Influence of shot peening on corrosion behavior of low alloy steel

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Abstract
Surface modification is an important technique for maintaining relatively favorable mechanical properties to surface properties and corrosion resistance. In this study, Surface shot peening technology is applied to low alloy steel production nanocrystallines. The microstructure near the surface layer was characterized by x-ray diffraction, transmission electron microscopy and electron backscatter diffraction. The corrosion behavior of the shot-treated surface layer was analyzed by polarization and pitting test, and the surface morphology of the corroded sample was observed by a scanning electron microscope. The results showed that the surface layer of the alloy after shot peening can be divided into three parts: equiaxed nanoparticle layer (NG), ultrafine grain layer (FG) and elongated fine grain layer (EG). Surface nanocrystallization improved the potential polarization behavior of low alloy steel in 3.5% NaCl solution. The microhardness of the near surface region showed a significant increase compared to the as-received steel sample, showing a more stable electrochemical performance. Shot peening also significantly reduced the pitting rate and maximum pitting depth in 10% FeCl3 solution. The surface nano-layer structure produced by the shot peening process could provide more nucleation sites, thereby improving the uniformity and compactness of the passivation film, resulting in better corrosion resistance. The above experimental results clearly showed that the overall and local corrosion resistance of the low alloy carbon steel in the chloride ion-containing solution can be improved by shot peening.

1. Introduction
Nanocrystalline (nc) materials structurally characterized by nano-sized grains with a large number of grain boundaries have been found to exhibit many unique properties relative to their coarse grain state [1–4]. Nanostructured metal materials have high strength and high fatigue strength due to their high grain boundary density. There are many ways to prepare nanocrystalline metal. It is an interesting research field to prepare nanocrystalline metals by surface nanocrystallization. Various surface treatments have been applied to produce nanostructured layers on the outer surface of metal materials such as shot peening [5], ultrasonic shot peening [6] (USSP), laser shock peening [7], surface mechanical wear reduction treatment (SMAT) [8], high pressure torsion [9]. Severe shot peening (SSP) is a developed technology for preparing gradient structure with grain size varying from nanometer to micrometer without changing the overall chemical compositions of a metal. Shot peening involves repeating impact of the hard ball on the surface of the sample, resulting in work hardening of the workpiece surface due to severe plastic deformation and compressive residual stress in the surface area. At this high strain rate, strong plastic deformation occurs, and shot peening produces an ultrafine grain structure in the surface region. The shot peening process forms a nano-scale grain layer on the surface of the alloy while introducing a large residual stress which has a positive effect on the corrosion resistance and crack initiation resistance of the workpiece.

Low carbon and low alloy steel has been widely used in transportation, automobile and other industries due to its reasonably strong plasticity, desired machinability and weldability. Low carbon and low alloy steels are
usually limited by unsatisfactory strength, fatigue and corrosion properties. It has been proved that the nanostructure has a positive effect on the hardness and fatigue properties of the materials. It has been proved that the surface hardness and fatigue properties of the material can be improved by nano surface treatment. However, research on corrosion is very limited in terms of low carbon and low alloys. Wang He Yu’s research showed that the surface of 1Cr18Ni9Ti stainless steel was surface nanocrystallization after high-energy shot peening treatment, and the sample had excellent pitting resistance in chloride solution [5]. Onizawa and Islam et al. reported that shot peening improved the corrosion resistance and fatigue properties of austenitic stainless steel [10]. However, there are conflicting views on the corrosion behavior of nanostructured layers on the metal surface. Qian Zheng’s observed that cracks were produced in the passivation film during shot peening, which led to the decrease of corrosion resistance [11]. The corrosion behavior of low carbon austenitic stainless steel 316 L was previously studied by Kalainathan. Their study is elucidated that the thermal mechanical treatment can produce higher surface roughness, selective ablation near inclusion, thus reducing the corrosion resistance [12, 13].

In order to better understand the effect of surface nanocrystallization on the corrosion resistance of low carbon and low alloy steel, shot peening was selected to prepare the surface layer of nanostructure on the steel surface in this study. Through the analysis of the microstructure, surface hardness of the sample, the corrosion behavior of the sample after shot peening was studied.

