Effects of Copper Addition on Mechanical Properties of 0.15C–1.5Mn–1.5Si TRIP-aided Multiphase Cold-rolled Steel Sheets

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The main emphasis of the present study was placed on understanding the effects of copper addition on the mechanical properties and microstructures of low-carbon TRIP-aided multiphase cold-rolled steel sheets. These steel sheets were intercritically annealed at 790–800°C, and isothermally treated at 430°C for various times. Tensile tests were conducted, and the changes of retained austenite volume fractions as a function of tensile strain were measured using X-ray diffraction. The copper addition increased the volume fraction of retained austenite, although it did not affect the stability. However, the hardness of ferrite in Cu containing steel was higher than that of Cu free steel. As a result, the strain-induced transformation of retained austenite was sustained up to the high strain region, thereby leading to the simultaneous enhancement of strength and ductility. These findings indicated that when copper, a representative tramp element, was positively utilized in cold-rolled steel sheets, excellent mechanical properties could be achieved.

KEY WORDS: TRIP; multiphase steels; Cu effect; mechanical properties; retained austenite.

1. Introduction

As one of the high-strength steel sheets of new concept, C–Si–Mn TRIP-aided steel sheet has been introduced for the last two decades,^{1,2)} since it showed both high strength and high ductility by the transformation induced plasticity (TRIP) effect arising from the martensitic transformation of retained austenite.^{1–4)} Particularly, the C–Si–Mn TRIP-aided steel, whose basic structure is composed of ferrite, bainite, and retained austenite, has a simple alloying composition, and is accepted as one with excellent environmental consciousness.

Meanwhile, recycling of steel scraps has become a very important concern from the standpoints of efficient use of energy and resources as well as environment preservation. When recycling steel scraps, some elements called tramp elements are retained and accumulated inside steels since they are not completely eliminated even during the refining process.⁵⁾ In particular, copper, a representative tramp element, has been known to have harmful effects such as hot embrittlement, high-temperature surface cracking, and poor cold-forging performance.^{6,7)} Studies to develop copper-added high-strength steel products have been actively pursued because of the recent reports of visible enhancement in mechanical properties of TRIP-aided cold-rolled steel sheets when added with copper.^{8–10)} It can possibly harden ferrite grains due to additional solid solution hardening or precipitation of fine ϵ -copper particles.^{8,10)} Active development of copper-added high-strength TRIP-aided steel products to replace the existing ones would contribute to solving the problem of high burden for environmental preservation as well as to the conservation and efficient use of resources

achieved from scrap recycling. Despite the generally accepted knowledge of the excellent mechanical properties of copper containing TRIP-aided cold-rolled steel sheets, studies on actual evaluation of its mechanical properties are still insufficient and hardly studied. In the present study, low-carbon TRIP-aided cold-rolled steel sheets, to which copper was added, were fabricated, and the effects of copper on the tensile properties and microstructure were evaluated in detail.

2. Experimental Procedure

2.1. Fabrication and Heat Treatment of Cold-rolled Steel Sheets

Two kinds of steel ingots, named as ‘ECO-0’ and ‘ECO-Cu’, were fabricated by vacuum induction melting and aluminum-killing. The ECO-0 steel was the base steel having 0.15C–1.5Si–1.5Mn composition, to which 0.5 wt% of copper was added to fabricate the ECO-Cu steel, and their detailed chemical compositions are shown in **Table 1**. Steel ingots were rough-rolled into a 25-mm-thick slab. The slab was homogenized at 1250°C for 2 h, hot-rolled into a 3-mm-thick sheet. The hot-rolled steel sheet was pickled by a 10% HCl solution of 80°C, and was cold-rolled into 0.8-

Table 1. Chemical compositions of cold-rolled steel sheets used. (wt%)

Steel	C	Si	Mn	Cu	P	S	Al	Fe
ECO-0	0.16	1.42	1.47	-	0.0016	0.0036	0.046	Bal.
ECO-Cu	0.14	1.49	1.51	0.51	0.0012	0.0034	0.040	Bal.

Fig. 1. Optical micrographs of the ECO-0 and ECO-Cu steel sheets isothermally heat-treated at 430°C for 3 and 10 min (etched by 10% sodium metabisulfite solution).

mm-thick sheets. Two kinds of steel sheets were intercritically annealed for 5 min at 790–800°C, where the volume fraction ratio of ferrite and austenite is 50 : 50, isothermally treated at the martensite start (Ms) temperature of 430°C for 1–20 min, and then air-cooled.^{4,9,11} Intercritical annealing and isothermal treatment were conducted using salt baths.

