Inversed Phosphorus Segregation in Twin Roll Cast Strips for Improvement of Mechanical Properties and Weathering Resistance

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In the present paper, twin roll strip casting was applied to fabricating the strips of low carbon steels containing different P contents. P was spontaneously segregated near strip surfaces by the deformation in mushy zone during strip casting. Uniform surface layers enriched in P can be formed after subsequent processing of cold rolling and annealing, which can be used as surface coatings for the improvement of both weathering resistance and mechanical properties including toughness and elongation. In terms of plasticity, the elongation of conventional strips started drastically decreasing with P content beyond 0.15% by weight. By contrast, the elongation of the cast strips containing 0.26% P remained at the level of about 30%, with the tolerated ability of P being increased by about 0.1% by weight by twin roll strip casting. The ductile–brittle transition temperatures (DBTT) for the cast strips after cold rolling and annealing were measured to be lower than those for the conventional strips after hot rolling, cold rolling and annealing by 10–15°C. For 120 cycles of corrosion exposure, the weight gains of the 0.15 and 0.26P cast strips were reduced by more than 30% as compared with that on the conventional strip containing 0.08% P. It has been demonstrated that phosphate enriched layers could be formed beneath the corrosion scales of the 0.15 and 0.26P cast strips after cold rolling and annealing, which reduced the corrosion rate and improved the corrosion resistance.

KEY WORDS: twin roll strip casting; phosphorus; elongation; toughness; weathering resistance.
Table 1. Chemical compositions of the experimental steels.

| Samples     | C  | Si | Mn  | P     | Cr | Ni | Cu | S     |
|-------------|----|----|-----|-------|----|----|----|-------|
| 0.08P TRSC  | 0.080 | 0.391 | 0.360 | 0.085 | 0.591 | 0.430 | 0.310 | 0.0071 |
| 0.15P TRSC  | 0.076 | 0.341 | 0.326 | 0.150 | 0.510 | 0.410 | 0.325 | 0.0083 |
| 0.20P TRSC  | 0.075 | 0.352 | 0.320 | 0.260 | 0.505 | 0.407 | 0.317 | 0.0057 |
| 0.30P TRSC  | 0.078 | 0.346 | 0.325 | 0.300 | 0.508 | 0.406 | 0.322 | 0.0079 |
| 0.36P TRSC  | 0.075 | 0.345 | 0.330 | 0.360 | 0.509 | 0.409 | 0.321 | 0.0076 |
| 0.08P HCA   | 0.074 | 0.421 | 0.374 | 0.080 | 0.545 | 0.428 | 0.329 | 0.0048 |
| 0.15P HCA   | 0.082 | 0.405 | 0.371 | 0.150 | 0.549 | 0.424 | 0.343 | 0.0071 |
| 0.20P HCA   | 0.085 | 0.386 | 0.374 | 0.200 | 0.571 | 0.431 | 0.333 | 0.0057 |
| 0.30P HCA   | 0.083 | 0.422 | 0.383 | 0.300 | 0.521 | 0.426 | 0.310 | 0.0082 |
| 0.36P HCA   | 0.080 | 0.419 | 0.386 | 0.360 | 0.538 | 0.411 | 0.323 | 0.0077 |

TRSC: twin roll strip cast, cold rolled and annealed at 750°C; HCA: hot rolled, cold rolled, and annealed at 750°C.

2. Experimental Procedures

Low carbon steels were re-melted by using a 30 kg induction furnace to produce the compositions containing 0.08–0.36% P by weight under high vacuum. The molten steels were poured into the crucible of the furnace into a preheated tundish, and flowed through a nozzle into the twin roll strip caster to form thin strips, with the solidification rolls of 450 mm in diameter and 254 mm in length being internally cooled with running water. The initial roll gap and strip casting speed were set up to be 1.0 mm and 20 m/min, respectively. The as-cast strips were cold rolled to the thickness of 0.8 mm with the total reduction of 53% for 5 passes by using a pilot reversible 2-high rolling mill. The cold rolled strips were annealed at 750°C for 30 min. The as-cast, cold rolled and annealed strips are denoted as TRSC strips. As the comparison, ingots with P contents of 0.08–0.36% were made by using a vacuum induction furnace. Hot strip rolling and cold strip rolling were applied to produce the strips with thickness of 0.8 mm, and annealing treatments at 750°C for 30 min were carried out, which are denoted as HCA strips. Table 1 shows the compositions for both TRSC and HCA strips.

Tensile tests were carried out to measure the mechanical properties such as yield strength, tensile strength, and elongation of the strips after the annealing treatment. The samples cut from the TRSC strips were etched by using the Oberhoffer (OB) reagent (30 g FeCl3 + 1 g CuCl2 + 0.5 g SnCl2 + 50 mL HCl + 500 mL H2O + 500 mL alcohol) to reveal the presence of P, with light and dark regions in the microstructure showing relatively high concentration of P under optical microscope and SEM, respectively.19,20 A field emission electron probe micro-analyzer (FE-EPMA) of JXA-8500F was used to qualitatively and quantitatively measure the distribution profile of P concentration through strip thickness.

