Wear and corrosion properties of a low carbon steel processed by means of SMAT followed by lower temperature chromizing treatment

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Abstract

A duplex lower temperature chromizing treatment at 600 °C for 120 min followed by 860 °C for 90 min was performed on a low carbon steel plate with a nanostructured surface layer, induced by surface mechanical attrition treatment (SMAT) [Z.B. Wang, J. Lu, K. Lu, Acta Mater. 53 (2005) 2081]. Microhardness, wear and corrosion resistances of the chromized SMAT sample were measured, in comparison with those of the chromized coarse-grained counterpart and the as-annealed coarse-grained sample. Experimental results showed that these properties were improved markedly. The much enhanced properties of the chromized SMAT sample relative to the chromized coarse-grained counterpart might originate from its superior microstructures, i.e., a much thicker chromized surface layer with smaller grains and more homogenous phase-distribution, due to the employed processes of the SMAT and the duplex lower temperature chromizing treatment.

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1. Introduction

Chromizing is one of the widely used surface coating technologies to economically improve the performance of components. The chromized surface layer can substantially improve the surface hardness, wear resistance, corrosion resistance and high-temperature oxidation resistance of ferrous alloys [2–4]. However, nearly all conventional chromizing processes are carried out at temperatures above 1000 °C, limited by the diffusion and reaction kinetics involved. The thermochemical treatment of some ferrous alloys at these temperatures will induce serious distortion of the workpieces and severe degradation of the mechanical properties [5,6]. To prevent these negative effects and to widen the application of chromizing techniques to a larger variety of materials, it is a must to lower the treating temperatures.

In a previous work [1], lower temperature chromizing process was investigated on a low carbon steel plate after surface mechanical attrition treatment (SMAT) [7,8]. Due to the much enhanced atomic diffusivities [9] and chemical reaction kinetics [10] in the resultant nanostructured surface layer, a thicker chromized layer was formed in the SMAT sample than in the coarse-grained counterpart, especially at the temperature below 600 °C. Meanwhile, carbides and nitrides of chromium were formed predominantly in the surface layer at the temperature above 700 °C. To fabricate a much thicker chromized surface layer containing a large volume fraction of compounds, a duplex lower temperature chromizing process at 600 °C for 120 min followed by 860 °C for 90 min has been developed to chromize the SMAT low carbon steel [1]. The lower temperature process would allow an effective diffusion of Cr along grain boundaries, while keeping the nanostructures relatively stable, and the following higher temperature process would enhance the growth kinetics of the compounds layer. In this study, the hardness, the resistances to wear and corrosion of the low carbon steel sample processed by means of SMAT followed by the duplex lower temperature chromizing treatment were evaluated, in comparison with those of the chromized coarse-grained counterpart and the as-annealed coarse-grained specimen. The effects of the microstructure formed by the process of SMAT followed by chromizing on these properties were discussed.

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2. Experimental

A commercial low carbon steel plate, with compositions (wt. %) of Fe, 0.11C, 0.01Si, 0.39Mn, 0.024S (max), 0.01P (max), was used for the investigation. The as-received sample was submitted to annealing to obtain homogeneous coarse grains, followed by the SMAT. The details of set-up and SMAT processing were described previously [7,8]. The resultant microstructures were characterized in detail in [1]. In brief, a nanostructured surface layer of about 20 μm thick was achieved. The average grain size of ferrite in the top surface layer was about 9 nm and increased with the increasing depth.

The SMAT sample was cleaned and then chromized in the packed powder mixtures of Cr (50 wt.%), NH₄Cl (1.5 wt.%) and Al₂O₃ (48.5 wt.%), under a duplex lower temperature chromizing treatment [1] at 600 °C for 120 min followed by 860 °C for 90 min, in a double can designed by Meier et al. [3]. For comparison, the coarse-grained sample was also chromized under the same process. After chromizing, the treated surface was cleaned to remove adhering powders.

