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Effect of Copper on the Grain Size and Tensile Strength of Ultra-Low Carbon Steel

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Abstract

The paper presents a study on the grain size and tensile strength of annealed ultra-low carbon (ULC) steel containing 0.008 wt.% carbon (C) and various contents of copper (Cu). The annealing temperature was predetermined at 700, 800, and 900 °C with the same holding time of 15 minutes and a slow cooling rate. The microstructural result showed that the ferritic grain size of the steel increased with the annealing temperature, e.g. increased to 60 and 65 μm when the temperature raised to 900 °C for the 0.112 and 0.285 wt.% Cu steel, respectively. This phenomenon was attributed to the recrystallization of the steel during the annealing process. The coarser grains resulted in a decrease in the tensile strength of the steel despite that the tensile strength of the steel was found to improve with the increased Cu content. The low tensile strengths and good elongation remained in the ULC steel, for instance, the ultimate tensile strength stayed in the range of 234-350 MPa and the elongation remained in the range of 22-35 % dependent on the annealed temperature, and the Cu content. The results show that the content of Cu less than 0.3 wt.% did not have a negative effect on the tensile strength of the studied steel, but caused a deteriorated elongation of the steels annealed at 900 °C.

Keywords: ULC steel, copper in steel, grain size, recrystallization, tensile strength.

1. Introduction

Tramp elements in steel are those that remain after melting scrap and refining. It is very difficult for steelmakers to eliminate these elements so increased contents are expected in the future as steels need to be in the next recycling cycle. Consequently, they are considered detrimental to the steel's mechanical properties. This becomes a severe problem when such elements are present in high concentrations. Among tramp elements in steel scrap, copper (Cu) is known as causing some harmful effects including hot shortness that is the reason for loss of ductility and surface defects of the mild steel due to the preferential oxidation phenomenon on the Cu-rich surficial area [1, 2]. Since Cu has a melting temperature of about 1083 °C, such steel is usually sensitive to cracking during hot deformation in a temperature range of 1050-1200 °C. In this condition, the grain boundaries are usually adversely affected leading to the separation of grains by shear thereby deteriorating the steel's mechanical properties. Thus, the use of scrap for the production of steel has been related to a high incidence of transverse cracking during continuous casting. Another bad effect of Cu on steel is weldability which often causes a tendency to cold cracking. Because of its deterioration, the Cu content is required to be lower than a certain level in steel, causing a decreased ratio of the using scrap in the input materials. In general, removing Cu from scrap is possible, but in practical production, some impurities including Cu in the melt of steel scrap are difficult to remove due to the efficiency aspect. Instead of that, it is required to spend much effort to separate the low Cu-bearing scrap to provide for melting in the electric arc furnace (EAF) or blowing oxygen furnace (BOF).

However, the presence of Cu to a certain percentage has been remarked as a positive effect on the microstructure and mechanical properties of carbon steel. Since Cu has the ability to increase the corrosion resistance and strength of steel through precipitation hardening, it has been utilized as an effective alloying element for steel in recent years in terms of the promotion of recycling steel scraps. By adding 0.20 to 0.35 wt.% Cu, corrosion resistant property of the structural steel has been improved [3]. The addition of Cu from 0.25 to 0.5 wt.% into carbon steel and low alloyed steel improves significantly corrosion resistance in the atmosphere; these steels are known as weather-resistant steel [4]. A lot of studies in Cu-bearing steel have been carried out to clarify the precipitation behavior and strengthening mechanism, and moreover, Cu-bearing steel strengthened by Cu-precipitation has been developed. For example, Syarif *et al.* strengthened the Cu-bearing steel by air-cooling from the austenitic phase after solution treatment or aging at a dual-phase region after quenching [5]. Ray *et al.* performed an experiment to compensate for the lower strength of high-strength low alloy (HSLA) steel via the addition of a proper content of Cu into the steel [6]. According to Banadkouki *et*

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al., Cu-bearing HSLA steel has similarly been developed into a commercial grade for many steel producers [7]. Such HSLA steel is considered to have a good balance of strength and other mechanical properties such as ductility, toughness, fatigue resistance, and workability by forming, welding, and machining. Meiler *et al.* reported on the development of Precipitation-Hardenable-Ferritic-Pearlitic (PHFP) steel for energy-efficient and distortion-reduced production of cold-formed, high-strength structural components [8]. According to the Fe-Cu phase diagram, Cu has a relatively high solubility in austenite but is almost insoluble in ferrite. Hence, Cu precipitation is expected to take place in Cu-bearing steels in spite of that the precipitation of Cu in steels with relatively low Cu contents is still debatable.