2. Experimental materials and methods

Commercial steel with a chemical composition of 0.08 C, 0.57 Si, 0.65 Mn, 0.013 P, 0.006 S, 0.67 Cr, 1.80 Ni and 0.23 Mo were studied. The hardness and yield strength for the low alloy steel were 239 ± 14 HV and 473 MPa, respectively. The steel plate of 100 × 100 × 10 mm3 shall be polished with different grit of SiC sandpaper, and then evenly cut into two plates with the size of 100 × 50 × 10 mm3. The samples were rinsed with distilled water, followed by ultrasonic cleaning with acetone for 5 min. The shot peening specimen was prepared by using a steel ball with a diameter of 0.8 mm. The shot peening time and pressure were respectively five minutes and 0.5 MPa. The phase composition and average grain size were measured by x-ray diffraction (XRD; Rigaku D/ max–2500PC). X-ray diffraction (XRD) was used to analyze the phase change of the sample in the range of 20°~120 °. The scanning speed was 2° min⁻¹. In order to understand the microstructure evolution of the surface layer and the lower layer, the cross-section of the sample was cut, cold inlaid with phenolic resin, then polished with a series of silicon carbide sandpaper (150–2000 grit), and further polished with SiO2 suspension. Then, the polished cross section was chemically etched with nitric acid alcohol reagent (4 ml nitric acid, 96 ml ethanol) a for 5 s each time. All etched samples were observed with by Hitachi su–5000 scanning electron microscope. The section sample is cut into 600 μm thick sample by wire electrode discharging, then it is mechanically ground to 30 μm by 1500 sandpaper, and then it is thinned to perforation by TenuPol-5 twin-jet electropolishing device. The electrolyte used is composed of 7% perchloric acid and 93% glacial acetic acid at room temperature. The test voltage is 40 V. Microvickers hardness of the cross section of the sample was measured on FM–ARS9000 hardness tester with 100 g load.

The structure of sample cross-sections was characterized by electron backscatter diffraction (digiview EBSD camera) analysis. The cross section of the sample was ground and treated according to the same sample program sample as the scanning observation, followed by electrolytic polishing treatment. The composition of the polishing solution is 7% perchloric acid + 93% ethanol. The room temperature potentiodynamic polarization measurement of different samples was carried out in 3.5% NaCl solution by using CHI660A electrochemical workstation. The saturated calomel electrode (SCE) was used as the reference electrode to measure all potentials, and the platinum rod was used as the auxiliary electrode. The 10% FeCl3 solution was stored in a tank at 50 °C for pitting test. The Corrosion samples were ground for a few seconds using 2500 grit SiC paper to slightly remove the surface highest peaks caused by shot peening. The samples were immersed in the solution for 2 h, 4 h, 6 h, 9 h and 18 h respectively, and then washed with distilled water and ethanol. Mechanical method was used to determine the corrosion depth of corrosion samples.

3. Results

3.1. Microstructure

Figure 1 shows the XRD of the received and SP treated test steel. It can be seen that only the ferrite phase can be observed in the x-ray diffraction pattern after shot peening. Therefore, the phase composition had no effect on the corrosion behavior of the test steel. At the same time, due to the grain refinement, the half maximum width of Bragg diffraction peak on the shot peened surface was widened. The average size of test steel grain could be roughly calculated according to the scherrer formula [14, 15]. When the shot peening time was 5 min, the
average grain size of the surface layer decreased to about 70 nm, and the lattice parameters and the average micro strain are 2.8740 and 0.0021%, respectively.

The SEM observation results of the cross-section samples perpendicular to the shot peening surface for 5 min were shown in figure 2. The as-received sample was featured by equiaxed ferrite structure with an average grain size of 16 μm, as shown by the red arrow. After shot peening, the surface layer of the sample has obvious plastic deformation. It could be seen from the typical plastic flow that the maximum depth of the top surface is 30 μm. The grain boundary could not be clearly identified by SEM.

