Localized ageing in the heat affected zone of welded X5CrNiCuNb16-4 and X4CrNiSiTi14-7 sheets

S Sakhawat1, A Falahati2, H P Degischer2, K Spiradek3 and M Dománková4
1Pakistan Welding Institute, Islamabad, Pakistan
2Vienna University of Technology, Vienna Austria
3Austrian Institute of Technology, Seibersdorf, Austria
4Slovak University of Technology, Bratislava, Slovakia

Abstract. Localized ageing and corresponding microstructural developments as a result of welding heat in the heat-affected zone (HAZ) of two different precipitation-hardened Cr-Steels (X5CrNiCuNb16-4 and X4CrNiSiTi14-7) have been studied. The X5CrNiCuNb16-4 sheet was in solution annealed condition and X4CrNiSiTi14-7 sheet was in peak aged condition. The results showed that despite of initial heat treated condition, the fusion zone formed in both welded sheets has typical cast structure. The HAZ has different microstructure compared to fusion zone and base metal. The HAZ is found to be sensitive to the welding heat and was aged locally due to thermal effects of welding. This localized ageing forms regions in HAZ varying from over-aged to under aged, depending upon the initial ageing condition of the base sheet.

1. Introduction
Precipitation hardening martensitic stainless steels have 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. They are widely used in various industries such as nuclear, chemical, aircraft, and naval due to their favorable combination of mechanical properties, easy machinability, good weldability and adequate corrosion resistance. The unique ability of strength enhancement by age hardening makes these steels very attractive for high strength applications.

X5CrNiCuNb16-4 (a type of 17-4 PH) is very attractive to designers and engineers. This steel is strengthened by precipitation of copper rich phases in the martensitic matrix by aging treatment [1,2,3,4]. The second alloy type that is used in this study is X4CrNiSiTi14-7, which is a high tensile strength precipitation hardening stainless steel with martensitic microstructure. This alloy is hardened by G-phase precipitation[5,6].

These precipitates are sensitive to heat and significant changes in the microstructure of the weld and heat affected zone (HAZ) may occur as a result of welding. The high heat of welding produces stresses and local ageing in HAZ. This paper focuses on the microstructural investigation of the HAZ developed as a result of welding in different material condition, through optical metallography, EBSD, TEM and micro hardness measurements.

2. Material and experimental methods
Two types of precipitation hardening martensitic stainless steels are investigated in this work. They are X5CrNiCuNb16-4 (17-4PH) and X4CrNiSiTi14-7(15Cr-7Ni) sheets of thickness > 2mm. The chemical composition of these alloys is given in Table 1. The X5CrNiCuNb16-4 sheets were welded together in solution annealed condition and the X4CrNiSiTi14-7 sheets were welded together in peak
The welding was done by TIG welding technique, without using filler material and with two welding passes, one pass from each side. The first weld-pass was on the top and the second pass was from the bottom.

**Table 1. Chemical composition of the alloys (wt %) balance Fe**

| Elements | X5CrNiCuNb16-4 | X4CrNiSiTi14-7 |
|----------|----------------|----------------|
| Fe       | Balance        | Balance        |
| C        | 0.024          | 0.038          |
| Si       | 0.706          | 1.475          |
| Mn       | 0.78           | 0.35           |
| P        | 0.166          | 0.0258         |
| S        | 0.00005        | 0.0006         |
| Ni       | 5.04           | 7.03           |
| Cr       | 15.04          | 13.61          |
| Cu       | 3.3            | 0.6            |
| Ti       | 0.016          | 0.33           |
| Mo       | 0.115          | 0.79           |
| Nb       | 0.26           | 0.006          |
| Al       | 0.011          | 0.037          |
| V        | 0.072          | 0.037          |

Metallography was done to characterize the microstructure. The metallographic samples were prepared in transversal direction. Conventionally used etchant Nital did not reveal microstructural details. The etchant WII (16g FeCl\(_3\)·6H\(_2\)O in 50 ml H\(_2\)O dist. + 9g (NH\(_4\))\(_2\)S\(_2\)O\(_8\) in 50 ml H\(_2\)O dist mix in 60 ml of 32% HCl) with etching time of 3-6 s was able to etch the samples. Metallography was carried out on the base metal and the welded area to characterize their microstructure. Vickers micro hardness profiles across the weld, in the HAZ and base material were measured according to EN 6507 in Vickers HV 1 and were performed on universal hardness tester model Emco Test M1C010.