In combination with Cu additions, low carbon content is essential for attaining the desired effects, and many research works have been carried out to clarify the benefits of the alloyed Cu via hot rolling or heat treatment to make further gains in the quality of the Cu-containing steel. The demands for steel with excellent formability from the automotive industry have accelerated the progress in the steelmaking process, leading to the development of ultra-low carbon (ULC) steel containing carbon less than 0.01 wt.% [9, 10]. On the other hand, it has been found that the solute Cu can improve the mechanical properties of ferritic steel such as ULC steel. It could be expected that a combination of the solid solution strengthening by Cu and the dislocation strengthening, obtained by deformation, could be effective for further strengthening the steel. Although a small ratio of the scrap has been used to produce ULC steel in the BOF steelmaking route, the Cu content of the product may reach the level of 0.3 wt.% if the scrap has not been sorted carefully. It can be acknowledged that a few research works have been done to investigate the mechanical properties of Cu-containing ULC steel [4, 10]. Therefore, this paper focuses on the effect of a small Cu content on the microstructure and tensile strength of the annealed ULC steel.

2. Materials and Method

It is important to note that the microstructure of steel plays a crucial role in determining its properties. To achieve the desired properties in steel, it is necessary to carefully control both its composition and processing route. One way to enhance the mechanical properties of steel is through grain refinement, which can be achieved through the annealing process. The time and temperature of the annealing process must be carefully determined to achieve the desired grain size. The main experimental steps included melting the steel sample, the deformation, and heat treatment in accordance with the practical production. In this research, the steel samples were melted at Pohang University of Science and Technology (POSTECH, Rep. of Korea) using an induction furnace (Fig. 1) with an argon atmosphere.

Fig. 1. The induction furnace used for melting.

For the purpose of strengthening the ULC steel, some alloying elements were added in a predetermined range. Since the mechanical properties of the steel have been known to depend on the compositions, deformation, and heat treatment, the alloying elements, such as Si and Mn, which were added to compensate for the softening effect of ULC content, contribute to the strengthening by solid solution hardening. Mn has an important role in steel due to improving steel in terms of its hot workability, steel without Mn has a trend to be brittle at high temperatures [6, 9, 10].

Fig. 2. Image of the as-casted plate in this study.

The used raw materials consisted of graphite powder and high-purity metals such as electrolyzed iron (Fe), manganese (Mn), and copper (Cu) with the calculated ratios. After being completely melted in an alumina crucible, the liquid steel was kept at 1600 °C for 10 minutes for homogenization and then cooled down to room temperature. Fig. 2 is the image of the steel plate with a diameter of 40 mm and a thickness of 10 mm.

The chemical compositions of the two steel samples were analyzed using optical emission spectroscopy (Metal LAB 75/80J MVU-GNR), as given in Table 1.

Table 1. Chemical compositions of the steels (wt.%).

	C	Si	Mn	Cu	Fe
M-1	0.008	0.186	0.475	0.112	Bal.
M-2	0.008	0.154	0.464	0.285	Bal.

The steel plate was hot-forged in the temperature range of 1150-900 °C, then slowly cooled down to room temperature so that it remained good ductility for cold-rolling to the sheet with 1 mm thickness. After that, the steel sheet was cut with a wire electric discharge machine to prepare the specimens for the tensile test and microstructural observation. Dimensions of the tensile specimen were prepared according to the standard TCVN 197:2002, as seen in Fig. 3.