2.2. Microstructural Observation and Tensile Test

The steel sheets were etched in a 10% sodium metabisulfite solution ($\text{Na}_2\text{S}_2\text{O}_3 \cdot \text{H}_2\text{O}$ 10 g + H_2O 100 ml),^{4,11} and observed by an optical microscope. Room-temperature tensile tests were conducted on plate-type specimens (longitudinal direction) with a gage length of 25 mm and a gage width of 6.3 mm at a crosshead speed of 2.5 mm/min.

2.3. Measurement of Volume Fraction and Stability of Retained Austenite

Volume fraction of retained austenite was measured using an X-ray diffractometer. Mo-K α characteristic ray was used, and the volume fraction of retained austenite, V_γ , was calculated from the integrated intensity of ferrite and austenite peaks using the following Eq. (1),^{12,13}

$$V_\gamma = 1.4I_\gamma / (I_\gamma + 1.4I_\alpha) \quad \text{.....(1)}$$

where I_γ and I_α are the average integrated intensity obtained at 220 $_\gamma$ and 311 $_\gamma$ peaks and that obtained at 211 $_\alpha$ peak, respectively. The average lattice constant, a_0 , of retained austenite was calculated from the following Eq. (2),¹⁴

$$a_0(\text{\AA}) = 3.578 + 0.033C \quad (\text{wt\%}) \quad \text{.....(2)}$$

The strain-induced martensitic transformation rate formula, which was recently suggested by Chung¹⁵ and Chang

et al.,¹⁶ was used to evaluate the stability of retained austenite.

$$\log[\ln f_s / (f_s - f)] = \log \kappa + m \log \varepsilon \quad \text{.....(3)}$$

Here, f_s and f refer to the saturated martensite volume fraction and the martensite volume fraction transformed during deformation, respectively, while ε and m refer to the true strain and the deformation mode coefficient, respectively. κ is defined to be the stability coefficient of retained austenite. The higher κ indicates the lower stability of retained austenite and the faster martensitic transformation.

3. Results

3.1. Microstructure

Figures 1(a) and 1(b) are optical micrographs of the two cold-rolled steel sheets. When etched by a sodium metabisulfite solution, it is easy to tell the phases, since gray parts are ferrites, black ones are bainites and martensites, and white ones are retained austenites.^{4,11} In both of the steels, retained austenites are relatively homogeneously distributed throughout the microstructure, and are mostly connected with nearby ferrites and bainites. However, the volume fraction of retained austenite increases to about 15% in the ECO-Cu steel from about 11% in the ECO-0 steel, indicating that the addition of copper has a beneficial effect in formation of retained austenite. Increasing the isothermal holding time slightly reduces the amount of retained austenite in both steels.

3.2. Tensile Properties

Figure 2 shows changes of mechanical properties and volume fractions of retained austenite in two steels as a function of isothermal holding time. As the isothermal

Fig. 2. Mechanical properties and retained austenite volume fractions of the ECO-0 and ECO-Cu steel sheets isothermally heat-treated at 430°C.

holding time increases, tensile strength of the ECO-0 and ECO-Cu steels slightly decreases from 770 MPa and 825 MPa, respectively, although yield strength increases remarkably. However, the yield strength was maintained almost constantly after isothermal holding for 5 min. The ECO-Cu steel shows higher tensile strength than the ECO-0 steel by 50–80 MPa. Despite its high strengths, it also shows higher elongation. Thus, the ECO-Cu steel shows better overall tensile properties than the ECO-0 steel. This might be associated with its higher retained austenite volume fraction of about 15%, compared with 11% in the ECO-0 steel. These results indicate that copper can be positively applied to increase the volume fraction of retained austenite and to improve the mechanical properties.

3.3. Stability of Retained Austenite

Figure 3 shows the change of retained austenite volume

Fig. 3. Retained austenite volume fraction changes of the ECO-0 and ECO-Cu steel sheets isothermally heat-treated at 430°C for 3 min as a function of true strain.

