Effect of heat treatment on the microstructure and yield strength of a cold-rolled enameling steel

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Abstract. The mechanisms of yield strength reduction of a cold-rolled enameling steel after enamel-fire annealing at 760°C by air cooling, and the effect of the tempering process on the microstructure and yield strength, are studied by combining experiments and thermodynamic calculations. The results show that after heat treatment at 760°C and air cooling, the lump phase, enriched with the element carbon, appears along the ferrite grain boundaries, which leads to yield strength reduction. After tempering at 200°C~400°C, the lump phase disappears gradually and is transformed to lamellar pearlite as the tempering temperature increases, resulting in the yield strength increasing.

1. Introduction

Enameling steels, produced by continuous casting and hot-rolling processes, and then subject to enamel-fire annealing (EFA), are used in industries that require chemical, corrosion, and weather resistance, and where colour or appearance is important [1]. The mechanical properties of enameling steels are not only impacted by casting, but also by the subsequent EFA process. When used for thin-walled pressure vessels, high yield strengths are crucial for safety [2]. However, during the EFA process that consists of heat treating in the range of 750~900°C, the yield strengths of the enameling steels decrease, requiring sufficient steel thicknesses to meet the safety requirements and the associated added expense. In an effort to reduce these added expenses, studies have been carried out to investigate the mechanisms of yield strength reduction during the EFA. Jiang et al. [3, 4] studied the strengthening mechanisms of both the hot-rolled and cold-rolled enameling steels by establishing empirical equations to relate the microstructure and yield strength. The results show that grain refinement strengthening and solid solution strengthening are the main strengthening mechanisms. The yield strength reduction results primarily from an increase in grain size and a decrease in dislocation density. By comparing the effects of different strengthening mechanisms, Mao et al. [5] reported that the precipitation hardening of nanometer TiC particles has the greatest contribution to the yield strength increase of a hot-rolled steel. Isasti et al. [6] observed that the addition of the element Mo to Nb-bearing steels provides a refinement of the precipitates and enhances the contribution of precipitate strengthening. The grain size contribution is found to be the most important strengthening factor, followed by dislocation density and precipitation.

In this work, a cold-rolled enameling steel produced by thin-slab continuous casting are exposed to various heat treatment processes to simulate the EFA process used in industry. The microstructures
and yield strengths of the enameling steel after different heat treatment processes were studied by combining experiments and thermodynamic calculations.

2. Experiment
A cold-rolled enameling steel was investigated in the present work. The chemical composition is given in table 1. The EFA was simulated by heat treating the samples with a size of 200×80×1.2 mm in a box type furnace. The samples were isothermally heated at 760°C for 5 min, and then air cooled (~5°C/s) or sand cooled (~2°C/s) to room temperature. The samples air cooled were then subjected to a tempering process in the temperature range of 200°C~400°C for 20 min.

| C   | Mn | Si | S   | P   | N   | Al | Cu | Cr | Mo | Nb | Ti | Fe   |
|-----|----|----|-----|-----|-----|----|----|----|----|----|----|------|
| 0.07| 1.22| 0.43| 0.001| 0.051| 0.006| 0.038| 0.1 | 0.04| 0.01| 0.002| 0.021| bal. |

The tensile specimens were prepared according to the standard for sheet tensile specimens (ASTM A370-05). Tensile tests were performed at a crosshead speed of 6 mm per min with a CMT5105 tensile machine. The microstructures were observed with a XL30 scanning electron microscope (SEM). Transmission electron microscopy analysis was performed on thin foils with a TECNAI G2 20 transmission electron microscope (TEM). The thin foils were prepared by mechanically thinning to 50 μm, and then perforated by twin-jet electropolishing.

The thermodynamic calculations of the equilibrium phases and element solubilities were performed using Pandat that is a phase equilibrium calculation software of multi-component alloys [7].

3. Results and discussion
3.1. Microstructure and yield strength
Figure 1 shows the SEM images of the samples as rolled and after isothermal heating at 760°C for 5 min and then quenching. As shown, the as rolled microstructure is ferrite and free cementite. In the quenched microstructure, free cementite nearly vanishes, and small amounts of martensite appear at the ferrite grain boundaries. The martensite shown in figure 1 (b) represents the morphology of austenite before quenching.

