

Effect of Laser Marking on Corrosion Performance of Metallic Materials in Different Environments

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ABSTRACT

This study was undertaken as an effort to understand the effect of laser marking on corrosion behavior of metallic materials. Two laser-marking companies and two metallic materials low alloy steel AISI 4140 (UNS G41400) and stainless steel AISI 420M (UNS S42000) were selected for this study. The obtained results indicate that the laser marking process created a thin black oxide layer on the metal surfaces without significantly affecting the base materials. In term of corrosion performance, the obtained results suggest that the laser marking does not have a significant effect on pitting corrosion resistance after 72 testing hours per ASTM G48¹ or general corrosion resistance after 42 days of salt spray test per ASTM⁽¹⁾ B117² or Sulfide Stress Cracking (SSC) resistance after 720 hours per NACE⁽²⁾ TM0316³ of the low alloy steel. However, in the case of stainless steel, the laser marking process was found to slightly to significantly affect the general corrosion resistance and SSC resistance of the stainless steel. One set of the laser marked stainless steel failed the SSC test while the unmarked specimen, tested in the same testing batch, passed. This illustrates the need to understand the potential effect of laser marking on corrosion resistance for a given material grade.

Key words: Laser marking, corrosion, SSC, low alloy steel, stainless steel.

INTRODUCTION

Laser marking of materials, especially metallic materials, has been widely used in many industrial fields from automotive to aerospace to decorative applications among others thanks to its fast marking time and its ability to work on a lot of materials. However, laser marking is a thermal process that could modify the metallic surface property without significantly changing the basic material properties⁴. It forms one or more layers of oxides and/or nitrides (depending on the operating conditions) on the metal surface⁵. Therefore, the corrosion behavior of the marked area could be different from that of the unmarked area. There were several studies on the effect of laser marking parameters on the corrosion resistance of metallic materials^{6,7}, although most research until now has been focusing on studying the

⁽¹⁾ ASTM International, 100 Barr Harbor Dr., West Conshohocken, PA 19428-2959.

⁽²⁾ National Association of Corrosion Engineers.

readability and repeatability of the marking⁸⁻¹⁰. In this study, we aim to systematically compare the corrosion performance of different metallic materials in a variety of corrosive environments from atmospheric corrosion to pitting corrosion and CO₂/H₂S corrosion. Low alloy steel and stainless steel are selected for Phase I of this study. Other materials such as duplex stainless steel and Nickel based alloys will be studied at a later stage.

EXPERIMENTAL PROCEDURE

One heat of low alloy steel AISI 4140 quenched and tempered to 80 ksi (552 MPa) Minimum Yield (MY) with 22 HRC max hardness and two heats of stainless steel AISI 420M quenched and tempered to 80 ksi (552 MPa) MY with 22 HRC max hardness were used for the study. The specimens for the various tests were machined to the same dimension of 70 mm x 25 mm x 10 mm (Figure 1) except the Sulfide Stress Cracking (SSC) test which utilizes the standard specimen of 115 mm x 15 mm x 5 mm per NACE TM0316. The chemical compositions of each heat of material used in the study are given in Table 1. Do note Heat C was quite similar to Heat B. All testing, except SSC testing, in this study was done on Heat A for 4140-80 (i.e. AISI 4140 with 80 ksi MY) and Heat B for 13Cr-80 (i.e. AISI 420M with 80 ksi MY). Yttrium Aluminum Garnet (YAG) laser was used for the laser marking. The laser marking companies typically do not disclose any process details (wavelength, pulse, frequency, focal diameter, scanning speed, laser intensity, etc.) related to the laser marking process as they are considered proprietary. In the first part of the study all the test specimens used in this project were laser marked by one company. We also had three additional sets of SSC specimens of 4140-80 and 13Cr-80 materials marked by a second company and which were used to replicate the SSC test. The test plan is detailed in Table 2.

Table 1: Chemical composition of material heats

Material	Heat ID	%C	%Si	%Mn	%P	%S	%Cr	%Mo	%Ni	%Al	%Cu
4140-80	A	0.41	0.30	0.95	0.012	0.004	1.06	0.21	0.13	0.019	0.21
13Cr-80	B	0.20	0.29	0.67	0.013	0.002	12.91	0.01	0.10	-	0.02
13Cr-80	C	0.20	0.46	0.51	0.016	0.001	13.08	-	0.16	-	0.02



Figure 1: Front side and back side of the marked specimens.