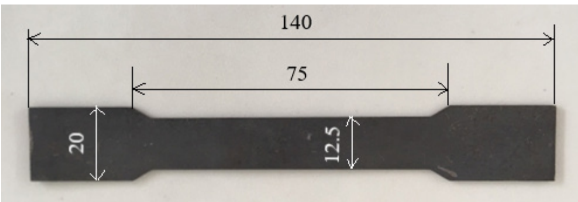
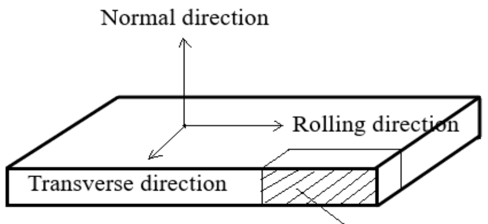
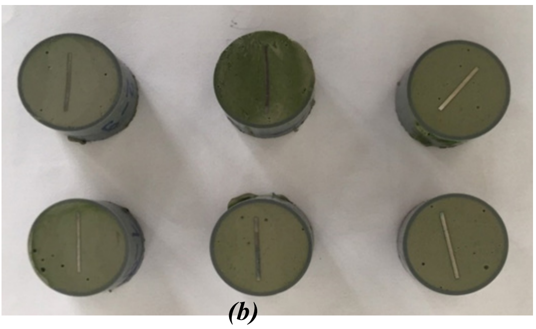


Fig. 3. Dimensions of the specimen for the tensile test (unit: mm).



(a)



(b)

Fig. 4. Cutting position (a) and specimens for the microstructural observation (b).

Similar to the heat treatment of cold rolled coil (CRC) in the industry, the annealing step is usually performed in the range of 700-900 °C to remove the residual stress and improve the ductility of the steel. Thus, the specimens were heated up to 700, 800, and 900 °C, hold for 15 minutes, and slowly cooled down to room temperature naturally together with the furnace (in ambient air). The tensile test was carried out on the machine (INTRON) using the strain rate of 10^{-2} mm/s.

Annealed specimens were cut longitudinally in the rolling direction (Fig. 4a), mounted in the epoxy (Fig. 4b), ground, polished, and etched with 2 % nital-solution for microstructural examination by optical microscopy (Axioviert 25A). The grain size of the steel was defined as the average diameter which was measured by the linear intercept approach over the optical micrograph. Several of the measurements have been done to get the final result.

3. Results and Discussions

The analyzed result of the steels in Table 1 showed that the compositions stayed at the predetermined values. The content of C, Si, and Mn was almost the same in both steel samples symbolized as M-1 and M-2. The alloyed Mn increases strength and toughness after rolling by lowering the austenite decomposition temperature during cooling to give ferritic grain refinement and a reduction in grain size [11]. Similar to Mn, Si is found in all steel grades; however, its content is usually lower than that of Mn; but still increases the strength and hardness of steel [6, 11]. The difference between these two samples was in the content of Cu which was 0.112 and 0.285 wt.%. This resulted from the careful preparation of the input materials and melting in the argon atmosphere.

Fig. 5 shows optical micrographs of the annealed steels, in which the recrystallized microstructure is seen to be homogeneous across the thickness of the sheet. It is noteworthy that one of the strengthening effects must be done by grain refinement controlled through the annealing process, so the annealing parameters are considered very important. This is completely consistent with the microstructural findings when the annealing temperature was 700, 800, and 900 °C. The ferrite grains appeared equiaxed in shape, and the annealing temperature changed the size. Small grains were found to embed in large ones for the steel annealed at 800 and 900 °C. Clearly, the annealing temperature has affected the grain size of the steel through the occurrence of the recrystallization phenomenon by which deformed grains were replaced by new grains that nucleated and grew until the original grains were entirely consumed. Recrystallization may occur in a discontinuous way where distinct new grains form and grow, or in a continuous way where the microstructure gradually evolves into a recrystallized microstructure. During the annealing time, various thermally activated processes may occur, resulting in more and larger equiaxed grains forming but some small grains still stayed beside large ones when the steel was kept at a high temperature for a longer time [4]. Therefore, recrystallization is usually accompanied by a reduction in the strength and hardness of steel and a simultaneous increase in ductility.