Charpy V-notch impact tests were carried out to measure the impact energy of thin strips by using a pendulum impact tester, with a special specimen holder being used to avoid the specimen’s distortion upon impacting. The actual specimen temperature was calibrated by calculating the temperature increase using the finite element method (FEM) in the period from the specimen leaving the low temperature medium to being held in the holder. The details for the impact test and temperature calibration are described in the Appendix.

For the corrosion exposure test, samples cut from the cold rolled and annealed sheets were polished down to 5 μm, which were sealed in epoxy resin with one surface in the size of 30 mm in length and 30 mm in width being exposed. Before the corrosion test, the corrosive liquid in solution of 0.005 mol/L NaHSO3 with pH of 4.5 was sprayed to each sample in the density of 40 μL/cm². The exposure was carried out in a dry and wet cyclic manner at 30°C in the humidity of 60%. After each cycle for 12 hrs, the samples were retreated to measure their mass changes. Then, they were cleansed with distilled water, sprayed with the corrosive liquid, and replaced into the chamber. The cross-sections of rusts after 120 cycles were observed and analyzed by using SEM and EDX. The details of the corrosion exposure test were described elsewhere.21

3. Results

Table 2 shows the mechanical properties measured through tensile testing and grain sizes for all strips.

Figure 1 shows the relationships between elongation and P content in the HCA and TRSC strips. Elongations of the HCA strips begun to drastically decrease when P content was greater than 0.15% by weight. Elongation of the TRSC strips, by contrast, remained to be at high level until P content was greater than 0.26% by weight, indicating that the safe content of P in the TRSC can be increased by about 0.1% by weight in terms of plasticity. Figure 2(a) shows the relationships between impact energy and the test temperature for TRSC and HCA strips. It can be seen that the DBTT value for the HCA strips containing 0.08% P was measured to be less than −60°C, in good agreement with previous measurements of the DBTT for the steel with 5 mm thickness,22 indicating that the temperature calibration had a reasonably good accuracy. The DBTT value for the 0.08P TRSC strip was measured to be about −75°C.
The DBTT values for the TRSC and HCA strips containing 0.15% P were measured to be about −45°C and −35°C, respectively. The DBTT values for both HCA strip containing 0.20% P and TRSC strip containing 0.26% P were measured to be about −25°C. Figure 2(b) shows the relationship between DBTT values and P content in both strips, which indicates that the DBTT values for the TRSC are lower than those for the HCA strips by 10–15°C for the present P content range.

Figures 3(a), 3(b) and 3(c) show the microstructures in the HCA strips containing 0.08, 0.15 and 0.20% P, respectively. It can be seen that typical central P segregations had been formed in all strips. Figures 4(a), 4(b) and 4(c) show the solidification structures of the 0.08, 0.15 and 0.26P cast strips, respectively. Significant P enriched zones have been formed near the cast strip surfaces. In both the 0.15 and 0.26P cast strips, the depths of surface P enriched zones were about 200 μm. There are more P enriched/segregated spots in central regions of the 0.26P cast strip than those in the 0.15P cast strip. Figure 4(d) shows the SEM high magnification observation of typical local interface between P enriched surface layer and matrix of the 0.26P cast strip, with the dark areas representing the relatively enriched presence of P. It indicates that the P enriched layer is in connection with P rich “reservoirs” through fine channels, with the interface between the P enriched layer and substrate being rather flat.

Figures 5(a), 5(b) and 5(c) show the microstructures of the 0.08, 0.15 and 0.26P TRSC strips, respectively. The original P enriched/segregated zones had become to be uniform layers of about 50 μm in both strips after the subsequent processing of cold rolling and annealing. Elongated P segregated zones can be observed in the bulk of 0.26P TRSC strip, while few P enriched spots can be found in the bulk of 0.08 and 0.15P TRSC strips.

Figure 6 shows the SEM photos of the fracture morphologies for the TRSC and HCA strips after impact tests. For the 0.15P HCA strip, big cleavage area can be observed after the impact at −45°C. For the 0.15P TRSC strip, however, the fracture morphology is comprised of ductile dimples, in good agreement with the measurement of DBTT values for the two strips. For the 0.20P HCA strip, only inter-granular fracture morphology can be observed after the impacting test at −35°C. For the 0.26P TRSC strip, by contrast, the fracture morphology is consisted of smooth granular facets and micro voids after the impacting test at −35°C, implying that ductile dimples could have been formed to result in some degree of ductile fracture.

