Sensitization of laser-beam welded martensitic stainless steels

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Abstract

Ferritic and martensitic stainless steels are an attractive alternative in vehicle production due to their inherent corrosion resistance. By the opportunity of press hardening, their strength can be increased to up to 2000 MPa, making them competitors for unalloyed ultra-high strength steels. Welding, nevertheless, requires special care, especially when it comes to joining of high strength heat treated materials. With an adopted in-line heat treatment of the welds in as-rolled as well as press hardened condition, materials with sufficient fatigue strength and acceptable structural behavior can be produced. Because of microstructural transformations in the base material such as grain coarsening and forced carbide precipitation, the corrosion resistance of the weld zone may be locally impaired. Typically the material in the heat-affected zone becomes sensitive to intergranular cracking in the form of knife-edge corrosion besides the fusion line. The current study comprises of two text scenarios. By an alternating climate test, general response in a corroding environment is screened. In order to understand the corrosion mechanisms and to localize the sensitive zones, sensitisation tests were undertaken. Furthermore, the applicability of a standard test according to ASTM 763-83 was examined. It was found that the alternative climate test does not reveal any corrosion effects. Testing by the oxalic acid test revealed clearly the effect of welding, weld heat treatment and state of thermal processing. Also application of the standard which originally suited for testing ferritic stainless steels could have been justified.

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1. Introduction

Intergranular corrosion of stainless steels is due to the intergranular precipitation of chromium rich M23C6 type carbides resulting in the reduction of chromium content in the adjacent matrix surrounding the grain boundaries. If the chromium percentage in the stainless steels falls below the amount required for the formation of passive oxide layer, corrosion occurs along the chromium depleted regions. The precipitation of chromium carbides occurs when the material is slowly cooled through 550-850°C, as the carbide precipitates are stable below 850°C and the diffusion of chromium is sufficiently rapid above 550°C (Frankenthal. and Pickering. 1973, Grubb 2011, Kim et al. 2010). This loss of corrosion resistance of stainless steels when cooled in a particular temperature range either during heat treatment or welding is called sensitisation.

Ferritic stainless steels with low carbon, martensitic stainless steels with medium carbon find their application in wide range of fields. A less time consuming yet effective technique was required to understand their corrosion behaviors. Electrochemical corrosion tests are nondestructive and rapid, making them the developer’s choice for intergranular corrosion detection. Oxalic acid etch test is used to detect the presence of sensitisation and compare the severity of sensitisation in the various zones of the weld. It is described under the standards ASTM 763-93 Practice W (ASTM 2015) and ASTM A262 Practice A (ASTM 2013) are allotted for ferritic and austenitic stainless steels respectively. The correlation of these standards to the martensitic stainless steels is carried out in this work.

### Nomenclature

| Abbreviation | Description |
|--------------|-------------|
| HAZ          | heat-affected zone |
| HT           | high temperature |
| RT           | room temperature |
| TMs          | martensite start temperature |

2. State of the art

The alternating climate test according to VDA 621-415 (VDA 1982) simulates the environmental effects on single specimens or a structure in a standardized and controlled atmosphere. With this global test complete structures consisting of a base material and a coating can be tested. Detailed information on the material’s response of material in different states to environmental effects are not target of this method.

Ferritic stainless steel welds were extensively studied by several authors (Alonso-Falleiros., Magri and Falleiros 1999, Amuda and Mhrida 2011, Greeff and du Toit 2006). It is understood from their work that the control of weld heat input and cooling rate plays a major role in sensitisation. Overlapping of the heat affected zones during multiple welds, welding at low heat input followed by continuous cooling of the welds are specified as some of the reasons for sensitisation. It is understood that the fast cooling rates of ferritic stainless steel due to low heat input or without any preheating of the samples suppressed the austenite formation leading to sensitisation by the formation of ferrite-ferrite grain boundaries. Whereas slow cooling led to austenite formation and grain boundary martensite when cooled further. This slow cooling was found to prevent sensitization (Du Toit, van Rooyen and Smith 2012). The cooling rates are dependent on section thickness and heat input (Alvarez-Moreno 1992, Akselsen et al. 2004). With increase of the carbon content the carbides become the origins of sensitisation. The chromium-depleted zones are attacked by the etchant (Grubb 2011). The degree of corrosion depends on the nature of carbides. In laser remelted layers, fine and homogenously distributed carbides can lead to an improvement of corrosion resistance (Fischer, B., Neidel 2014, Kwok 2003). All these studies and criteria are suitable only for as rolled and annealed ferritic stainless steels. Tempering of martensitic stainless steels at 400°C or below showed the martensitic structure without any grain boundary carbides (Alonso-Falleiros., Magri and Falleiros 1999). Not much has been explored in the intergranular sensitization of welding of martensitic stainless steels and also for press hardened materials. So this study is aimed at understanding the effect on these materials (Herbsleb and Schwaab 1986, Pistorius and Coetzee 1996).
3. Materials and Methods