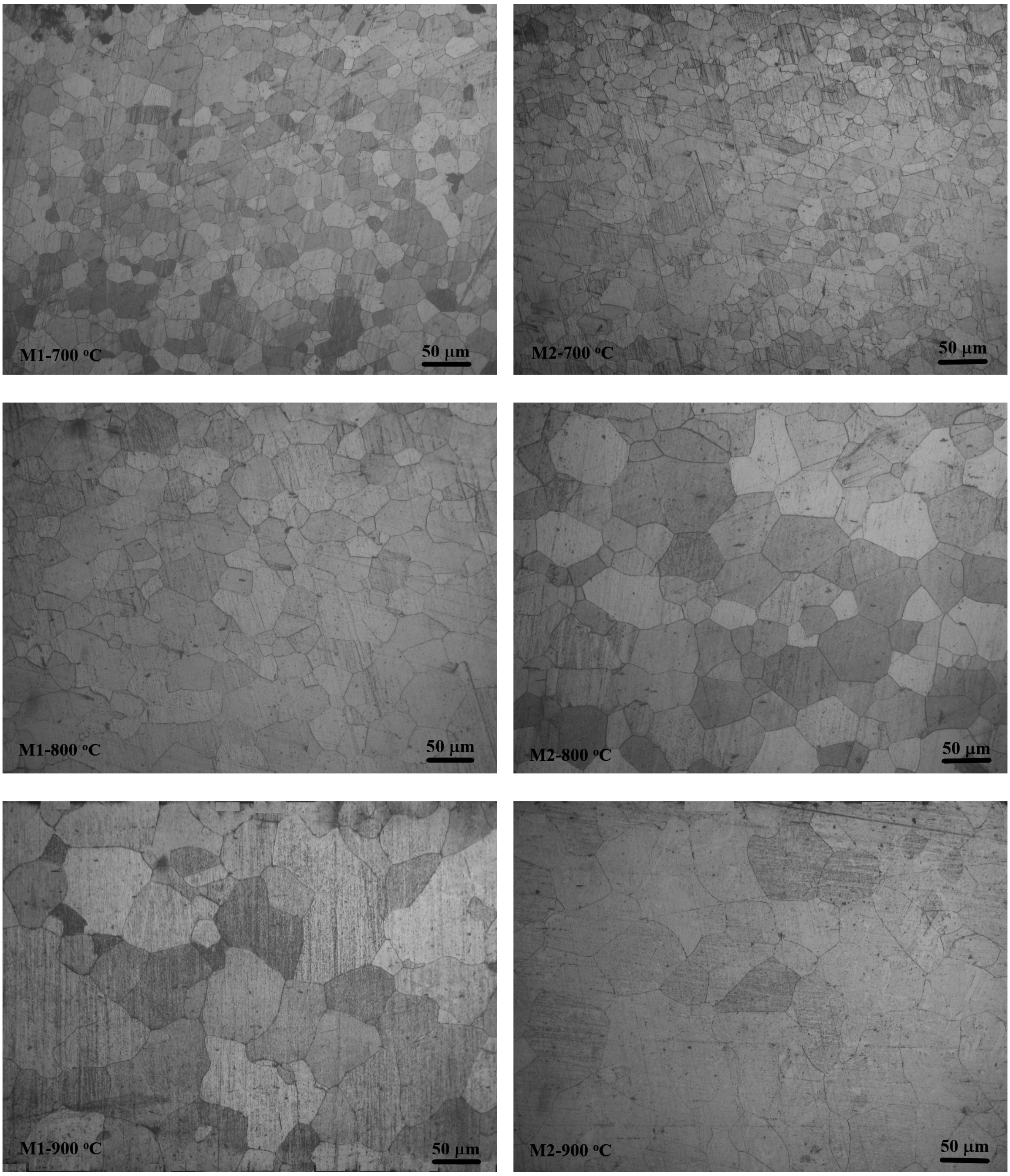


Fig. 5. Microstructures of the annealed steels.

The effect of annealed temperature on the grain size of the steel is shown in Fig. 6, where the grain size has changed from 25 to 60 µm for the steel M-1 and 30 to 65 µm for the steel M-2 when the annealing temperature has increased from 700 to 900 °C, respectively. This finding is in agreement that recrystallization not only releases much larger amounts of stored energy but new, larger grains are formed by the combination of the nucleation of stressed grains and the joining of several grains to form larger ones [4, 9]. Despite that, there are several factors that affect the rate of recrystallization for a given temperature, and the annealing steel must be decided and carefully controlled in practical production. The mechanical properties of steels are strongly connected to the annealed microstructure that generally brings a good hardness or tensile strength with sufficient ductility. The obtained finer grain microstructure of 700 °C-annealed steel must have enhanced the mechanical properties of the steel obviously. In addition, alloying can lead to the solution which can further influence the mechanical properties of the steels. As a result, the strength of the steel M-2 has been improved by adding Cu. In the steelmaking industry, the hot rolled steel that stays in the austenitic region can be directly quenched by water spraying to obtain the martensitic phase and fine grains, resulting in adequate mechanical properties. Thus, further study on the effect of cooling rate must be carried out.