![Figure 1](image1.png)

Figure 1. SEM images of the samples (a) as rolled and (b) after isothermal heating at 760°C for 5 min and then quenching to retain the austenite morphology.

Figure 2 shows the SEM images of the samples after isothermal heating at 760°C for 5 min and then sand cooled or air cooled to room temperature. It is seen that the main differences between the two microstructures are the amount and features of the phases distributed at the ferrite grain boundaries. In the microstructure of the sand cooled sample, there are small amounts of pearlite and lump phase at the ferrite grain boundaries (figure 2 (a)). However, in the case of the air cooled sample, nearly no pearlite appears, and the amount of lump phase is higher than in the sand cooled sample as
shown in figure 2 (b). By comparing figure 2 with figure 1 (b), it is apparent that the pearlite and lump phase along the ferrite grain boundaries are transformed from the retained austenite during cooling.

The samples air cooled were then tempered at 200°C~400°C for 20 min. The SEM images of the tempered samples are presented in figure 3. It is noted that the microstructure after tempering at 200°C (figure 3 (a)) remains nearly unchanged compared to the sample air cooled (figure 2 (b)), except for the appearance of extremely small amounts of lamellar pearlite at the ferrite grain boundaries. After tempering at 300°C, the transformation from lump phase to pearlite proceeds further, and the two phases coexist along the grain boundaries (figure 3 (b)). When the tempering temperature is 400°C, the lump phase almost completely transformed into lamellate pearlite as shown in figure 3 (c).

![Figure 2](image1.png)

**Figure 2.** SEM images of the samples after isothermal heating at 760°C for 5 min and then (a) sand cooled and (b) air cooled.

![Figure 3](image2.png)

**Figure 3.** SEM images of the samples tempered at different temperatures of (a) 200°C; (b) 300°C; and (c) 400°C for 20 min after heat treatment at 760°C and then air cooled.
Figure 4 shows the stress-strain curves of the samples as rolled and after heat treatment at 760°C and then sand cooled or air cooled. It is found that the sample after heat treatment by sand cooling presents the higher yield strength and longer yield platform than the as rolled sample. However, for the sample after heat treatment by air cooling, the yield strength is decreased and the yield platform becomes short compared to the as rolled sample as shown in figure 4.

Figure 5 shows the stress-strain curves of the air cooled samples before and after tempering at different temperatures. It is found that for the air cooled samples, after tempering at various temperatures for 20 min, the yield strength gradually increases and the yield platforms become longer with increasing tempering temperature.

Table 2 presents the yield strengths of the samples as rolled, after heat treatment at 760°C and then sand cooled and air cooled, and tempering at different temperatures. The yield strengths of the samples after heat treatment at 760°C by sand cooling and air cooling are ~50 MPa higher and ~40 MPa lower than that of the as rolled sample, respectively. After the air cooled samples are tempered at different temperatures, the yield strengths increase with increasing the tempering temperature. When the tempering temperature is 400°C, the yield strength is higher than that of the samples as rolled, sand cooled, and air cooled by ~60 MPa, 10 MPa, and 100 Mpa, respectively.

It is known that yield strength and yield platform features are closely related to the formation of high concentration Cottrell atmosphere by the interstitial elements C and N pinning dislocations [8, 9]. Thus, it is considered that the different yield strengths obtained from the different heat treatments might be caused by the impact of different heat treatment processes on the formation of high concentration Cottrell atmosphere and related to the amount of lump phase distributed at grain boundaries.

![Figure 4](image1.png)

**Figure 4.** Stress-strain curves of the samples as rolled and after heat treatment at 760°C and then sand cooled and air cooled.