Fig. 4. Martensite transformation ratios of the ECO-0 and ECO-Cu steel sheets isothermally heat-treated at 430°C for 3 min as a function of true strain.

fraction in the steel sheets isothermally heat-treated at 430°C for 3 min as a function of true strain. In the ECO-0 steel, the volume fraction of retained austenite is gradually decreasing, while in the ECO-Cu steel, it decreases gradually at the beginning of deformation and drastically decreases in the range of true strain 0.08–0.1, and again gradually decreases. Figure 4 presents the volume fraction of transformed martensite normalized from the changes in retained austenite volume fraction as a function of true strain. In both steels, martensitic transformation persists up to the high strain region before fracture. In the region where the true strain is below 0.08, the martensitic transformation ratio of the ECO-0 steel is slightly higher than that of the ECO-Cu steel. As the strain increases, the transformation ratio of the ECO-Cu steel abruptly jumps far higher than that of the ECO-0 steel. The final transformation ratio is about 80% in the ECO-0 steel, whereas it reaches almost up to 90% in the ECO-Cu steel.

The relationship between $\log \varepsilon$ and $\log[\ln f_s/(f_s - f)]$ was interpreted by applying Eq. (3) to the results of Fig. 3, and is graphed in Fig. 5. The slope of straight lines, m , in Fig. 5 and Eq. (3), being the deformation mode coefficient, equals 1.0 in C–Si–Mn TRIP-aided steels, which is known to have specific values depending on alloying compositions.¹⁶⁾ The stability coefficient of retained austenite obtained from the

Fig. 5. Relationships between $\log[\ln(f_s/(f_s-f))]$ and $\log(\epsilon)$ for the ECO-0 and ECO-Cu steel sheets isothermally heat-treated at 430°C for 3 min.

straight line of Fig. 4, κ , does not vary much in the ECO-0 and ECO-Cu steels, being 10.4 and 9.6, respectively. This indicates that the effect of the copper addition on the stability of retained austenite is negligible.

4. Discussion

4.1. Effects of Copper Addition on Microstructure

According to the data of Figs. 1 and 2, the copper addition causes the increased retained austenite volume fraction. Copper, as an austenite stabilizer, plays a role in increasing the stability of retained austenite formed during intercritical annealing. Thus, the ECO-Cu steel can have the higher retained austenite volume fraction than the ECO-0 steel because of the effect of austenite stabilization by copper. This higher volume fraction of retained austenite results in the improvement of tensile strength, elongation, and the balance of strength-ductility. In the meantime, the ECO-Cu steel shows higher yield strength than the ECO-0 steel, implying that some other mechanism is working in increasing yield strength, since the effect of increasing the retained austenite volume fraction is negligible in the increase of yield strength in TRIP-aided multiphase steels.^{1,3,4,15)}

It is generally known that the copper addition leads to the effect of precipitation strengthening as fine ϵ -copper particles are precipitated in ferrite grains.¹⁷⁾ In this study, the micro-hardness of ferrite grain of both steels isothermally aged for 3 min at 430°C was measured using nano-indentation tester with the load of 1 g. The hardness value of the ECO-0 was Hv 200 and that of the ECO-Cu was Hv 243. In order to investigate the additional strengthening effect of the copper addition in the ECO-Cu steel, its microstructure was observed by a transmission electron microscope, but copper-related precipitates were not found. According to previous reports,^{18,19)} the precipitation strengthening effect in the case of the 1.0% copper addition is visible only when aged for several tens of minutes in the temperature range from 400 to 700°C. However, it is hard to expect ϵ -copper precipitation in the present study, because (1) the copper addition in the ECO-Cu steel is only 0.5%, (2) the isothermal treatment temperature is somewhat low at 430°C, and

(3) the treatment time is short for 3 min. Thus, the higher hardness of ferrite grain of the ECO-Cu steel might be from the solid solution hardening effect or clustering effect of copper in ferrite grains. The superior mechanical properties of the ECO-Cu steel than the ECO-0 steel are attributed to the strengthening of ferrite grains as well as the TRIP effect.

4.2. Strain-induced Transformation Behavior of Retained Austenite

According to previous studies on TRIP-aided multiphase steels, it is generally recognized that the stability and volume fraction of retained austenite are the most crucial factors affecting the strain-induced transformation and the TRIP behavior. The stability of retained austenite is determined by the carbon concentration inside austenite, which is largely affected by the chemical composition and the heat-treatment time and temperature. Because the ECO-0 and ECO-Cu steels have almost identical chemical compositions except the addition of copper in the latter and because the intercritical annealing and isothermal treatment conditions are the same, the difference in the austenite stability could be associated with the addition of copper. Although the carbon concentration in austenite measured by X-ray diffraction is 1.08% in the ECO-0 steel and 0.91% in the ECO-Cu steel, their stability coefficients are in the same level as shown in Fig. 4. Thus, it is found that the carbon concentration in austenite is not the only factor which determines the stability of austenite. The above findings mean that the strengthening of ferrite grains owing to the copper addition affects the strain-induced transformation behavior of retained austenite, *i.e.* transformation rate.