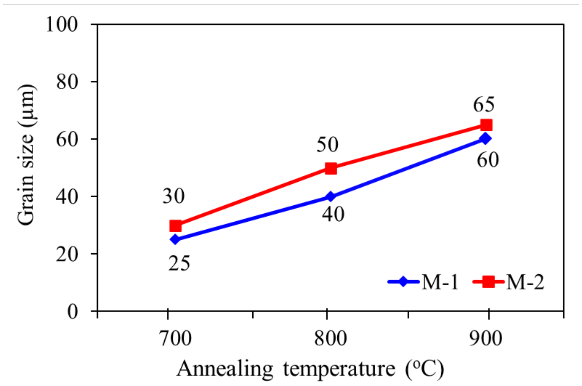


Fig. 6. Variation of the grain size with the annealing temperature.

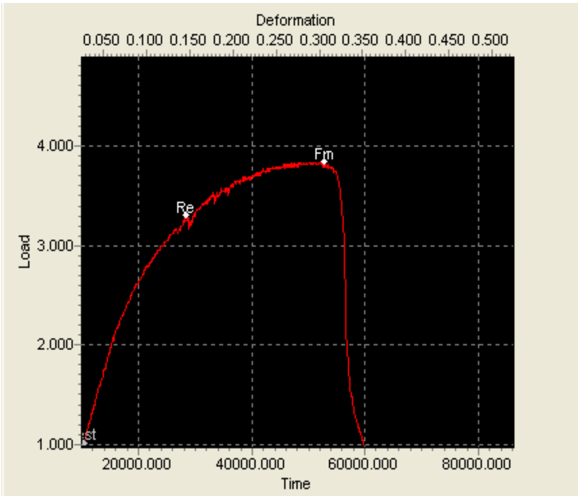


Fig. 7. The stress-strain curve of steel M1 annealed at a temperature of 700 °C.

Fig. 7 shows a typical stress-strain curve for the annealed steel, of which the total elongation is high value, i. e. the ductility is good for this type of ULC steel. The calculated results of the tensile tests including ultimate tensile strength (UTS), yield strength (YS), and elongation (EL) of the present steels are given in Table 2, and plotted in Fig. 8. It is seen that the UTS and YS of both the steels are quite low, for instance, 234-350 MPa in UTS and 160-252 MPa in YS dependent on the annealed temperature and the Cu content. The fact that the strengths decreased with the increased annealing temperature is completely consistent with the microstructural observation of the steel annealed at an increased temperature from 700 to 900 °C. The study found that, in the case of ULC steel containing Cu, this tramp element did not have a negative effect on the mechanical properties. The study showed that by annealing the steel at 700 °C, a balance of strength and ductility in the Cu-containing steel can be attained.

Table 2. Result of the tensile tests.

Steel M-1			
	700 °C	800 °C	900 °C
YS (MPa)	212	169	160
UTS (MPa)	316	285	234
EL (%)	35	30	22

Steel M-2			
	700 °C	800 °C	900 °C
YS (MPa)	252	241	189
UTS (MPa)	350	303	261
EL (%)	34	30	22

