calculated 0.2% proof stress was estimated using the Bailey–Hirsch equation, obtained from relation between the 0.2% proof stresses and measured dislocation densities of cold-rolled ferritic steels, as shown in Eq. (7).²¹⁾

$$\sigma_y = 0.1 + 0.5 G b \rho^{1/2} \dots \dots \dots (7)$$

It is found that the measured 0.2% proof stresses approximately equal to the calculated values. Although the calculated 0.2% proof stresses are slightly smaller than the measured values in the martensitic 0% Cu steel and the martensitic 1% Cu steel, therefore, it can be concluded that the increment of the yield strength of the martensitic Cu steel is mainly dominated by the increment of the dislocation strengthening due to Cu addition. On the other hand, the solid solution strengthening by Cu has small influence on the increase in the yield strength of the martensitic Cu steel.

3.3. Microstructures of Work-hardened Fe–Cu Alloys

To evaluate the effect of the dislocation density on the contribution of the solid solution strengthening by Cu, the dislocation densities of the ferritic Cu steels were varied by the cold-rolling, and then tensile tests were carried out for

Fig. 7. Optical micrographs showing recrystallized specimens of the pure iron (a) and the ferritic 1% Cu steel (b).

Fig. 8. Change in dislocation density of the pure iron and the ferritic 1% Cu steel as a function of reduction of thickness by cold-rolling.

the steels. **Figure 7** represents OM images of the as-annealed steels (CR 0%): pure iron (a) and ferritic 1% Cu steel (b). Both of the steels exhibit ferritic structure and the mean grain sizes of the pure iron and the ferritic 1% Cu steel were 110 μm and 90 μm , respectively. Although there is a slight difference in grain size, it is thought that grain refinement strengthening and microstructural development due to cold-rolling are almost the same in the steels. The TEM observation and measurement of lattice parameter of ferrite using the X-ray diffractometry indicate that Cu atoms were in solid solution. **Figure 8** shows the change in the dislocation density of the pure iron and the ferritic 1% Cu steel, plotted as a function of reduction of thickness. Although the dislocation densities of the ferritic 1% Cu steel are slightly higher than those of the pure iron at any reduction, increments in the dislocation densities are similar in both steels; that is, they abruptly increase about 10^{14} m^{-2} up to reduction of 10%, and level off at about 10^{15} m^{-2} after cold-rolling at reductions of 70% or more. The saturated dislocation densities are in the same order as those of the martensitic steels. **Figure 9** displays TEM images of the 70% cold-rolled steels; the pure iron (a) and the ferritic 1% Cu steel (b). TEM images reveal that typical stratified structures were formed and no significant difference is observed in substructures of the steels after cold-rolling.

Fig. 9. TEM images of the pure iron (a) and the ferritic 1% Cu steel (b), cold-rolled up to 70% in reduction of thickness.

Fig. 10. Relation between Cu content and the 0.2% proof stress of the cold-rolled ferritic Cu steels.

3.4. Contribution of the Solid Solution Strengthening by Cu to the Yield Strength in the Work-hardened Ferritic Steels

Figure 10 shows relation between Cu content and the 0.2% proof stress of the cold-rolled ferritic Cu steels at different reductions. The 0.2% proof stresses increase linearly with square root of atomic percentage of Cu in all of the steels. The increment of the 0.2% proof stress in the as-annealed steels can be regarded as the solid solution strengthening by Cu because the dislocation density is sufficiently low. It is found that the increment of the 0.2% proof stress due to Cu addition becomes smaller as the reduction is enlarged, especially when the reduction is above 70%. For instance, a slope in the as-annealed steel is 57 $\text{MPa}/(\text{at.}\%)^{1/2}$, however, it decreases to 31 and 30 $\text{MPa}/(\text{at.}\%)^{1/2}$ in the 70% and 90% cold-rolled steels, respectively. In order to show the relation between the dislocation density and the contribution of the solid solution strengthening, the difference in the yield stresses between the ferritic 1% Cu steel and the pure iron, *i.e.* the solid solution strengthening by 1% Cu, was plotted as a function of dislo-

Fig. 11. Change in the contribution of the solid solution strengthening as a function of dislocation density.

cation density of the ferritic 1% Cu steel as shown in **Figure 11**. The contribution of the solid solution strengthening by Cu decreases with increasing the dislocation density and almost disappears when the dislocation density becomes more than $1.8 \times 10^{15} \text{ m}^{-2}$. This is indicative of the fact that the dislocation density has great influence on the solid solution strengthening by Cu. Moreover, it is found that the contribution of the solid solution strengthening by Cu in the cold-rolled ferritic Cu steel corresponds to that in the martensitic Cu steel having high dislocation density of around $3.0 \times 10^{15} \text{ m}^{-2}$. Although above-mentioned results have not been clarified yet, it is thought to be due to next-stated reasons: an interaction between a moving dislocation and other dislocations is predominant than an interaction between the moving dislocation and the solute Cu atoms,^{†2} or elastic stress field due to the solute Cu atom is offset by that due to the dislocation.

The high strength steels for practical use are often strengthened by the combination of the strengthening mechanisms *e.g.* the grain refinement strengthening, the dispersion strengthening, the solid solution strengthening and the dislocation strengthening. However, the summation of multiple strengthening mechanisms could not be applied for further strengthening as shown in this study. Therefore, in order to establish a guideline for strengthening the steel, it is important to clarify the contribution of each of the strengthening mechanisms when they are combined.

4. Conclusions

The effect of the solute Cu on the yield strength of the dislocation-strengthened steel such as the martensitic steel and the work-hardened ferritic steel was discussed, and the following findings were obtained.

(1) The yield strength of the martensitic steel increases with increasing solute Cu content. However, the increment of the yield strength is smaller in the martensitic steel than in the ferritic steel whose strength is dominated by the solid solution strengthening by Cu. The increase in the yield strength of the martensitic steel is not due to the solid solution strengthening, but mainly dominated by the dislocation strengthening.

(2) In the dislocation-strengthened steel, the addition rule of the solid solution strengthening and the dislocation strengthening is applied when the influence of the dislocation strengthening is small. However, the contribution of the solid solution strengthening by Cu to the yield strength deteriorates and disappears when the dislocation density increases to be 10^{15} m^{-2} or over.

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^{†2} In terms of the strengthening mechanism based on the theory of dislocation, the strength of a material is reflected by the stress, needed for a moving dislocation to become bowing and passing through obstacles. The bowing angles are 90° and less than 2° in the dislocation strengthening and the solid solution strengthening, respectively. Thus, it is thought that the bow of the dislocation strengthening is predominant that of the solid solution strengthening.