The hardness variation along depth in the chromized sample was examined on the cross-sectional sample (mechanically polished carefully with diamond powder to 1 μm) by using a Nano Indenter XP™ (Nano instruments) fitted with a Berkovich indenter. The nanoindentor was calibrated by using a SiO₂ standard specimen. The maximum indentation depth for the as-received sample was 200 nm and the distance between any two neighboring indentations was at least 10 μm. The load-displacement data obtained during unloading were analyzed using the Oliver–Pharr method to determine the hardness [11]. At least 5 measurements along a line parallel to the chromized surface were averaged to get the hardness value and error bar at each depth. Limited by the dimension of the plastic deformation zone around the indent, the closest zone measured on the cross-sectional sample should be 3 μm away from the chromized surface in the present work. Thus, the microhardness of the top chromized surface was monitored on a plane-view sample (i.e., on the as-chromized surface) by using an MVK-H₃ Vickers microhardness tester, with a load of 1 N and duration of 10 s. Nanoindentor was not employed here because the as-chromized surface was not smooth enough.

A ball-on-disk SRV® Optimol tribometer with an oscillating ball was used to test unlubricated wear resistances under ambient laboratory conditions (25 °C, 45% relative humidity). Tests were carried out against a WC–Co ball (10 mm in diameter) under normal loads of 5, 10, 15 and 20 N, respectively, with oscillating amplitude of 2 mm and frequency of 5 Hz, over sliding duration of 30 min. The wear volume loss \( W \) was calculated as

\[
W = \frac{D^2L}{4} \left\{ \arcsin \left( \frac{H}{D} \right) - \frac{1}{2} \sin \left[ 2 \arcsin \left( \frac{H}{D} \right) \right] \right\},
\]

where \( D \) is the diameter of the WC ball, \( L \) is the length of the wear scar and \( H \) is the width of the wear scar (measured by using a reading optical microscope). The surface morphologies of wear scars were observed by using a JEM-6301F scanning electron microscope (SEM). The specimens were ultrasonically cleaned in acetone before SEM observations.

To investigate the corrosion behaviors of chromized SMAT sample in the environments with and without chloride ions, potential dynamic measurements were conducted in 0.5 M NaCl + 0.05 M H₂SO₄ and 0.25 M Na₂SO₄ + 0.05 M H₂SO₄ solutions, respectively. The tests were conducted on a Potentiostat instrument (EG and G, Model 273) with a scanning rate of 0.33 mV/s under the ambient temperature. A three-electrode cell was employed with a Pt auxiliary electrode, a saturated calomel reference electrode, and a working electrode of the tested sample with the treated surface exposed (an area of 10×10 mm²).

3. Results and discussion

3.1. Microstructure characterization of the chromized surface layer

Detailed microstructural characterization of the surface layer of the SMAT sample after the duplex chromizing treatment by SEM, TEM observations and XRD analyses, together with the underlying enhanced chromizing kinetics of diffusion and phase formation due to numerous grain boundaries with a high excess stored energy in the nanostructured surface layer induced by SMAT, can be found in [1]. Fig. 1(a) and (b) show the cross-sectional SEM morphologies of the chromized SMAT sample (sample A) and the chromized coarse-grained counterpart (sample B), respectively. Meanwhile, distributions of Cr in the chromized surface layers were monitored by using a fully quantitative (Oxford programs) X-ray energy dispersive spectroscopy (EDS), as shown in Fig. 1(c). It is clear that a continuous chromized surface layer of about 20 μm was formed in sample A, much thicker than that in sample B (≈4 μm). The atomic concentration of Cr is about 70 at.% in the top surface layer of sample A. It is a little lower than that in the top surface layer of sample B (≈90 at.%), due to the fast diffusion kinetics of the deposited Cr in the SMAT surface layer.

Meanwhile, TEM observations and XRD analyses [1] demonstrated that a cemented surface layer (composed of (Cr, Fe)₂₃C₆ and (Cr,Fe)₂N phases) of about 5 μm thick was formed in sample A, much thicker than that in sample B, and a larger volume fraction of (Cr,Fe)₂₃C₆ in sample A than in sample B was detected. The average grain size of chromium compounds in the top surface layer of sample A was 100–200 nm, apparently smaller than that in sample B (500–700 nm). In addition, large-sized (Cr,Fe)₂₃C₆ grains (~2 μm) could be observed in sample B, which might formed from the initial cementite phases in the as-annealed low carbon steel.