The SEM-EBSD technique was used for resolving microstructural details of HAZ. The samples were mechanically ground and polished down to 1µm diamond paste. For good quality of EBSD patterns, it is important to remove the residual deformation in the surface layer of the specimens by electro-polishing. Different polishing solutions were tried for the purpose and finally a solution of 20 vol.% perchloric acid (HClO\(_4\)), 70 vol.% ethanol (C\(_2\)H\(_5\)OH) and 10 vol.% ethylene glycol monobutyl ether (CH\(_3\)(CH\(_2\))\(_3\)OCH\(_2\)CH\(_2\)OH) at 20°C, with the voltage of 28V for 10 s was found successful for giving a good EBSD signals from the sample [7]. SEM-EBSD investigations were performed on FEI Quanta 200 FEGSEM operated at 20kV. EBSD scan were carried out in the middle of the specimen, with a step size of 50nm. During experiment the samples were maintained at standard 70° tilt by using special specimen holder.

The investigation of the HAZ of welded X5CrNiCuNb16-4 sheets has been performed with the transmission electron microscope CM20STEM and the high resolution electron microscope (HRTEM) Tecnai F20 operating at 200kV at Austrian Institute of Technology, Seibersdorf, Austria. Thin foils were prepared by mechanical grinding and subsequent electro polishing. The structure was analyzed in bright field and dark field imaging; and the precipitation was identified by electron diffraction, and with reference to the distance between the specific crystal planes in HRTEM.

Carbon extraction replicas were prepared for examination by TEM and analysis by EDX to identify the precipitates in X4CrNiSiTi14-7 alloy. The samples were etched in etchant consisting of 1-2 g of picric acid, 10 ml of ethanol, and 5 ml of water. The surface was coated by a C-layer and the replicas were removed from the sample surfaces electrochemically at 20 V using 3% nital as electrolyte. TEM observations were performed in a microscope JEOL 200CX operating at 200 kV.
3. Results and Discussions

The X5CrNiCuNb16-4 sheets were in precipitation free (solution annealed and rolled) condition before welding together. The microstructure in this condition was martensitic with an average grain size of about 25 μm. Figure 1 shows the macrostructure of cross section of the weldment showing the different regions developed. The first weld-pass was on the top and the second pass from the bottom. During welding the temperatures surpassed locally the solidus temperature, but the time of exposure to such high temperatures was very short, thus producing a temperature gradient in the weld and in the areas which were adjacent to the weld. As a result the microstructure varied from the fusion zone to the base material.

![Macrograph of the cross-section of welded region (X5CrNiCuNb16-4)](image1)

![Microstructure of the weld zone (X5CrNiCuNb16-4)](image2)

![Microstructure of heat affected zone (X5CrNiCuNb16-4)](image3)

![Microstructure of black tinted region (X5CrNiCuNb16-4)](image4)

The microstructures of the fusion zone is shown in Figure 2. The fusion zone is a typical cast structure, characteristic of solidification at rapid cooling. The HAZ is shown in Figure 3. As can be seen in Figure 1 that there is some black region in HAZ on both sides of the weld in the macrograph, which is shown in detail in Figure 4 depicting a strongly etched sample and remains unresolved by optical microscopy. Since this area appears black in metallographic images, hence termed as “black tinted region”. There is a coarse grained structure adjacent to the fusion boundary in Figure 3. The black tinted region that remained unresolved by optical micrography was successfully resolved by EBSD. The microstructure is mostly martensitic with ca. 2% of austenite (Figure 5). The grain size has been found to be extremely small with 40% grains between 1-2 μm. The largest grain found in the area is less than 4 μm (Figure 6).
Figure 7 presents the EBSD phase mapping of weld and HAZ. Big ferritic grains (>20μm) are mixed with small laths (<10 x 5 μm) present in the weld (Figure 7a). The grain size decreases and the small grains look rounder in Figure 7b. Very small grains (< 0.5 μm Φ) or highly distorted crystal structures, presumably both are found in the black region (Figure 7c). The grain size starts increasing outside dark region (Figure 7d). The possible explanation for this heterogeneity in HAZ is recrystallization, which occurs by the nucleation and growth of the new grains. The stored energy is the driving force for recrystallization in work hardened materials. During rapid heating of welding, the recrystallization temperatures may increase because it requires diffusion which takes time. During welding, the martensite in the coarse-grain region will transform into austenite and this reformed austenite subsequently transforms back into laths martensite during cooling with some retained austenite islands as suggested in literature [8].