Recently, Jacques *et al.*²⁰⁾ studied the strain-induced martensite transformation behavior after diverse heat treatment on TRIP-aided multiphase steels. An interesting result from their finding is that strain-induced transformation rate of specimen having more carbon concentration in retained austenite is higher than that of specimen having less carbon concentration in retained austenite. That is, the strain-induced transformation of retained austenite is influenced not only by the carbon concentration of retained austenite but also by the properties of the other phases like ferrite and/or thermal martensite. One of the possible mechanism is that the solid-solution strengthening effect due to copper in this study leads to a higher stress partition toward the ferrite matrix, and to bring about a shielding effect, reducing the rate of stress increase in austenite.

The transformation rate of retained austenite during plastic straining is expressed as the following Eq. (4).²⁰⁾

$$\ln[(V_\gamma - V_{\gamma u})/(V_{\gamma 0} - V_{\gamma u})] = \ln k - n\epsilon \dots \dots \dots (4)$$

Here, $V_{\gamma u}$ is the volume fraction of retained austenite remaining untransformed at saturated true uniform strain (2.4% in the ECO-0, and 2.6% in the ECO-Cu), $V_{\gamma 0}$ is the initial volume fraction of retained austenite, and ϵ and k are true strain and a constant, respectively. In the Eq. (4), n is a constant determining the transformation rate, indicating that the larger the n , the higher the transformation rate. Figure 6 can be obtained by applying the Eq. (4) into Fig. 3, and the slope of the line in the figure is n value. The n values of the ECO-0 and ECO-Cu steels are 11.5 and 14.4,

Fig. 6. Relationships between $\ln[(V_\gamma - V_{\gamma u})/(V_{\gamma 0} - V_{\gamma u})]$ and ε for the ECO-0 and ECO-Cu steel sheets isothermally heat-treated at 430°C for 3 min.

respectively, meaning that the transformation rate of the ECO-Cu is slightly higher than that of the ECO-0 steel. Considering the relation between the carbon concentration of retained austenite and n value from the result of Jacques *et al.*,²⁰⁾ n value increases 10–15 as the carbon concentration of retained austenite decreases about 0.1%. In this study, however, the increase of n value is only 3 despite the fact that the carbon concentration of retained austenite of the ECO-Cu steel is less than that of the ECO-0 steel by 0.17%. This results from the reduction of transformation rate by the strengthening of ferrite grains owing to the copper addition. Therefore, the higher strength and better ductility ECO-Cu steel can be explained from the higher volume fraction of retained austenite and similar stability in spite of its lower carbon concentration in retained austenite.

From the above findings, it was confirmed that a small amount of copper addition to the C–Mn–Si TRIP-aided multiphase steels enhanced the yield and tensile strength, and elongation as well as high volume fraction of stable retained austenite. As mentioned above, the stability and volume fraction of retained austenite are the most crucial factors affecting the strain-induced transformation and the TRIP behavior. For developing low carbon TRIP-aided multiphase steels having limitations in increasing the volume fraction and stability of retained austenite, the addition of copper can be a new direction of alloy design for coping with the limitations.

5. Conclusions

In the present study, the effects of the copper addition on the mechanical properties and microstructure of low carbon cold-rolled steel sheets were investigated, and the conclusions are summarized as follows:

(1) When copper was added to low-carbon TRIP-aided cold-rolled steel sheets, the retained austenite volume fraction increased, and ferrite grains were strengthened. As a result, the strain-induced transformation of retained austenite was sustained up to the high strain region, thereby leading to the simultaneous enhancement of strength and uniform strain.

(2) The copper addition increased the volume fraction of retained austenite, but did not affect the stability. The stability of retained austenite is influenced not only by the carbon concentration but also the properties of surrounding phases.

(3) With the copper addition, high strength, ductility, and formability could be simultaneously achieved from the increased volume fraction of retained austenite and strengthening of ferrite grains. When copper, a representative tramp element, was positively utilized, cold-rolled steel sheets with excellent mechanical properties could be fabricated.

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