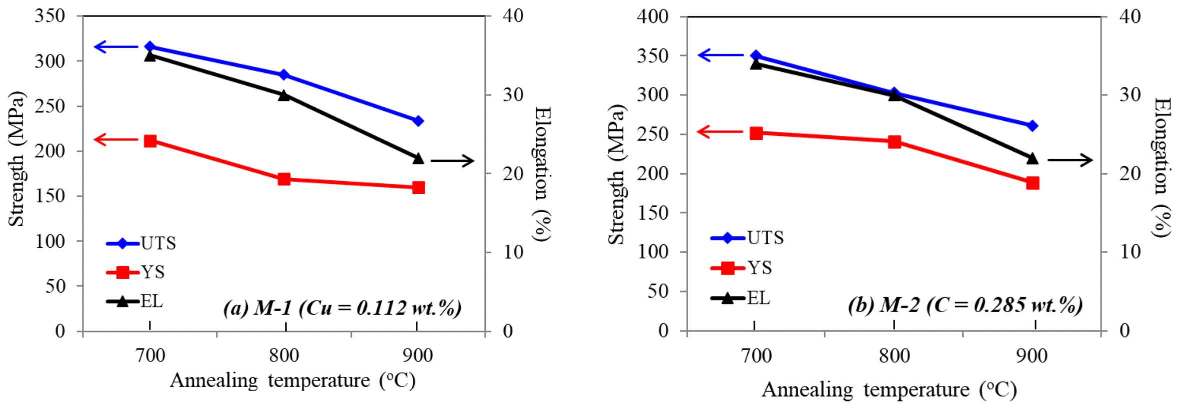


Fig. 8. Tensile test results of the steel samples.
(a) Steel sample M-1 (C = 0.112 wt.%), (b) Steel sample M-2 (C = 0.285 wt.%)

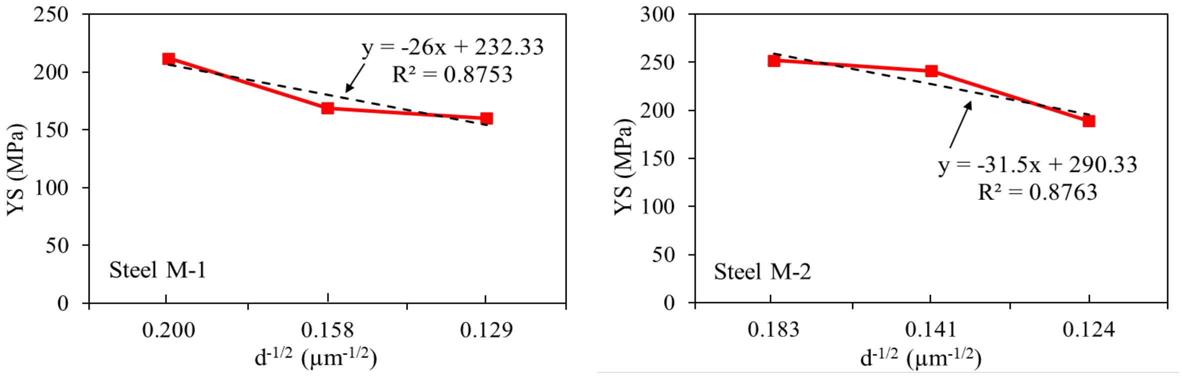


Fig. 9. Relationship of the strength and the grain size of the steel.

During the annealing process, two phenomena occurred: removal of residual stress caused by deformation and recrystallization [4, 5]. Thus, both recrystallization and removal of the residual stress have been expected to occur when the steels were annealed in this study, resulting in the strength has been decreased for the steel annealed at a higher temperature. Low strength and moderate ductility were attributed to the small amount of strengthening elements such as Si and Mn in the steel. Therefore, this Mn-Si alloying ULC steel is expected to fulfill the requirement for this type of steel which is usually applied in stamped products.

The combination of mechanical properties and microstructure of the steels suggests that the steel with recrystallized microstructure had a high ductility and low strength, meanwhile, the steel with higher Cu content (i.e. M-2) had the same ductility and a little higher strength in comparison with the steel M-1. It showed that the steel containing Cu obtained a better compromise of strength and ductility. This is essential for the application of ULC steel in agreement with Ray *et al.* who concluded that HSLA steel was more attractive when Cu was alloyed in an appropriate amount for precipitation hardening by the formation of Cu-rich particles during an aging treatment [6]. Evenly, Meiler *et al.* proposed a technology for the production of screws based on the precipitation-hardening effect of Cu for increasing strength by aging while avoiding the final quenching of steel with high Cu content [8]. A better result could be obtained; the strength and ductility of steels alloyed with Cu were at a high level in case of low C content, the addition of nickel (Ni), and also prior grain refinement during controlled rolling.