Contains 3.3 wt% Cu which precipitates out upon ageing and produces precipitation hardening [1,2]. Before welding the X5CrNiCuNb16-4 sheets together, they were super saturated with Cu. During continuous cooling of the welded sheets in air, some regions of the HAZ have passed through temperatures, which were suitable to age these regions locally and as a result to precipitate Cu. The TEM investigations near the black-tinted region show a very fine and high density of spherical Cu precipitates of the size < 20 nm. One of the precipitate is shown in Figure 8. The HRTEM image in this figure shows some noncoherency of the precipitate with the matrix. Figure 9 shows the EDX spectra of matrix and precipitate and it clearly indicates that this precipitate is enriched with Cu. Hence the region close to the fusion line (points 6, 7, 12 and 13 in Figure 10) will be in solutionized condition, after which overaging (point 8 in Figure 10) might occur further away from the fusion line towards the region of peak hardness (point 3 and 16 in Figure 10) and thereafter follows the underaged region (point 1, 18 and 19 in Figure 10) until the base-material hardness is reached (about 1mm after max. hardness peak).
Figure 7. EBSD grain size mapping (X5CrNiCuNb16-4), a) weld, b) Weld and adjacent coarse grained HAZ, c) HAZ and black tinted region, d) outside black region. No EBSD signal obtained from black areas.

Figure 8. HRTEM, lattice fringe contrast, indicating some non-coherency of precipitate in X5CrNiCuNb16-4

Figure 9. Overlapping EDX spectra of matrix and precipitate, clearly indicating the Cu enrichment of the precipitate shown in Fig.8.
The second material studied in this work was X4CrNiSiTi14-7. The sheets were in peak age hardened condition before welding together with a hardness value of 477 HV. Figure 11 shows the macrostructure of cross section of the weldment showing the different regions developed. The first weld-pass was on the top and the second pass from the bottom. The microstructures of the fusion zone and HAZ formed after welding X4CrNiSiTi14-7 aged sheets together are shown in Figure 12 and 13 respectively. The “black tinted region” was also found on both sides of the weld in the macrograph and is shown in Figure 14. The fusion zone, like as formed in X5CrNiCuNb16-4 solution annealed sheets, is a typical cast structure, characteristic of solidification at rapid cooling.

Figure 15 presents the phase mapping of weld, HAZ and . Big ferritic grains (>20μm) are mixed with small laths (<4μm) in the weld (Figure 15a). The grain size decreases in Figure 15b. Very small grains (<1μm Φ) or highly distorted crystal structures, presumably both are found in black the region (Figure 15c). The black region consists of very small grains (Figure 15d) mostly unresolved by EBSD.
Figure 10 shows the micro hardness profile done along cross sections of the weld, HAZ and base metal. The average hardness in the weld region is ~340 HV, whereas the hardness of the base material is ~350 HV. This small decrease in hardness indicates that melting and re-solidification in the weld zone has removed cold rolling effects. Since no prominent difference in hardness exists in between the weld zone and base material, this indicates that the martensite formed in the weld zone is precipitation free and is in untempered condition. The peak hardness (> 455HV) is about 0.5- 1mm outside of black tinted region in the HAZ on both sides of the weld seam. The weld seam has the lowest hardness values (320-335HV). This increase in hardness can be explained on the basis of precipitation hardening. The X5CrNiCuNb16-4 alloy

Figure 13. Microstructure of heat affected zone (X4CrNiSiTi14-7)  
Figure 14. Microstructure of black tinted region (X4CrNiSiTi14-7)

