1 Introduction

Precipitation hardening martensitic stainless steel has been developed to overcome the limitation of fully austenitic and fully martensitic stainless steels on account of strength, ductility, toughness and high temperature performance capability. It is widely used in various industries such as nuclear, chemical, aircraft, and naval due to its favourable combination of excellent mechanical properties, good weldability and adequate corrosion resistance. One of the most commonly used alloys of this type is DIN 1.4542 which is identical with the type 17-4 PH stainless steel (ASTM A705 Grade 630). It has very low carbon content and approximately 3 wt % Cu is added to achieve significant hardness and strength.

The microstructure of this steel in solution annealed condition comprises largely of precipitation-free martensite containing a minor fraction of elongated δ-ferrite. The martensite phase consists of lath structure with very high density of dislocations [1]. Atom probe analyses of the solution annealed martensite phase has shown that the martensite is in a supersaturated solid solution containing all solute atoms homogeneously distributed [2].

On ageing, precipitation of coherent copper-rich clusters occur increasing hardness notably. On overageing, these coherent precipitates transform in to incoherent fcc epsilon-phase precipitates [2, 3] and hardness decreases gradually [1]. The resistance of the alloy to hydrogen embrittlement is primarily affected by the hydrogen concentration, the microstructure and the state of hydrostatic stresses. The internal characteristics of trapping sites for hydrogen play a very important role on the hydrogen embrittlement susceptibility of the material [4].

A solution annealed precipitation hardening martensitic stainless steel is exposed to high temperature during welding. Significant changes in the microstructure of the weld and heat affected zone (HAZ) may occur. The residual stresses induced during cooling of the weldment increase the susceptibility of the material to stress corrosion cracking and hydrogen embrittlement [5].

The purpose of this paper is to report the results of the hydrogen loading of a thin sheet weldment and the cracks generated in the heat affected zone of solution treated and welded samples.

2 Material and experimental methods

Two pieces of stainless steel sheet type DIN 1.4542 in solution annealed (SA) condition with a thickness of 1.6 mm were welded together. Welding was done by TIG without filler material with two welding passes from both sides (see Fig. 1). Chemical composition of the material is given in table 1. After welding, the welded sheets were exposed to hydrogen loading during galvanic Cr-
plating. Some cracks perpendicular to the seam weld were noticed. Dye penetration check and radiography (Fig. 2) were carried out on the samples. Dye penetration shows that one side of the plate has more open cracks to the surface than the opposite side.

**Table 1. Chemical composition of the material**

<table>
<thead>
<tr>
<th>Elements</th>
<th>C</th>
<th>Si</th>
<th>Mn</th>
<th>P</th>
<th>S</th>
<th>Ni</th>
<th>Cr</th>
<th>Cu</th>
<th>Nb</th>
<th>Fe</th>
</tr>
</thead>
<tbody>
<tr>
<td>Composition (wt%)</td>
<td>0.03</td>
<td>0.48</td>
<td>0.70</td>
<td>0.025</td>
<td>0.001</td>
<td>4.9</td>
<td>15</td>
<td>3.08</td>
<td>0.25</td>
<td>Balance</td>
</tr>
</tbody>
</table>

X-ray micro radiography has been performed by using a phoenix|225s microfocus tube at 120 kV and 100 µA and a PerkinElmer RID 1640 flat panel detector with 1024×1024 pixel averaging over 200 frames of 400 ms recording time. A resolution down to (10 µm)^2/pixel has been chosen for imaging the weld-seam and the crack region. Micro radiography shows that all the cracks with different lengths begin periodically along the weld seam. Metallography was carried out on the base metal (Fig. 3 and 4) and the welded area (Fig. 5 and 6) to characterize their microstructure. Two different types of etchants were used, W II and Beraha I [6] to check delta ferrite. Micro hardness profiles across the weld, in the HAZ and base material (ST-section) were measured according to EN 6507 in Vickers HV 1 and is presented in Fig. 7.

**Figure 1:** Macrograph of the cross-section of welded region / Etched with W II (Wallner)

**Figure 2:** X-ray micro radiography image of the welded sheet: cracks are visible on the both sides perpendicular to weld-seam

To study the crack initiation and growth, cracks identified with the help of radiography were opened by tensile testing perpendicular to the direction of the cracks at room temperatures. The fracture surfaces were studied with scanning electron microscopy to locate and identify the crack tip (Fig. 8) and the fracture mode (Fig. 9 and 10). Location and position of the susceptible microstructure were identified and samples prepared thereof investigated by targeted high resolution transmission electron microscopy (HRTEM) (Fig 11 to 13).
Figure 3: Base metal with typical martensitic microstructure appearing brown and blue. No delta ferrite is visible in this micrograph (LT plane, etched with Beraha 1)

Figure 4: Base metal etched with W II (Wallner), average grain size is about 25 µm (ST plane)

Figure 5: Grain structure in the HAZ close to the weld seam

Figure 6: Microstructure of black tinted region in the HAZ adjacent to Fig. 5

Figure 7: Microhardness measurements along cross section of the weld and HAZ
3 Results and discussion