3.1. Materials and welding process

Three different stainless steel grades with varying microstructures and properties were considered to analyze their tendency for sensitization after laser welding. The compositions of these stainless steels are given in Table 1. These stainless steels were welded in as rolled condition and hot pressed condition. These were also welded in as rolled condition and then hot pressed to eliminate the difference in properties that arise during welding in heat affected zone (HAZ) and base material. The constituents of these stainless steels are listed in the table below. Hot stamping is a non-isothermal forming process in which the material is heated to the austenitising temperature, formed to a required shape and then cooled to obtain a martensitic structure thereby resulting in the increased strength and hardness.

Table 1 Chemical composition (weight %) of the stainless steels

|   | C     | Cr    | Mn    | Si    | Ni    | P    | S    | N    |
|---|-------|-------|-------|-------|-------|------|------|------|
| 1.4003 | 0.030 max. | 10.5-12.5 | 1.50 max. | 1.00 max. | 0.30 - 1.00 | 0.040 max. | 0.015 max. | 0.030 max. |
| 1.4021 | 0.16-0.25 | 12.0-14.0 | 1.50 max. | 1.00 max. | -     | 0.040 max. | 0.015 max. | -     |
| 1.4034 | 0.43-0.50 | 12.5-14.5 | 1.00 max. | 1.00 max. | -     | 0.040 max. | ≤ 0.03 | -     |

Table 2. Heat treatment parameters during welding

| Condition | Pre-heating | Intercooling | Tempering | Dwell time |
|-----------|-------------|--------------|-----------|------------|
| 1         | RT          | -            | none      | -          |
| 2         | RT          | -            | 400°C     | 300 s      |
| 3         | T_{ms}      | None         |           | -          |
| 4         | T_{ms}      | 200°C        | 400       | 300 s      |

During welding, some trials were conducted by preheating to their respective martensite start temperatures which were 400°C, 350°C and 300°C for 1.4003, 1.4012 and 1.4034, respectively. In some trials, the specimens were tempered at 400°C for 5 minutes and then cooled down to room temperature. In the rest, both preheating and tempering was carried out (table 2).

3.2. Alternating climate test

In order to investigate the susceptibility against crevice corrosion under condition of an incomplete cathaphoretic primer an alternating climate test according to the standard VDA 621-415 was carried out. Specimens of all materials in all states, welded at room temperature as lap joints of similar material at an input energy of 48 kJ/m, were opened to from a wedge and dip coated with Cathoguard 800. Following coating the wedge was opened in order to break the primer. In this condition the specimens were introduced to the testing chamber. Seven cycles, one week each, were run in a salt spray chamber. The specimens were inserted in both, hanging and standing position in order to evaluate the effect of fogging and to ensure the removal of corrosion products. After weathering the specimens were opened and the wedge was removed, analogously to the test carried out for resistance spot welds. The specimens then were opened fully by inserting a cylinder with diameter 45 mm. Termination criterion was the fracture of the specimen of a bend angle of more than 180°.
3.3. Oxalic acid test

Round specimens with one inch diameter for oxalic acid test were laser cut from the welded sheets in a way that the specimens contain the regions of base material, HAZ and weld zone. The welds were located at the centerline of the plates. These specimens were then ground followed by fine polished with 2\(\mu\) diamond paste. Then the specimens are electrolytically etched using 10% aqueous oxalic acid solution under a current density of 1 A-cm\(^2\) for 90 seconds.

4. Results and discussion

4.1. Alternating climate tests

Upon opening the specimens after the climate test it became obvious that the primer approached only 10 to 15 mm distant from the weld. No corrosion damage of the weld was determined. Fig. 1 shows photographs of the inner surface of a specimen from 1.4021. The primer remained intact, showing that the opening angle by the wedge was too small to introduce cracks.