Figure 15. EBSD grain size mapping of X4CrNiSiTi14-7 weldment, a) weld, b) just outside weld, c) HAZ, d) black tinted region. No EBSD signal obtained from black areas (very distorted/ fine grained structure). (Color scale is shown on the right)
Figure 16 shows the micro hardness profile along cross sections of the weld, HAZ and base metal. The hardness of the weld seam (350-360HV) is lower than that of the base metal (~ 480 HV). Weld seam has the hardness of 350-360 HV. There is a hardness drop in HAZ near to the black tinted region, the lowest hardness value across the profile is at 1mm from the black tinted region in HAZ on both sides of the weld seam and the minimum hardness value is 317HV and then it increases again towards the base metal. This behavior can be explained on the basis of precipitation hardening. This high hardness of basematerial is due to the presence of fine G-phase precipitates [5,6] and shown in Figure 17. During welding the heat was sufficient to cause melting in the centre of weld zone. This melting also caused the dissolution of the G-phase precipitates present in the material. Since enough time was not available during re-solidification hence re-precipitation of G-phase did not takes place in the weld zone. As a result softening takes place due to the loss of precipitation hardening which was initially acting as a hindrance to dislocation motion. The microstructure is martensitic (precipitation free and in untempered condition) with some small islands of retained austenite. The weld became softer (340 Hv), which is very close to the hardness of the as-received condition with out ageing (335HV). This shows that weld zone will always be in solution annealed condition despite of the initial heat treated condition of the base material. A similar condition exists in the region next to weld zone, where the temperatures were above the solution temperatures and were sufficient to dissolve the G-phase precipitates during heating, thus resulting in softening. Hence hardness values are also lower like in the weld zone (see for example points 5 and 12 in Figure 16). Beyond “near weld region” the temperatures were still high but lower than the solution temperature. The exposure to these temperatures causes overaging of the already aged base metal (points 2, 3 and 14 in Figure 16). The regions where the temperature in the heat-affected zone is not above the original ageing temperature, or for only a very short time, the hardness is not significantly affected [9].
Figure 17. Transmission electron micrographs of X4CrNiSiTi14-7 showing precipitates

4. Conclusions
Microstructural changes in the HAZ of two types of precipitation hardening stainless steels have been characterized, and compared with the aging behavior.

During welding the HAZ is submitted to an “ageing” treatment producing strengthening and loss in ductility. Peak hardening is achieved at the borders of HAZ for X5CrNiCuNb16-4 sheets without heat treatment. In X4CrNiSiTi14-7 peak aged sheets, the hardness is reduced to the solution treated level close to the weld seam and outside where austenization did not occur, over-ageing takes place reducing the hardness further.

The “black tinted region” indicates very fine recrystallized regions representing either a precipitation strengthened region for an originally solution treated condition (X5CrNiCuNb16-4), or an overaged region (soft) for an initially peak aged sheet (X4CrNiSiTi14-7).

5. Acknowledgement
The work was partially supported by the Austrian FFG. The authors thank Higher Education Commission of Pakistan (HEC) for sponsoring PhD studies.

6. References
[1] Hsiao C N, Chiou C S and Yang J R 2002 Materials Chemistry and Physics 74 134-142
[2] Mirzadeh H, Najafizadeh A 2009 Materials Chemistry and Physics 116 119-124
[3] Murayama M, Katayama Y and Hono K 1999 Metall. Mater. Trans A 30A 345-353
[4] Wang J, Zou H, Cong L, Peng Y, Qiu S andShen B 2006 Nuclear Engineering and Design 236 2531-2536
[5] Sakhawat S, Falahati A and Domankova M 2010 Prakt. Metallogr. 47 500-516
[6] Murata Y, Ohashi S and Uematsu Y 1993 ISIJ International 33 711-720
[7] Jia N, Peng R L, Chai G C, Johansson S andWang Y D 2008 Materials Science and Engineering A
[8] Bhaduri A K and Venkadesan S 1989 Steel Research 60 509-513
[9] Messler W R 2004 Principles of welding (Wiley VCH Weinheim) pp 540-542