Electrochemical analysis and SEM-EDX characterization of laser-treated weathering steel plate

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1. Introduction Weathering steel (WS) structures are expected to have corrosion resistance due to protective corrosion layer formed on the surface. However, some of the WS structures located in a highly corrosive environment may still suffer from airborne sea salt caused severe corrosion problems, thus proper surface preparations are required. Laser surface treatment is a promising technique, with advantages of effective cleaning and environment-friendly. The principle of laser cleaning is based on laser ablation to remove the surface contaminations. This study reports a comparative study on electrochemical properties of WS pretreated by continuous wave (CW) laser and milling process, laser irradiation was performed under three different laser energy densities. The surface chemical composition was identified by using scanning electron microscope-energy dispersive X-ray spectrometry (SEM-EDX), then open circuit potential (OCP) and potentiodynamic polarization of specimens were measured under identical test condition.

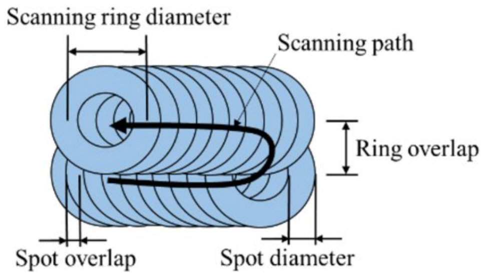
2. Specimen and test method The chemical composition of WS as shown in Table 1. The whole steel plate surface was irradiated with certain laser ring, velocity and direction. To ensure a thorough coverage for laser treatment. The adjacent laser ring was overlapped in ring width (equals to laser spot diameter), and each parallel laser path was overlapped in ring diameter, these two overlapped areas were labeled as spot overlap and ring overlap respectively, as shown in Fig.1 (b). The laser output energy divided by irradiated area was defined as energy density. Three different laser energy density of 3077, 1739 and 600 J/cm^2 were adopted in the irradiation procedure and classified into W-A, W-B and W-C, as shown in Table 2. On the other hand, WS plate treated by milling process is used as a comparison to laser surface treatment.

SEM-EDX was used to identify the elements distribution of Iron and Oxygen on the specimen surface. For the electrochemical measurements, OCP and potentiodynamic polarization curves were performed in 3.5 mass% NaCl aq solution as an electrolyte at room temperature, with an electrochemical cell consisting of three electrodes. A platinum plate as a counter electrode, the WS plate as the working electrode, and Ag/AgCl in saturated potassium chloride (Sat.KCl) solution as the reference electrode. The potentiodynamic polarization curves were performed after one-hour immersion in electrolyte to reach stable stage, then tested from -250 mV to +250 mV (vs. OCP) with the scanning speed of 0.167 mV/s.

Table 1 Chemical composition of weathering steel (mass%)

Chemical composition	C	Si	Mn	P	S	Cu	Ni	Cr	Mo
Mass (%)	0.11	0.25	0.68	0.01	0.02	0.32	0.11	0.49	0.10

(a) Laser-treated area



(b) Overlap area

Fig.1 Schematic image of laser surface treatment

Table 2 Energy density of different laser condition

Laser condition	W-A	W-B	W-C
Energy density (J/cm^2)	3077	1739	600

3. Test results The surface observation by SEM along with EDX mapping indicates that the laser-treated surface presents an oxide layer. As shown in Fig.2, the highest and lowest oxygen content among laser-treated WS were W-A and W-C specimens, present 19.0 mass% and 10.5 mass% of oxygen respectively. With the laser energy density increases, the Oxygen content increases on the surface. Comparing with the unirradiated W-Milling specimen contents of 1.15wt%, the Oxygen content sharply increased to over 10% after laser treatment. With higher energy density, the W-A and W-B showed clearly Oxygen concentration along the laser scanning path.

Fig.3 shows the OCP distributions of four specimens under 24 hours immersion time. From the transients, it is obvious that the milling specimens present more cathodic values compared to the laser specimens. Results of 24 hours immersion time indicated the laser-treated specimens maintain higher potential with time-lapse. W-A and W-C specimens exhibit most anodic and cathodic

Keywords: Weathering steel, Electrochemical properties, Laser irradiation, Corrosion resistance, SEM-EDX analysis
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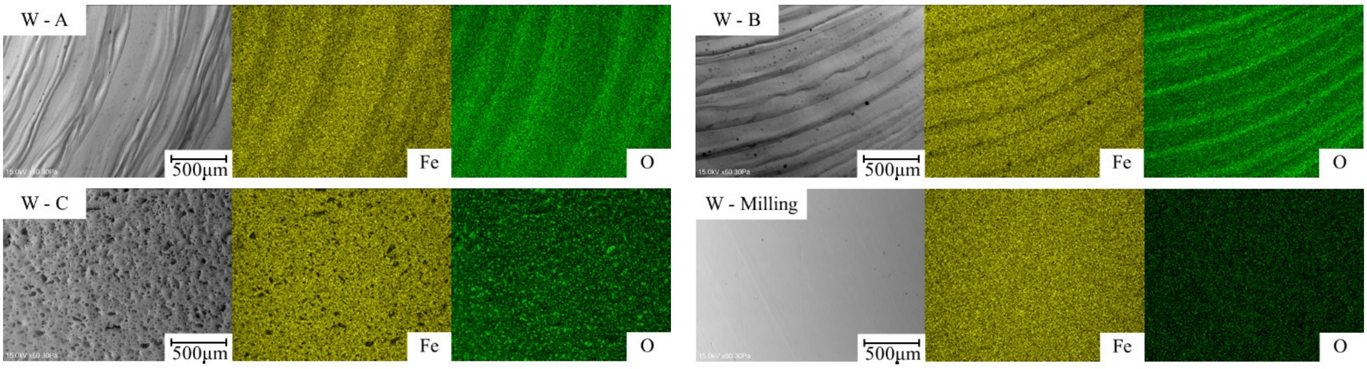