Table 2: Test plan

Material	Heat ID	Laser-marking Company	Planned Tests
4140-80	A	I	- Hardness measurement - Micro-examination - Salt spray test - Pitting corrosion test - SSC test
	A	II	- SSC test
13Cr-80	B	I	- Hardness measurement - Micro-examination - Salt spray test - Pitting corrosion test - SSC test
	C	I	- SSC test
	C	II	- SSC test

Characterization

Hardness Measurement

After being marked, all specimens of 4140-80 (Heat A) and 13Cr-80 (Heat B) were hardness inspected by Rockwell method per ASTM E18¹¹ to provide a quick hardness comparison between the marked and unmarked areas.

Micro-examination

The cross-section of the marked area of 4140-80 (Heat A) and 13Cr-80 (Heat B) was also examined by an optical microscopy and a microhardness tester using HV10. The hardness testing followed ASTM E92¹².

Salt Spray Test per ASTM B117

The salt spray test was conducted by a third-party lab in accordance with ASTM B117. Two specimens (one marked and one unmarked) each from Heat A and Heat B were machined and tested in the same chamber under a neutral salt spray for a duration of 42 days with a daily visual inspection to detect the first rust spot of each specimen. The test conditions are provided in Table 3. At the end of the test, the specimens were carefully removed, gently washed in clean flowing water not warmer than 38°C to remove salt deposits, and then immediately dried.

Table 3: Salt spray test conditions

Concentration of Sodium Chloride	5 wt.%
pH of Fallout (Average)	6.8 (Range: 6.5 to 7.2)
Fallout Rate (Average)	1.6 ml (Range: 1 to 2) / 80 cm ² / hour
Specific Gravity (Average)	1.030 g/ml (Range: 1.025 to 1.040)
Test Duration	42 days
Temperature	23 ± 3°C

Pitting Corrosion Resistance Test per ASTM G48 (Method A)

The pitting corrosion resistance test was conducted in accordance with ASTM G48 (Method A). Multiple test specimens of 4140-80 (Heat A) and 13Cr-80 (Heat B) were tested in ferric chloride solution at 25°C and then decreased to 5°C for 72 hours. All the test specimens have the same dimension (Figure 1) with one surface marked and the others unmarked. After 72 hours, all surfaces were cleaned by flowing water, photographed, and weighed. Pit depth was also measured when pitting was observed.

Sulfide Stress Cracking (SSC) Test per NACE TM0316

To understand the effect of laser marking on corrosion resistance of a material in sour service, a SSC test was performed per NACE TM0316 (four-point bend test). This testing was done on specimens from Heat A (4140-80) and Heat B (13Cr-80) marked by Company I per Table 2. Based on the results on Heat B; SSC testing was done on Heat C (13Cr-80) also laser marked by Company I. Finally to further replicate the results of the SSC testing, testing was also conducted on specimens from Heat A (4140-80) and Heat C (13Cr-80) marked by Company II. Each SSC test consisted of three marked specimens and one unmarked specimen which was used as a benchmark for comparison. The testing condition of SSC test is provided in Table 4 in accordance with NACE TM0316 for each material grade. After 720 hours of testing, both marked and unmarked specimens were visually examined and then non-destructively inspected by magnetic particle inspection (MPI). The cross-sections of all specimens were also observed under a microscope with magnification of 500X.

Table 4: SSC test condition

Material	4140-80	13Cr-80
Sample Dimension	115 mm × 15 mm × 5 mm	115 mm × 15 mm × 5 mm
Surface Preparation	800 grit	800 grit
Test Duration	720 hours	720 hours
Applied Stress	80% AYS	100% AYS
Test Solution	NACE TM0177 Solution A [13]	NACE TM0177 Solution B [13]
pH Requirement	Initial: 2.7 ± 0.1 (maximum 4.0 during testing)	Initial: 3.5 ± 0.1 (maximum 4.0 during testing)
De-aeration (by N₂)	20 hours	8 hours
Test Gas	100% H ₂ S (1 bar)	10% H ₂ S (0.1 bar) + balance CO ₂
Test Temperature Requirement	23 ± 3°C	23 ± 3°C