Concerning the dependence of yield strength on microstructural parameters, the Hall-Petch relationship (1) is usually used [9]:

$$\sigma_y = \sigma_o + k_y d^{-0.5} \quad (1)$$

where σ_o is the internal stress, d is the ferrite grain size, and k_y is a constant. On the other hand, the term σ_o includes the contribution from friction stress, solid solution effect, strengthening from precipitation, and dislocation hardening. The variation of strength (YS) with the grain size is plotted in Fig. 9, in which values of σ_o and k_y were approximately estimated based on the experimental results and (1). The change in the strength was in good consistency with the microstructural evolution (i.e. grain size) and also indicated the effect of annealing temperature. This result was in the agreement with the strengths that appeared in Table 2, as other studies confirmed that the steel with smaller grains gained higher tensile strength [2, 10]. Similar findings were remarked in the study in which a refined microstructure resulted in a good combination of strength and toughness [6]. As shown in Fig. 9, the value of σ_o was calculated as 232 and 290MPa for steel M-1 and steel M-2, respectively. This means that the internal stress of steel M-2 is higher than that of steel M-1 in spite of that both steel samples have been processed in the same procedure. In this case, the compositions must be the reason for the difference in the internal stress of these steels. Once the content of elements such as C, Mn, and Si was almost the same in both steel M-1 and M-2, the Cu content must have a certain influence on the mechanical properties of the steel.

Several semi-empirical correlations have been published to quantify the strength of low-C steels. One accepted expression to calculate the lower yield stress is given in the following equation, including the contribution of substitutional solute elements (Mn, Si, and Cu), and grain size [11]:

$$YS = 62.6 + 26.1\times(\text{wt.\% Mn}) + 60.2\times(\text{wt.\% Si}) + 212.9\times(\text{wt.\% Cu}) + 19.7\times d^{-0.5} \quad (2)$$

(d is the grain size in mm).

The difference between calculated YS and measured values, as given in Table 3, shows that this equation can be used to estimate the YS which can be controlled through the following parameters as chemical compositions and grain size of the steel.

Clearly, the difference between them becomes larger when the grain size is larger.

Table 3. The calculated and measured yield strength of both the steels.

Steel	Annealing temp. (°C)	*d* (mm)	YS_{Cal} (MPa)	YS_{Meas} (MPa)
M-1	700	0.025	235	212
	800	0.040	209	169
	900	0.060	190	160
M-2	700	0.030	269	252
	800	0.050	233	241
	900	0.065	222	189

Since Cu does not interact with C, the two elements are essentially immiscible. Therefore, all Cu in mild steel is dissolved or precipitated in ferrite, resulting in a slight hardening effect. It has not been fully recognized that along with the improved corrosion resistance, evenly to date, the precipitation of Cu can make a significant contribution to the mechanical properties of steel [12]. Some literature has clarified the effect of the solute Cu on the mechanical properties of ferritic steel and reported that hardness has a relationship with Cu content [5]. Research shows that additional strengthening occurs as a result of the precipitation of fine particles enriched in Cu after fast cooling. In addition, Cu is known to have the ability to strengthen the steel through the precipitation of fine Cu particles in the Cu-bearing steel [5, 8]. This steel has been developed to use for hot stamping high-strength parts without additional heat treatment; however, steels containing high Cu content (e.g. more than 1 wt.%), in contrast to steels with a lower content or without the presence of Cu after annealing, demonstrate deteriorated strength [12]. The increase in the YS of the present steel was not due to the solid solution strengthening elements such as Mn and Si, but also Cu. However, the increment of the internal stress (σ_o) which resulted in the improvement of the tensile strength was dominated by the Cu presence in the steel.

4. Conclusion

The effect of low Cu content in ULC steel has been investigated. Experimental melt, deformation, and annealing were carried out for the steel with 0.008 wt.% C and various contents of Cu (0.112 and 0.285 wt.%). The effect of the Cu content and the annealing temperature on the grain size and the tensile strength of the steel was discussed, and the following findings were obtained.

1) The microstructure of the steel included only the ferritic phase. A homogeneous microstructure has been found across the thickness of the steel sheet.

2) The grain size was increased with the annealing temperature from 25 to 60 µm for the 0.112 wt.% Cu-bearing steel or from 30 to 65 µm for the 0.285 wt.% Cu-bearing steel when the temperature increased from 700 to 900 °C. The coarser microstructure was attributed to the higher content of Cu in the present steel.