Fig.2 SEM micrograph and EDX mapping results of specimens

Table 3 Content of oxygen in different laser condition

Laser condition	W-A	W-B	W-C	W-Milling
Oxygen(mass%)	19.04%	17.15%	10.48%	1.15%

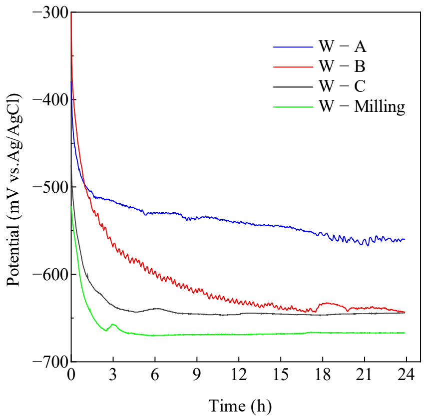

Fig.3 Open circuit potential of the weathering steel in 3.5 mass% NaCl aq for 24 hours

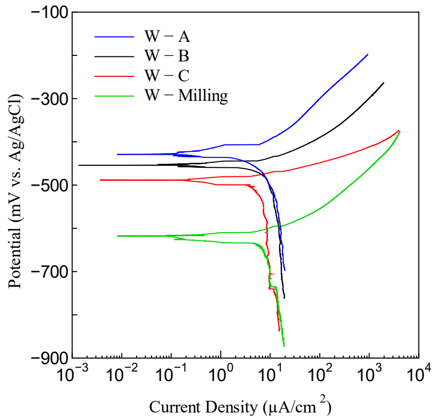

Fig.4 Polarization curves of the weathering steel in 3.5 mass% NaCl aq.

Table 4 Potentiodynamic polarization fitting results and protective efficiency rates of the WS in 3.5 mass% NaCl aq solution

Specimen	E_{corr} (mV vs. Ag/AgCl)	i_{corr} (μA/cm^2)	P_{EF}(%)
W-A	-448	4.13	60.3
W-B	-513	5.81	44.2
W-C	-589	5.84	43.9
W-Milling	-623	10.41	—

value respectively, which related to the highest and lowest laser energy density. After 1h OCP test to stabilize the specimen condition, the potentiodynamic polarization curves have been conducted to evaluate the instantaneous corrosion behavior of WS[1], as shown in Fig.4. The corrosion potential (E_{corr}) of the WS shifted to the positive value compared with the milling specimens. The corrosion current (i_{corr}) was seen as the most critical parameter to evaluate the corrosion performance, the lower i_{corr} indicates the better corrosion resistant performance, as shown in Table 4. W-A specimen possessed the highest E_{corr} of the -448 mV, along with the lowest i_{corr} of 4.13 μA/cm^2. However, the E_{corr} reduced to -589 mV and i_{corr} increased to 10.41 μA/cm^2 for W-B. Thus higher energy density results in more significant potential shifting of laser-treated specimens. From the calculated protective efficiency (P_{EF})[2] in Table 4, where the $i_{corr,0}$ represents corrosion current density of the milling WS plate, and the $i_{corr,N}$ represents the corrosion current density of the laser-treated WS plates. It is obvious that all laser conditions show beneficial effects. W-A specimens possessed the most positive potential among the others. The i_{corr} of laser-treated specimens are lower than milling specimen, present slower corrosion rate. The most significant i_{corr} decreasing appeared under W-A condition, results in the highest protection efficiency of 60.3%, which confirmed the effects of laser irradiation on electrochemical properties are strongly related to energy density.

4. Summary 1) The laser surface treatment has a positive effect on the corrosion resistance of WS. 2) Along with the increasing energy density, the corrosion resistance of laser-treated WS improved. 3) Higher laser energy density results in more oxide on the treated surface, which improved corrosion resistance further.

Reference 1) U. Trdan and J Grum: Evaluation of corrosion resistance of AA6082-T651 aluminum alloy after laser shock peening by means of cyclic polarization and EIS methods, Corrosion Science, Vol.59, pp.324-333,2012. 2) Q. Ma, Z. Tong, and W. Wang, G. Dong: Fabricating robust and repairable superhydrophobic surface on carbon steel by nanosecond laser texturing for corrosion protection, Applied Surface Science, Vol. 455, pp.748-757, 2018.