Formation of a much thicker chromized surface layer in the SMAT sample, with smaller grain sizes, more homogenous distributed phases and a larger volume fraction of (Cr,Fe)₂₃C₆, results from the enhanced diffusivity and phase formation kinetics, as discussed in [1]. In brief, a large volume fraction of grain boundaries with a high excess stored energy promote the diffusion of Cr and increase the nucleation and growth rates of chromium compounds in the nanostructured surface layer induced by SMAT.
3.2. Microhardness and wear properties

The variation of hardness along depth in sample A is determined in Fig. 2, in comparison with that in sample B. At the depth of about 30 μm in sample B, it is noted that the hardness obtained by nanoindentation is larger than the Vickers microhardness. It might result from the indentation size effect. As shown by nanoindentation results in Fig. 2(a), a hardened layer of about 25 μm thick forms in sample A. The hardness is more than 5 GPa at the depth of 3 μm and decreases gradually to that of the matrix (≈2.5 GPa) with the increasing depth. It is clear that both the thickness and hardness of the hardened layer are much larger than those in sample B (see Fig. 2(b)). The difference between the measured thickness of the hardened layer (≈8 μm) and the value of the chromized layer (≈4 μm, see Fig. 1(b)) in sample B might be mostly attributed to the dimension of the plastic deformation zone around the indent (with a diameter ≈7 μm in this study), which makes the measured hardness not decrease sharply in such a small distance.

As expected, the Vickers microhardness of the treated surface of sample A (≈7.4 GPa) is significantly higher than that of sample B (≈2.3 GPa) and untreated sample (or the matrix of sample B, ≈1.3 GPa). The much lower Vickers microhardness of the top surface than the nanoindentation value at the depth of...
Fig. 4. Typical surface morphologies of wear scars on (a) sample A, (b) sample B and (c) sample C under the load of 10 N. The patterns of EDS elements counting of the zones labeled D, E and F on the wear scars are shown in (d), (e) and (f), respectively.
3 μm in sample B, as shown in Fig. 2(b), might be attributed to the fact that the chromized layer of this sample is too thin and brittle to support the employed load. After Vickers microhardness testing, serious cracks were observed around indents in sample B by using optical microscope, while no obvious cracks could be detected in sample A.

In Fig. 3, the variation of wear volume loss with the load for sample A is compared with those for sample B and the as-annealed coarse-grained one (sample C). It is clear that the wear loss values of chromized samples (A and B) are much lower than that of sample C under the same load, indicating the wear resistance of the low carbon steel sample has been improved significantly by the chromizing treatment. Moreover, the wear loss value of sample A is only about 1/6–1/3 that of sample B. The process of the SMAT followed by the duplex lower temperature chromizing treatment apparently further improves the wear resistance of the low carbon steel plate.

The SEM morphologies of wear scars and the corresponding EDS elements counting patterns shown in Fig. 4 shed light on the wear mechanisms. Under the load of 10 N, the wear loss of sample A occurs on a very small scale: the worn surface shows less evidence of fracture or plastic deformation, as shown in Fig. 4(a). While on sample B, there are apparent grooves formed by plowing action and microcutting under the effect of abrasive particles and few spalling pits formed by adhesive wear (marked by ‘D’), as shown in Fig. 4(b) and (d). That is to say, wear behaviors on both sample A and sample B are dominated by abrasive wear mechanism. Fig. 4(c) shows typically adhesive wear has happened on sample C: adhesive wear tracks of tearing and material-transferring bestrew on the worn surface. The dark regions in Fig. 4(b) and (c) (marked by ‘E’ and ‘F’, respectively) have been confirmed with the composition of W, as shown in Fig. 4(e) and (f). They might be transferred from the WC ball.