Figure 3(a) shows the Inverse pole figure (IPF) of the shot peened specimen. The surface layer of the severe shot peening sample showed gradient grain structure, which confirmed the sem observation results. For severe shot peening, the thickness of grain refinement layer is estimated to be about 50 μm. During shot peening, the surface of the sample deforms seriously, and the average confidence index of surface layer was larger than that in the central region. It can be seen from figure 3(b) that at a depth of 90 μm from the shot peening surface, the grain morphology of the alloy changes significantly, and the equiaxed grains become slender grains. The EBSD grain size distribution chart showed significant grain refinement on the surface layer of all shot peened samples, as showed in figure 3(c). The grain size increased from nanometer to micrometer, showing a gradient distribution. Surface layer of shot peening was nanocrystalline layer. The matrix was a grain layer with a grain
size of Micron. In this region, there were serious work hardening and high-density dislocations in the grains/sub grains. Dislocation slip was involved in the plastic flow of ferrite at this depth. Combined with the above observation and analysis results, the surface layer of the alloy after shot peening could be divided into equiaxed nanocrystalline layer (NG), ultrafine grain layer (FG) and elongated fine grains layer (EG) stretched along the depth direction.

3.2. Mechanical characteristics
The microhardness distribution of the cross section of the sample was measured in figure 4. It can be seen in this graph that the microhardness of the base material was about 270HV. Shot peening significantly increased the hardness near the sample surface and the surface of sample had the maximum value (350HV). Also, the microhardness value gradually decreased from the surface to the center of the sample.

3.3. Corrosion characteristics
Figure 5 shows the potentiodynamic polarization curves of shot peened and as-received samples in 3.5% NaCl solution. Shot peening reduced the passivation holding current density (imax) and reduced the corrosion current density (icorr) and the free corrosion potential (Ecorr),as shown in Table 1. In addition, it increased the breakdown potential (Etr) of the passivation film. Therefore, the polarization behavior of the current steel could be improved by shot peening.
After the shot peening sample was immersed for 2 h, no pits were found. With the increase of time to 4 h, the depth of the pit was slightly deeper than 2 h, but the corrosion rate increases sharply from 4 h to 6 h with time, as shown in Figure 6. After the sample was more than 6 h, the rate remains basically unchanged. In addition, for the sample received, pitting corrosion was evident even after soaking for 2 h, and the corrosion rate remained substantially unchanged. The results were consistent with the special morphology of the NG surface layer shown in figure 3, indicating that shot peening could inhibit the formation of pitting corrosion of low alloy steel.

The morphology of the eroded surface of the two state samples was further observed by scanning. As can be seen from figure 7, there are a large number of large pits on the surface of the received sample surface as compared with the shot peened sample. Therefore, it can be concluded that the surface of the nanocrystals caused by shot peening can enhance the pitting resistance of the low alloy steel in the Cl⁻ solution.

4. Discussion

4.1. Microstructure analysis

After the shot peening, the deformed surface layer has a thickness of about 100 μm. The SEM micrograph of the sample clearly showed ferrite and a small amount of pearlite. The coarse ferrite grains were refined, and the
respective phases become indistinguishable. When surface nanomaterials were prepared by shot peening, micro stresses were also introduced on the surface of the sample [16]. Because of the sharp plastic deformation of the shot peened sample, it is difficult to distinguish the conventional scanning microstructure characteristics. The microstructure of the sample was analysed by transmission electron microscope.

The TEM image and the corresponding selected area diffraction (SAD) image of the surface microstructure of the shot peened sample are shown in figure 8. It can be seen that the equiaxed nanocrystals are formed in the near surface layer of the shot peened sample. Depending on the statistics of grain size by section method, the average grain size of the surface layer was about 19.3 nm.

From the bright field image in figure 9, it could be observed that at a depth of 10 μm from the shot peening surface, the grain morphology of the alloy was also equiaxed. From the electron diffraction pattern of the selected area

### Figure 6

The maximum depth of pit corrosion for the as-received and shot-peened samples in 10% FeCl3 solution at 50 °C varied with corrosive time.

### Figure 7

Typical SEM micrographs of corrosive surface morphologies of the as-received (a) and shot-peened (b) samples immerged in 10% FeCl3 solution at 50 °C for 2 h.

### Table 1

Results of electrochemical corrosion at different surface conditions.

| Conditions    | Current density Icorr (μA cm⁻²) | Potential, Ecorr (Vscce) |
|---------------|---------------------------------|--------------------------|
| shot-peened   | 28.79                           | -0.6765                  |
| as-received   | 39.30                           | -0.6700                  |
in figure 9(a), the continuity of the diffraction ring was weaker than that of the shot peened surface, indicating that the grain size was larger than the grain size of the surface layer. The grain size of the steel at a depth of 10 μm from the shot peening surface was determined by quantifying several dark field images. The average grain size was 23.1 nm.