Figure 7 shows the relationship between weight gains and corrosion exposure time. The weight gains of the 0.15
and 0.26P TRSC strips were measured to be about 9.9 and 9.5 mg/cm² after 120 cycles of exposure, respectively, lower than those of the 0.08, 0.15 and 0.20P HCA strips by approximately 30% and 33%, 23% and 26%, 13% and 17%, respectively. Figures 8(a), 8(b) and 8(c) show the SEM photos of the cross sections of the corrosion scales formed on the HCA and TRSC strips after 120 cycles of corrosion exposure test. It can be seen that the structure of the corrosion scales formed on TRSC strips is denser and their thickness is thinner than those formed on the HCA strips. Figure 8(d) shows the composition analyses by EDX at the interfaces between rust scales and 0.15P TRSC and 0.15P HCA strips after 120 cycles of corrosion exposure test. They clearly indicate the P enrichment at the rust/substrate interface for the 0.15P TRSC strip but no P presence at the rust/substrate interface for the 0.15P HCA strip.

4. Discussion

In directional casting, surface inverse segregation of the low melting point elements can be formed near the chilled surface driven by the back flow due to the solidification
During strip casting, the surface inverse segregation of solute is believed to be mainly caused by squeezing the solute-rich liquid to flow back to the strip surfaces through channels between dendrite arms. During strip casting, solidification first occurs on the strip surfaces, resulting in the formation of gaps between casting rolls and strip surfaces and channels between dendrite arms due to the solidification shrinkage. Simultaneously, the deformation in mushy zone takes place to squeeze the P rich liquid through the channels to strip surfaces and form the P enriched zones. Figure 4(d) shows that the P enriched layer has a flat interface with the as-cast strip, and it is connected with P rich “reservoirs” through fine channels. The observation may indicate the typical scenario that the P enriched liquid had been squeezed out of the solidified surface through the gaps between dendrite arms and rolled flat, although more work is still needed to better clarify the mechanism for the formation of P enriched layer by strip casting.

With the contents of Cu and S in all experimental steels used in this work, nano particles of copper sulfides could possibly be formed in the cast strips, which may have great influence on mechanical properties. In this work, all steels contained almost the same contents of Cu and S, and they had been subjected to the same processing of strip casting.
casting and heat-treatments. Therefore, the effect of copper sulfides was believed to be constant for all steels and only the effect of P contents on mechanical properties and weathering resistance had been considered.

By using the field emission EPMA, accurate quantitative analysis of the distribution of P concentration through strip thickness becomes possible because of the enhancement of probe current. Figure 9 shows the distribution profile of P...
concentration through thickness for 0.15P TRSC and HCA strips. In the TRSC strip, the average P concentration on the surface was measured to be about 0.26% by weight, while the average P concentration on the HCA strip was measured to be less than 0.14% by weight, with the difference of more than 0.12% by weight. In the bulk of 0.15P TRSC strip, the average P concentration was measured to be about 0.135% by weight; while the average P concentration in the bulk of 0.15P HCA strip was measured to be about 0.152% by weight, with the increase by about 0.017% by weight or with the relative increase by more than 15%.

The more P having been added in steel, the more segregation of P along grain boundaries tends to take place, which may weaken grain boundaries to cause the occurrence of inter-granular rupture. In the HCA strips containing different P contents, P central segregations were formed, with P being depleted near surface regions; while in the TRSC strips, segregations were formed on surfaces, with P depleting in the bulk. During impact test, the impacting force was mainly loaded on the bulk of the specimen. If the grain boundaries in the bulk have been deteriorated by P segregation, the whole resistance against rupture can certainly be decreased. According to Seah, the P concentration along grain boundaries, $C_{gb}$, can be estimated by Eq. (1).

$$\frac{C_{gb}}{1 - C_{gb}} = C_0 \cdot \exp \left( \frac{\Delta G}{RT} \right)$$

Where, $C_0$ is the concentration of P in the bulk near grain boundary; $\Delta G$ the segregation free energy of P for Fe–P alloy; $R$ and $T$ the gas constant and temperature in Kelvin, respectively. For a semi-quantitative estimation, it is reasonable to assume that the values of $\Delta G$ are the same for all strips. It can be estimated from Eq. (1) that if the P concentration in bulk is relatively reduced by about 15%, concentration of P in the grain boundary can be reduced by about 10%, which is corresponding to the case for the 0.15P TRSC and HCA strips. According to Song et al., the empirical equation of DBTT ($°C$)=$3.38C_{gb}−91.95$ may be used for the relationship between the DBTT and the average P concentration along grain boundaries, from which it can be seen that the increase of $C_{gb}$ by 10% can result in the increase of DBTT by about 10°C. In the present work, the DBTT values for the 0.15P TRSC strip has been measured to be lower than that of the 0.15P HCA strip by about 10°C, Fig. 2(a), which can, therefore, be mainly attributed to the decrease of P in the bulk of the 0.15P TRSC strip having reduced P segregation along grain boundaries and lessened inter-granular weakening effect.