The microstructure of the unaffected SA base metal is shown in optical micrograph (Fig. 3). As can be seen the base metal is a typical martensitic microstructure and no delta ferrite is visible in the micrograph. As can be seen in Fig. 4 the average grain size of the base metal in SL direction is about 25 µm. Fig. 1 shows the macrostructure of cross section of the weldment showing the different regions developed. The first weld-pass is on the top and the second pass from the bottom. The weld zone has a cast microstructure, characteristic of solidification and rapid cooling and martensitic structure. Fig. 5 shows cast structure of the weld seam (right), coarse-grain structure of about 50 µm size adjacent to fusion boundary (in the middle) and a fine-grained structure. Although the duration of heating is very short, the martensite in coarse-grain region will transfer to austenite and part of the reformed austenite subsequently transform to laths martensite during cooling (partially could remain as retained austenite too [3]). Because the austenitising temperatures experienced in this narrow region during welding is generally higher than the SA temperature used, grain growth produces coarse grained structure. Adjacent to the coarse grains is a fine-grained structure region of about 70 µm width. The HAZ region just next to the fine grained has a grain size
similar to that of the base material. As can be seen in Fig. 1 there are also some black tinted regions on both side of the weld in the macrograph [4], which is shown in detail in Fig. 6 depicting a strongly etched sample. The cracks observed on the surface are limited by that black tinted region (see Fig. 2). The microstructure is martensite with some horizontal segregation lines. Fig. 7 shows the micro hardness profile across the weld. As can be seen the peak hardness is about 0.25 mm outside the black tinted region which implies that full width of the HAZ is not visible and recognizable by optical micrographs.

HAZ consist of retransformed martensite (and reformed austenite [7]), overaged martensite and underaged martesite. Regarding precipitation hardening, the region close to the fusion line (retransformed martensite) could be in SA condition, after which overaging might occur further away from the fusion line to the region of peak hardness and thereafter, underaged region, to the region where the base-material hardness is reached (about 1 mm after max. hardness peak). Fractography of the tore crack is shown in Fig. 8. The crack seems to penetrate into the plate limited by borders roughly perpendicular to the surface. White crack propagation lines are found by SEM within the cracks revealed in the fractured surface. They are found to converge close to the bottom side of the plate. Reconstructing the origin of the crack from those white lines, it seems to be 0.2-0.3 mm beneath the surface of the plate, but may have started along a line of 0.3 mm width parallel to the surface. They are situated approximately outside the black tinted region which limits the propagation towards the weld seam. Cracks are found to initiate and propagate trans-granular through the material (see Fig. 9). In contrast, the fracture area outside the crack’s region demonstrate dimples, characterizing ductile fracture (Fig. 10). The TEM investigation in Fig. 11-12 near the black-tinted region shows a very fine and high density of spherical Cu precipitates of the size < 20 nm. The HRTEM images in Fig. 13 show one set of crystallographic {111} planes within the very small precipitates with and without coherency with the matrix.

The uptake (diffusivity and solubility) of hydrogen is influenced by microstructure and chemical composition [5]. The microstructure showing highest hardness and strength levels are normally most prone to hydrogen embrittlement [4]. Trapping sites for hydrogen could be various lattice defects (point defects, dislocations), precipitates, grain boundaries etc. The SA condition contains martensite with high density of dislocations.

Considering the coincidence of the highest hardness position and the crack locations, the condition of Cu-precipitates in the peak aged region of the HAZ seems to be the most susceptible structure for hydrogen embrittlement.

Although the Cu precipitates in the semicoherent-incoherent stage, besides improving hardness, may trap more hydrogen [5]. If the peak hardness is attainable at a state of coherent copper precipitation [8, 9], then crack initiation has occurred close to it. After crack initiation, crack has propagated perpendicular to the weld-seam to the surface and into the plate. The width of the crack is limited by the black tinted region at one side and growing forwards the base metal. Accordingly, initially over-aged specimens are more resistant to hydrogen embrittlement than solution-annealed which suffer ageing locally in the HAZ during welding.

As was mentioned earlier, dye penetration tests revealed that one side of the plate has less cracks in compare to the other side. The reason is due to tempering and stress relieving effect of the second pass on the HAZ of the first pass. Reducing residual stresses decreases the risk of hydrogen embrittlement.
4 Conclusion

The heat-affected zone of a solution treated and welded sample of precipitation hardening martensitic stainless steel has been investigated. The optical micrographs are usually not enough to reveal the details and to characterize the microstructure of the martensite and the HAZ. The HAZ consists of three distinct microstructural zones: retransformed martensite (and reformed austenite) with Cu in solid solution, followed by region with Cu precipitates in the sequence overaged, peak aged and underaged. Cu precipitates increase the local hardness in the HAZ. Cracks due to hydrogen embrittlement seem to initiate near the peak hardness region below the surface of the plate. After crack initiation, cracks propagate perpendicular to weld seem in the direction of the under aged region in to the base metal and is limited by the overaged region. Initiation and propagation of cracks occur trans-granularly through the material.

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6 References