3) The tensile strength of the steel increased with the higher content of Cu, resulting in the solid solution strengthening. UTS and YS exhibited an increase in values as Cu content increased from 0.112 to 0.285 wt.%. For the steel annealed at 700 °C, UTS increased from 316 to 315 MPa, and YS increased from 212 to 252 MPa when the Cu content was changed from 0.112 to 0.285 wt.%. However, the tensile strength of both steel samples deteriorated in the case of the higher annealing temperature.

4) The scrap sorting combined with the adoption of an efficient annealing method would be useful to increase the recycled ratio of Cu-containing scrap in the production of ULC steel. The Cu content of steel products less than 0.3 wt.% could guarantee their mechanical properties.

References

[1] H. S. Jin, B. Mishra, Minimization of copper contamination in steel scrap. In Energy Technology 2020: Recycling, Carbon Dioxide Management, and Other Technologies. The Minerals, Metals & Materials Series. Springer, pp. 357-364. https://doi.org/10.1007/978-3-030-36830-2_34.

[2] O. I. Sekunowo, S. I. Durowaye, O. P. Gbenebor, Effect of copper on microstructure and mechanical properties of construction steel, Int. J. Chem. Nucl. Metall. Mater. Eng., vol. 8, no. 8, 2014, pp. 785-789.

[3] S. K. De, S. Srikanth, A. K. Bhakat, A. Saxena, B. K. Jha, Copper bearing steels from SAIL and its application, Int. J. Metall. Eng., vol. 5, no. 1, 1-8, 2016. https://doi.org/10.5923/j.ijmee.20160501.01

[4] P. Sellamuthu, P. Hodgson, N. Stanford, Effect of copper on microstructure, recrystallization and precipitation kinetics in strip cast low carbon steel, Mater. Res. Express, vol 6, no 12, ID article 1265j5, 2020. https://doi.org/10.1088/2053-1591/ab7310

[5] J. Syarif, K. Nakashima, T. Tsuchiyama and S. Takaki, Effect of solute copper on yield strength in dislocation-strengthen steels, ISIJ Int., vol. 47, no. 2, pp. 340-345, 2007. https://doi.org/10.2355/isijinternational.47.340

[6] P. K. Ray, R. Ganguly, A. Panda, Optimization of mechanical properties of an HSLA-100 steel through control of heat treatment variables, Mater. Sci. Eng. A, vol. 346, no. 1-2, pp. 122-131, 2003. https://doi.org/10.1016/S0921-5093(02)00526-9

[7] S. S. G. Banadkouki, D. P. Dune, Formation of ferritic products during continuous cooling of Cu-bearing HSLA steel, ISIJ Int., vol. 46, no. 5, pp. 759-768, 2006.

https://doi.org/10.2355/isijinternational.46.759

[8] S. Meiler, F. Hoffmann, H. Schwich, R. Kawalla, W. Bleck, U. Prahl, Copper-alloyed precipitation-hardenable-ferritic-pearlitic steel for energy-efficient and distortion-reduced production of cold-formed, high-strength structural components, Steel Res. Int., vol. 90, no. 6, Article ID 1800432, 2019. https://doi.org/10.1002/srin.201800432.

[9] A. H. Bui, H. Le, Strength and microstructure of cold-rolled IF steel, Acta Metall. Slovaca, vol. 22, no. 1, pp. 35-43, 2016. https://doi.org/10.12776/ams.v22i1.690

[10] A. S. Ghorabaei, M. Nili-Ahmadabadi, Effect of prior austenite grain size and phase transformation temperature on bainitic ferrite formation in multi-constituent microstructures of a strong ultra-low-carbon steel, Mater. Sci. Eng. A, vol. 815, Article ID 141300, 2021. https://doi.org/j.msea.2021.141300

[11] P. D. Hodgson, R. K. Gibbs, A mathematical model to predict the mechanical properties of hot rolled C-Mn and microalloyed steels, ISIJ Int., vol. 32, no. 12, pp. 1329-1338, 1992. https://doi.org/10.2355/isijinternational.32.1329

[12] P. Salvetr, A. Gokhman, Z. Novy, P. Motycka, J. Kotous, Effect of 1.5 wt% copper addition and various contents of silicon on mechanical properties of 1.7102 medium carbon steel, Materials (Basel), vol. 14, no. 18, 2021, ID article 5244. https://doi.org/10.3390/ma14185244