![Figure 5](image2.png)

**Figure 5.** Stress-strain curves of the air cooled samples before and after tempering at different temperatures.

| Yield strength/MPa | As-rolled | Sand cooled | Air cooled |
|--------------------|-----------|-------------|------------|
| 336±4              | 389±4     | 291±12      |
| Tempering temperature | 200°C   | 309±10      | 324±8      | 397±6      |

### 3.2. Analysis of the lump phase

According to the microstructures and yield strengths of the samples exposed to different heat treatments presented in section 3.1, it is noted that the yield strength is closely related to the volume fraction of lump phase distributed at the ferrite grain boundaries. Thus, the detailed analysis of the
lump phase was performed by applying SEM and TEM analysis, and by applying thermodynamic calculations using Pandat software.

Figure 6 and table 3 show the energy dispersive spectrometer (EDS) results of the lump phase and the ferrite matrix of the sample after heat treatment at 760°C and then air cooled. It is found that the average carbon concentration in the lump phase is higher than that in the ferrite matrix.

Figure 7 shows the morphology and the selected area electron diffraction (SAED) pattern of the lump phase. It is found that there is a sharp interface between the lump phase and the ferrite matrix. Evident dislocation tangles are observed inside the lump phase. According to the diffraction pattern shown in figure 7 (b), the lump phase has a bcc lattice. Therefore, it considered that the lump phase is a type of bainite-ferrite phase [10], namely, a supersaturated ferrite phase.

Figure 8 shows the fractions of ferrite and austenite, the solubilities of elements C, Mn, and Si in ferrite, austenite, and precipitates, respectively, varying with temperature; the data was calculated using Pandat. It is seen that the phase transformation from ferrite to austenite starts at ~700°C, and finishes at ~890°C. Thus, the heat treatment temperature at 760°C is within the ferrite-austenite two-phase region. The solubility of element C in ferrite is significantly lower than in austenite. When the matrix is the ferrite phase, most carbon atoms are tied up as precipitates as shown in figure 8 (b). The solubility of Mn in ferrite is slightly lower than in austenite when the temperature is around 500–700°C, and gradually decreases with decreasing temperature (figure 8 (c)), while the solubility of element Si is nearly identical in austenite and ferrite as shown in figure 8 (d).

![Figure 6](image1.png)

**Figure 6.** EDS analysis of the sample after heat treatment at 760°C and then air cooled: (a) lump phase; (b) ferrite matrix.
Table 3. EDS analysis of the sample after heat treatment at 760°C and then air cooled.

| Content (wt.%) | C   | Si  | Mn  | Fe  |
|---------------|-----|-----|-----|-----|
| Lump phase    | 6.00| 0.75| 1.94| 91.31|
| Ferrite matrix| 3.45| 0.64| 1.83| 94.08|

Figure 7. Morphology and SAED of the lump phase: (a) TEM image; (b) diffraction pattern.

(a) Lump Phase
(b) Diffraction Pattern

Figure 8. Variations of (a) the equilibrium phases of ferrite and austenite; and the solubilities of (b) carbon; (c) manganese; (d) silicon in ferrite, austenite, and precipitates with temperature.
Based on the above analysis, during isothermal heating at 760°C, within the ferrite-austenite two-phase region, ferrite-to-austenite phase transformation takes place, and the formed austenite is primarily distributed along the ferrite grain boundaries. Since the solid solubilities of interstitial elements, C and N, in austenite are higher than that in ferrite, while the diffusivities of interstitial atoms in austenite are lower than that in ferrite [11], these interstitial elements are enriched in the austenite grains. During the subsequent cooling processes from 760°C to room temperature, austenite-to-ferrite phase transformation occurs. When the temperature is cooled down to a certain temperature, the retained austenite is transformed to pearlite or supersaturated ferrite through allotropic transformation. It is known that austenite to pearlite phase transformation is controlled by carbon diffusion. When the cooling rate is relative slow, more time is available for phase transformation and carbon diffusion. Thus, it is understandable that in the sand cooled sample there are small quantities of pearlite and lump phase at the ferrite grain boundaries, while in the air cooled sample, nearly no pearlite is observed, and the amount of lump phase is higher than that in the sand cooled sample, as shown in figure 2. Since the lump phase at the grain boundaries is enriched with the element carbon, the carbon atoms cannot diffuse sufficiently to pin the dislocations and to form high concentration Cottrell atmospheres, leading to the reduction of dislocation strengthening [12]. In addition, the microsegregation of carbon atoms at grain boundaries reduces the solid solubility in the ferrite matrix, which weakens the contribution of solid solution strengthening [13]. Dong An et al. [14] simulated the carbon concentration distribution after the cooling processes from 760°C to room temperature at the cooling rates of 2°C/s and 5°C/s using a cellular automaton (CA) model. It is found that after cooling at 2°C/s, the carbon concentration field is nearly uniform, while a higher cooling rate of 5°C/s results in a non-uniform carbon concentration field. Accordingly, the air cooled sample presents a lower yield strength and a shorter yield platform than that of the sand cooled sample, and even than that of the as rolled sample, due to that fact that the fast cooling rate is unfavourable for the formation of high concentration Cottrell atmospheres and weakens the solid solution strengthening component.