The relationship between weight gain and exposure time is usually described by the empirical formula, Eq. (2).

$$\Delta W = K t^n$$

Where, $K$ and $n$ are constants, $t$ in hour. By using standard regression method, $K$ and $n$ can be obtained from the experimental results. Table 3 shows $K$ and $n$ values for the HCA and TRSC strips in the first and last 60 cycles. It is well accepted that if the corrosion is controlled by diffusion process, the kinetics should follow a parabolic law, with the value of $n$ being close to 0.5. If the value of $n$ is greater than 0.5, it indicates that there are cracks in the rust to accelerate the corrosion process, while the value of $n$ smaller than 0.5 indicates that the diffusion process is blocked due to the formation of dense layer in the rust. In the last 60 cycles, the values of $n$ for both strips were regressed to be about 0.60, indicating that cracks had been formed in the rusts at the early stages of corrosion. In the last 60 cycles of the corrosion exposure, the value of $n$ was regressed to be 0.46 for the 0.08P HCA strip, showing that the corrosion process was controlled by diffusion. The values of $n$ for both 0.15P and 0.26P TRSC strips, however, were only half of 0.5, implying that dense layers could have been formed at the interfaces between rusts and substrates to block the diffusion.

According to the ternary Fe–P–O phase diagram, the critical P concentration in steel for the formation of phosphate is greater than 0.24% by weight, implying that the bulk concentration of P in a conventional slab must be higher than this value if the steel is to be weathering resistant, which could deteriorate the mechanical properties due to severe central segregation. In the present work, it has been shown by the accelerated corrosion tests that phosphate enriched layers could have been formed beneath corrosion scales on 0.15P the TRSC strip, and the scale thickness was reduced by about 60% as compared with the HCA strip with 0.08% P. As indicated by the quantitative analysis, the P concentration near the surfaces of the 0.15P TRSC strip was measured to be higher than 0.24% by weight, being just enough for the formation of phosphate enriched layer between corrosion scale and substrate to improve the weathering resistance.
5. Conclusions

In the present work, it is found that P can be spontaneously segregated near strip surfaces by the deformation in mushy zone during strip casting, which can form uniform P enriched surface layers after subsequent processing of cold rolling and annealing. The P enriched layers can be used for the improvement of both weathering resistance and mechanical properties including toughness and elongation. As far as elongation is concerned, the elongation of conventional strips started drastically decreasing with P content more than 0.15% by weight. By contrast, the elongation of the TRSC strips containing 0.26% P remained at the level of about 30%. The tolerated ability of P can be increased by about 0.1% by weight by twin roll strip casting. The DBTT values for the TRSC strips were measured to be lower by 10–15°C than those for the HCA strips. In terms of corrosion resistance, the surface enriched layers of P can be used as surface coatings for the improvement of weathering resistance. Dense and phosphate enriched layers can be formed at the interfaces between corrosion scales and the TRSC strips. After 120 cycles of corrosion exposure, the weight gains for the 0.15 and 0.26P TRSC strips have been measured to be less than that formed on the HCA strip containing 0.080% P by more than 30%.

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Appendix

In the present work, the Charpy impact tests were carried out for the strips with thickness of 0.8 mm. In order to avoid the specimen distortion upon impacting, a special specimen holder has been designed and used in the impact testing, as shown in Fig. A-1. The specimens with the width of 10 mm and length of 55 mm were cut from the TRSC and HCA strips, with a V-notch being machined on each specimen. Liquid nitrogen and isopetane were mixed in different proportions in a container for different low temperature environments. Specimens were immerged in this container for the period of 2 min to get the specimen temperature to be equalized. They were then transferred to the specimen holder, with the transferring time in air and the time in contact with the holder having been about 5 and 2 s, respectively, which could result in dramatic temperature increase in thin gage strips by radiation and thermal conduction. Therefore, calibration for the actual specimen temperature prior to the impact must be performed. In the present work, the temperature change was calculated by using the finite element method (FEM) integrated within a commercially available software ANSYS. Figures A-2(a) and A-2(b) show the grids of the specimen and the holder for the temperature calculation and the temperature distribution in the specimen prior to the impact, respectively. It can be seen that the temperature in the region around the V-notch is the lowest and its distribution is homogeneous. Figure A-3 shows the relationship between the actual temperature, \( T_{act} \), around the V-notch in the specimen and the temperature, \( T_1 \), when it left the low temperature container.
Fig. A-2. (a) The grids of the specimen and the holder for the temperature calculation, and (b) the temperature distribution in the specimen prior to the impact.

Fig. A-3. The relationship between the actual temperature, $T_A$, around the V-notch in the specimen and the temperature, $T_L$, when it left the low temperature container.