It is well known that chromizing treatments markedly enhance the surface hardness and wear resistance of ferrous alloys due to the formation of carbide layers. The much enhanced surface hardness and wear resistance of sample A relative to those of sample B might result from its superior microstructure, i.e., a much thicker cemented surface layer with smaller grain size. Microstructural refinement is expected to enhance hardness following the well-known Hall–Petch relationship [12,13], and then to result in the improvement in wear resistance according to Archard’s law of wear [14], i.e.,

\[ W = K \frac{P}{H} \]

where \( W \) is volume worn per unit sliding distance; \( P \) is the applied load; \( H \) is the hardness of the worn surface and \( K \) is the wear coefficient. Evident improvements of friction and wear properties were achieved in a low carbon steel plate with a hardened surface layer due to surface nanocrystallization by means of SMAT [15]. The fact that the measured hardness values of both chromized surfaces in the present work are much smaller than that of the conventional chromized surface (∼16 GPa) is expected to be further investigated.

3.3. Corrosion resistance

The potentiodynamic polarization curve of sample A measured in the sulfuric acid solution of NaCl was presented in Fig. 5(a), in comparison with those of sample B and sample C. All the tested surfaces show apparent pitting morphologies, observed either by using naked eyes or an optical microscope. Clearly, relative to the corrosion potential (\( E_{corr} \)) of sample C (about −0.52 V), \( E_{corr} \) was increased by the chromizing treatment, reaching about −0.45 V for sample A and sample B. This increase represents a nobler electrode potential being achieved, thus indicating the improvement of corrosion resistance of low carbon steel after the formation of a chromized surface layer.

Corrosion current density is commonly utilized as an important parameter to evaluate the kinetics of corrosion reactions. The corrosion rate is normally proportional to the corrosion current density measured through polarization [16]. As shown in Fig. 5(a), the chromized samples (A and B) corrode far more slowly than the untreated sample C once the corrosion potential is surpassed. Furthermore, by comparing the current density at the same polarized potential, a significant reduction of dissolution current for sample A than sample B can be observed. This represents the lower corrosion rate of the chromized SMAT sample.

![Fig. 5. Potentiodynamic polarization curves of sample A in the solutions (a) of 0.5 M NaCl+0.05 M H₂SO₄ and (b) of 0.25 M Na₂SO₄+0.05 M H₂SO₄, in comparison with those of sample B and sample C.](image-url)
In the sulfuric acid solution of Na$_2$SO$_4$, it is also found that the corrosion resistance is enhanced significantly by the lower temperature chromizing treatment, as well as that the corrosion resistance of the chromized SMAT sample is further improved relative to that of the chromized coarse-grained counterpart. As shown by potentiodynamic polarization curves in Fig. 5(b), both sample A and sample B exhibit apparent self-passivation behavior in the tested medium, while sample C shows no self-passivation. The passivation-maintaining current density of sample B is about 2 orders of magnitude lower than the corrosion current density of sample C. Meanwhile, the passivation-maintaining current density of sample A is only about 1/3 that of sample B.

It is well known that the chromized layer exhibits excellent corrosion resistance due to plenty of Cr atoms in it. In this study, the enhanced corrosion resistance of sample A relative to that of sample B might be attributed not only to the much thicker chromized surface layer, but also to the smaller grain size and more homogenously distributed phases in the top surface, as depicted in Section 3.1. Investigations on the nanocrystalline surface layers of 304 stainless steel [17] and Alloy 22 [18] show that their corrosion properties were promoted markedly due to the nanostructures. The decrease in the grain size increases the diffusivities of passivation-promoting alloying elements, thus promoting the rapid formation of protective film.

4. Summary

A chromized surface layer of about 20 $\mu$m thick was produced on the SMAT sample after a duplex chromizing process at 600 °C for 120 min followed by 860 °C for 90 min. Microhardness, resistances to wear and corrosion of the chromized SMAT sample were investigated, in comparison with those of the chromized coarse-grained counterpart and the as-annealed coarse-grained sample. It was demonstrated that the chromized SMAT sample showed larger hardness and superior resistances to wear and corrosion. Relative to the chromized coarse-grained counterpart, the much enhanced properties of the chromized SMAT sample might be attributed to the much thicker chromized surface layer with smaller grain size and more homogenous phase-distribution. It is anticipated that the process of the SMAT followed by a duplex chromizing treatment might be developed to significantly modify conventional chromizing technologies and to widen the application of chromizing techniques to a larger variety of materials.

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