When the air cooled samples are then tempered at 200°C~400°C for 20 min, carbon diffusion takes place, which is beneficial for the formation of high concentration Cottrell atmospheres. As the diffusivities of the interstitial elements are temperature dependent, when the sample is tempered at 200°C, the diffusion of the interstitial atoms from boundaries to the locations of dislocations is still limited. The simulation results by An et al. [14] show that tempering at 200°C for 20 min has less effect on the carbon concentration field. Thus, after tempering at 200°C, the yield strength is only slightly increased, and the yield platform becomes slightly longer compared to the air cooled sample. With the tempering temperature increasing, the diffusivities of the interstitial elements increase, leading to more sufficient diffusion of the interstitial atoms to form high concentration Cottrell atmospheres. Therefore, yield strength increases and the yield platform becomes longer with increasing tempering temperature, as shown in figure 5. In addition, more sufficient carbon diffusion at higher tempering temperature also promotes the transformation of the non-equilibrium lump phase (supersaturated ferrite) to the equilibrium pearlite phase. Thus, as tempering temperature increases, the lump phase is gradually transformed to pearlite. After tempered at 400°C for 20 min, the lump phase at the grain boundaries nearly completely transformed to lamellate pearlite as shown in figure 3 (c).

4. Conclusions
A cold-rolled enameling steel was isothermally heated at 760°C for 5 min and then sand cooled or air cooled to room temperature. The microstructure of the sample sand cooled consists of the ferrite matrix and a small quantity of pearlite and lump phase distributed at the ferrite grain boundaries. However, in the microstructure of the sample air cooled, nearly no pearlite forms, and the amount of lump phase is significantly higher than in the sample sand cooled. The yield strengths of the samples sand cooled and air cooled are 50 MPa higher and 40 MPa lower than the as rolled sample, respectively.

After tempering at 200°C~400°C for 20 min, the lump phase in the samples air cooled is gradually transformed to pearlite with increasing tempering temperature. When the tempering temperature is
400°C, the lump phase almost completely decomposed into lamellate pearlite. Meanwhile, the yield strength gradually increases with increasing tempering temperature. After tempering at 400°C, the yield strength is higher than that of the samples as rolled, sand cooled, and air cooled by ~60 MPa, ~10 MPa, and ~100 MPa, respectively.

The results of the SEM and TEM analysis and the thermodynamic calculations show that the lump phase is a supersaturated ferrite phase enriched with carbon. During the air-cooling process from the ferrite-austenite two-phase region to room temperature, less time is available for austenite-to-ferrite and austenite-to-pearlite phase transformation and carbon diffusion. The retained austenite is thus transformed to the supersaturated ferrite (lump) phase through allotropic transformation. In this case, the carbon atoms cannot diffuse sufficiently to pin the dislocations to form high concentration Cottrell atmospheres, leading to yield strength reduction and yield platform shortening. When the samples air cooled are tempered at 200°C~400°C, carbon diffusion takes place, promoting the formation of high concentration Cottrell atmospheres. This results in the yield strength increasing. The effect of tempering on yield strength increases with increasing tempering temperature, due to the fact that the diffusivities of the interstitial elements increase with temperature.

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6. References
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