From the selected area electron diffraction pattern in figure 9(b), it could be seen that the ring of the diffraction point is incomplete at a depth of 30 μm from the shot peening surface, indicating that the number of grains in the corresponding selected area was significantly less than that of the projectile surface, and the grain size is further increased. It can be observed in from figure 9(c) that at a depth of 70 μm from the shot peening surface, the grain morphology of the alloy changes significantly, and the equiaxed grains become slender grains. In this region, there are severe work hardening and high-density dislocations in the grain / sub grain.

Dislocation slip is involved in the plastic flow of ferrite at this depth.

It was pointed out that the grain refinement mechanism of high stacking dislocation materials such as aluminum and steel during shot peening and the formation of dislocation slip deformation, dislocation entanglement, primary coarse grain subgrain boundary division and refinement blocks [17]. The division of the subgrain boundary of the body was related [18]. The surface organization was dislocation cells and local dislocation groups [19]. The main influencing factors of material hardness are grain size and work hardening degree. After shot peening, the average grain size of the sample gradually increased from the surface to the core, as shown in table 2.

Hardness and grain size meet the Hall-Petch relationship. As the grain size decreased, the microhardness of the
sample increased. Meanwhile the shot peening process formed a plastically deformed surface layer, which made the dislocation movement difficult and the hardness value increases [20].

4.2. Corrosion behavior
Previous studies have demonstrated that nanostructured surface layers accelerate the formation of passivation layers. The passivation layer is more dense, stable, and less susceptible to harm by corrosive media, and has a protective effect on the substrate. Chen’s demonstrates that the surface of the nanocrystal structure promotes the nucleation process of the passivation film and improves the compactness of the passivation film. Studies by gaberscek and pejovnik [21] have shown that the nucleation sites of the passivation film are mainly nucleated at the twin-corner, high-angle grain boundaries. Hills et al [22] described the nucleation process by an instantaneous nucleation model of nanocrystalline metal. Figure 10 is a nucleation and growth model of a surface passivation film of a low alloy steel sample. The microstructure of the un-peened sample is an equiaxed

| Distance from surface (μm) | Average grain size (nm) |
|---------------------------|-------------------------|
| 0                         | 19.3 ± 2.1              |
| 10                        | 25.1 ± 1.5              |
| 30                        | 36 ± 6                  |
| 70                        | 800 ± 300               |

Figure 9. TEM observations of the sample at different distances from the surface (a) 10 μm (b) 30 μm (c) 70 μm.
ferrite structure having a low grain boundary density. The passivation film was mainly nucleated at these interfaces. The surface layer of the sample formed nano-layered grains under shot peening conditions, and the grain boundary density increased sharply. Passive films nucleates instantaneously at these interfaces and grow uniformly in all directions along the surface plane.

In the nucleation model of the passivation film, the expansion process of the passivation film needs to overcome a certain resistance, and the corresponding equation is

\[ dF = 2\sigma L dx \]

\( dx \) is the growth distance for the film. The nano surface layer reduced the diffusion displacement of the passivation film and promoted the formation of a complete passivation film. After shot peening, the grains are refined, the wetting angle is reduced, and the adhesion work is increased. In addition, the micropores produced by shot peening generates a pressure difference (\( \Delta P \)) to compress the passive film and accelerate the dynamic process of passive film growth at the hole and dissolution at the bulge [23]. Therefore, the low alloy steel with shot peening had better electrochemical stability and corrosion resistance.

5. Conclusions

Nanocrystalline surface was obtained on low alloy steel by using high-energy shot peening. The grain size for nanostructure in the surface layer was ranged from 10–60 nm and averaged out to \( \sim 16 \) nm. The shot-peening-induced nanocrystalline surface can prominently improve the potentiodynamic polarization behavior of such a test steel in 3.5% NaCl solution by decreasing passivation-maintaining current density, corrosion current density and free Corrosion potential as well as raising the breakdown potential of passive film. The shot peening can also depress its pitting corrosion behavior in 10% FeCl₃ solution. The structure of nanocrystallines containing a high-density of grain boundaries can provide more activity sites, adhesion work and homogeneous capillary force to strengthen the passive film, definitely resulting in a better corrosion resistance.

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