![Fig. 1. View on the inner surface of specimen 1 (1.4021, KTL, suspended)](image)

From all materials a ductile behavior on crevice opening could be demonstrated for 1.4003 in both, rolled and hardened condition. In rolled condition some of the specimens broke in shear mode at bend angles of up to 135°. In general an opening angle of 180° was attained. The force that had to be applied for the opening was considered subjectively high. Specimens from the other materials broke at fairly low forces or even during clamping. The fracture occurred in the high-temperature HAZ. With respect to the failure mode no effect of the corrosive load could be identified. There was no difference between corroded and not corroded welds. An effect of the position in the salt spray chamber was not determined.
4.2. Sensitisation tests

The oxalic acid etch tests on the 1.4003 in the as rolled material that were carried out without any heat treatment and are found to oblige with the results obtained by Greeff and du Toit (2006). According to their work, it is found that no sensitisation occurs in the high temperature heat affected zone in the presence of grain boundary martensite. Also, the microstructures obtained in heat affected zones of 1.4021 and 1.4034 showed no evidence of sensitized or ditch structures. But the carbides in the material were etched during the test and the quantity of carbides is found to increase with the increase in carbon content in each material (Fig 2). The microstructure changes from ferrite with carbides to tempered martensite with carbides as the carbon content increases from 0.03 to 0.5 %.

Specimens of 1.4003 in hot pressed and welded condition with no heat treatment and only tempering at 400°C showed no evidence of sensitized structures in weld, HAZ and base material. But the samples that were preheated showed the dual and ditch structure in the HAZ. Fig 3 show the fusion zone, HAZ and base material of the material
preheated to 400°C held at 200°C during welding and then tempered at 400°C for 5 minutes. SEM images also confirm that the sensitized zones of HAZ and the presence of carbides in HAZ and along the fusion zone. The carbides that were segregated along the dendrites of the weld zone were etched during the test and are shown in the fig 3 (a) and 4(a).

Press hardened and welded 1.4021 and 1.4034 samples showed ditch structures in the low temperature heat affected zone for all heat treatment conditions whereas the base material and fusion zone stay unaffected during the oxalic acid etch test. The reason for this sensitization effect could be due to the cooling cycle during welding than heat treatment.

Hot pressing was carried out after welding to aid in better diffusion of alloying elements across the HAZ and the weld. Welded and then hot pressed samples showed the presence of carbides and martensite needles in all the stainless steels. Few dual structures were observed in HAZ and fusion zone of 1.4034. Figure 4b shows the martensitic carbides that are etched during the test.

5. Conclusions

In the alternating climate test on press hardened materials no effect on the fracture of the specimens was observed. The fracture behaviour remained unchanged compared to not corroded specimens:

- Ferritic 1.4003 exhibited ductile behaviour with bend angles greater than 180°C. If cracking occurred, the specimens failed in shear cracks.
- Ferritic-martensitic 1.4021 exhibited brittle failure. Cracking was observed in the high-temperature HAZ.
- Martensitic 1.4034 exhibited brittle failure. Cracking was observed in the high-temperature HAZ.

Also no effect of the position of the specimen in the weathering chamber could be found.

|                | RT/RT | T<sub>M</sub>/RT | RT/400°C | T<sub>M</sub>/400°C |
|----------------|-------|------------------|----------|---------------------|
| 1.4003 X2 CrNi 12) |       |                  |          |                     |
| Welding of hardened sheets | none | HAZ and BM ditched | none | HAZ ditched |
| Hardened after welding | none | - | none | - |
| 1.4021 (X21 Cr12) |       |                  |          |                     |
| Welding of hardened sheets | HAZ sensitized | HAZ sensitized | HAZ sensitized | Fused zone and HAZ sensitized |
| Hardened after welding | none | none | none | none |
| 1.4034 (X46 Cr13) |       |                  |          |                     |
| Hardened after welding | HAZ sensitized | HAZ sensitized | HAZ sensitized | HAZ and BM ditched |
| Welding of hardened sheets | none | HAZ ditched | HAZ ditched | Fused zone and HAZ ditched |

By the experiments on sensitisation it could have been shown that practice A of ASTM 262-13 is applicable for the investigation of welds in press-hardened and rolled martensitic stainless steels with a carbon content of up to 0.46 weight percent. Table 3 shows the complete results. The following reactions were found:

- The oxalic acid test is a screening test to understand the sensitization as it is less time consuming than other tests. The oxalic acid etch test is standardized for austenitic and ferritic stainless steels. The tests were effective in detecting the sensitization in martensitic stainless steels as well.
- In the as rolled condition at RT, all the materials were free from sensitization but the amount of carbides increased as the increase in C content from 1.4003 to 1.4034.
Weld heat treatment plays a major role in the process of sensitization. In the hot pressed and welded condition, 1.4021 and 1.4034 showed the presence of ditch/sensitized structure in HAZ under all heat treatment conditions. 1.4003 showed HAZ sensitization only in the preheated samples. In the welded and hot pressed condition, Carbides and martensite needles were observed in all the stainless steels. Few dual structures were observed in 1.4034 but complete sensitisation of the grains was not observed showing the reduced proneness to sensitisation as compared to hot pressed and welded specimens. To further understand the chromium depletion in the areas next to the sensitisation, Electron energy loss spectroscopy (EELS) should be conducted to highlight Cr depletion from the grain boundaries and Cr-enrichment on the grain boundaries where the carbides are present. Another technique could be electrochemical potentiostatic test where you control the potential in a range that causes Cr-depleted zones to dissolve, without attacking the matrix. It is performed in a 0.5M H2SO4 at 0 VSCE (saturated calomel electrode) for 300 seconds.

In order to increase the knowledge about the response of welds in ferritic and martensitic stainless steels on environmental conditions test on corrosion fatigue will be carried out. In conjunction with the results described above they will complete the knowledge on corrosion behavior of these classes of steels in hardened and welded state.

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References

Akselsen, O.M., Rørvik, G., Kvaale, P.E., van der Eijk, C, 2004. Microstructure-property relationships in HAZ of new 13% Cr martensitic stainless steels. Welding Journal Research Supplement, May 2004, 160 - 167
Alonso-Falleiros.N., Magri.M., Falleiros.I.G.S., 1999. Intergranular corrosion in a martensitic stainless steel detected by electrochemical tests. Corrosion 55, 769-778
Alvarez Moreno, L.F., 1992. Transformaciones de inequilibrio producidas pro ciclos anisotermicos in aceros inoxidables martensiticos tipo 13Cr y 14CrMoV, PhD thesis, Universidad Complutense de Madrid
Amuda, M.O.H., Mridha, S., 2011. An overview of sensitization dynamics in ferritic stainless steel welds. International Journal of Corrosion, Article ID 305793, 9 pages
ASTM 262, 2013: Standard practices for detecting susceptibility to intergranular attack in austenitic stainless steels. ASTM International, West Conshohocken
ASTM A763-15, 2.15. Standard Practices for Detecting Susceptibility to Intergranular Attack in Ferritic Stainless Steels, ASTM International, West Conshohocken, PA
Du Toit, M., van Rooyen, G.T., Smith, D.,2012. Heat affected zone sensitisation of low chromium stainless steels during welding. Proceedings of the IIW Regional Congress, Johannesburg, South Africa. 159-171
Frankenthal.R.P and Pickering.H.W., 1973. Intergranular Corrosion of a Ferritic Stainless Steel, Journal of the Electrochemical Society, 120 (1) 23-26
Fischer, B., Neidel, A., 2014. Intergranular corrosion in retaining rings made of X39CrMo17-1 and X39Cr13. Praktische Metallographie 51(6), 462 - 474
Greiff, M.L., du Toit, M., 2006. Looking at the sensitization of 11-12% chromium EN 1.4003 stainless steels during welding. Welding Journal Research Supplement, 243-s - 251-s
Grubb, J.F., 2011. Martensitic stainless steels. Uhlig’s Corrosion Handbook. John Wiley & Sons, Hoboken. 707 - 713
Herbsleb, G., Schwaab, P., 1986: Die Bedeutung des Oxalsäure-Tests für die Prüfung der Korrosionsbeständigkeit nichtrostender Stahle. Werkstoffe und Korrosion 37, 24-35.
Kim, J.K., Kim Y.H., Lee, J.S., Kim, K.Y., 2010. Effect of chromium content on intergranular corrosion and precipitation of Ti-stabilized ferritic stainless steels, Corrosion Science, 52 (5) 1847-1852
Kwok, C.T., Lo, K.H., Chen, F.T., Man, H.C., 2003. Effect of processing conditions on the corrosion performance of laser surface-melted AISI 440C martensitic stainless steel. Surface and Coatings Technology 166, 221 – 230
Pistorius, P.C., Coetzee, M., 1996. Sensitization of type 430 ferritic stainless steel during continuous annealing. The Journal of The South African Institute of Mining and Metallurgy. May/June 1996, 119-125
VDA, 1982. VDA-Prüfblatt 621-415 1982-02: Anstrichtechische Prüfungen, Prüfung des Korrosionsschutzes von kraftfahrzeuglackierungen bei zyklisch wechselnder Beanspruchung. Verband der Automobilindustrie, Düsseldorf