THE INFLUENCE OF SIGMA PHASE PRECIPITATION ON MECHANICAL PROPERTIES OF TP347H AUSTENITIC STEELS AFTER 100.000 HOURS SERVICE IN COAL-FIRED POWER PLANT

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Abstract

The Danish coal-fired Ultra Super Critical (USC) plant, Nordjyllandsværket has now reached 100.000 hours of operation. Taking advantage of the boiler maintenance programme, tube sections were removed from more than 20 different locations in the boiler during the 2012 summer shutdown to assess the materials conditions of the boiler. The tubes have been investigated to document wall thickness, fireside corrosion and steamside oxidation rates and morphology and microstructure evolution after 100,000 hours exposure. The mechanical and fracture properties were obtained using small punch test technique (SPT) as well as using miniaturized test specimens. The present paper focuses on investigations and modelling of the influence of sigma phase precipitation on mechanical and thermal stability of the austenitic alloy TP347H that was used as a construction material for superheaters and re-heaters. Obtained results show that even very small amounts of sigma phase affects fracture behaviour significantly. Drop in fracture properties can be clearly identified using miniaturized test specimens or SPT.

Keywords: sigma phase, Tp347HFG stainless steel, miniaturized test specimens, SPT

1. INTRODUCTION

Very little data exists in the literature which describes long-term exposure of TP347HFG and TP347H although there are many articles on short term laboratory exposures and initial experiences in power plants. Sigma phase is an intermetallic Fe, Cr phase that forms in austenitic steels during long term exposure at high temperatures. The presence of sigma phase leads to embrittlement of the material at ambient temperatures. The presence of sigma phase is a problem for steels with a higher Cr content however has not been recognised as being present for TP347HFG. The microstructural evolution of TP347HFG has been discussed for exposures between 1000 – 50,000 hours, where sigma phase develops within 1000 hours at 700 °C and within the first 50,000 hours at 650°C [1]. Such temperatures ranges are not utilised at Nordjyllandsværket, however sigma phase is observed. This work is focused on quantification of the influence of sigma phase on material properties including fracture behaviour using miniaturized test specimens and small punch test.

2. INVESTIGATION METHODS

The superheater and re-heater materials had been in service for 100,000 hours. As there are no direct measurements of the tube wall temperatures, they were estimated based on flue gas and steam temperatures according to EN standard [2]. Service temperature varies between 550 and 585 °C depends on the position of tubes. Specimen rings from the exposed tubes were prepared according to standard metallographic preparation techniques. Specimens were etched electrolytically with 10% oxalic acid to reveal microstructure. The orientation of the tubes in the boiler has a great influence on the microstructure. Therefore all samples were orientated in the same way such that the side facing the furnace was marked as position 0° and the side facing away from the furnace was marked 180°. The microstructure of the TP347H and TP347HFG tubes was investigated with Light Optical Microscopy (LOM) and Scanning Electron Microscopy (SEM) equipped with Energy Dispersive X-ray Spectroscopy (EDS).

To understand effect of sigma phase on material properties and structure, various testing methods based on miniaturized test techniques have been used including small punch test method. The influence of sigma phase on mechanical and fracture properties of tubes were further investigated by the means miniaturized Charpy V-notch test, miniaturized Tensile Test (TT), Small Punch Test (SPT) and Fracture Toughness Test (FTT). Fig. 1 shows the placement of all specimens in the test tubes for both wall thickness, and drawings of the test samples with dimensions are shown in Fig. 3 and 4. All tests were carried out according to valid standard [3-5]. SPT were carried out according to recent version of draft of the standard for this test [6]. The Small Punch (SP) miniaturised test technique is an invaluable method capable of providing direct values for mechanical properties of materials. The small punch technique is an almost non-destructive technique for characterizing the mechanical properties especially of service-exposed plant components. The microscopic size of the specimens means that only negligible amounts of material have to be sampled.

The SP testing technique utilises a small disc specimen, 8 mm in diameter and 0.5 mm in thickness, clamped around its circumference and indented by a spherical punch up to failure [6,7]. Monotonic load vs. displacement records are used to derive estimates of tensile and fracture toughness parameters see Fig. 4 b). All tests presented in this work were performed at room temperature. Impact properties after exposure have been compared to values of impact energy in a virgin state of material TP347HFG used in work [7].

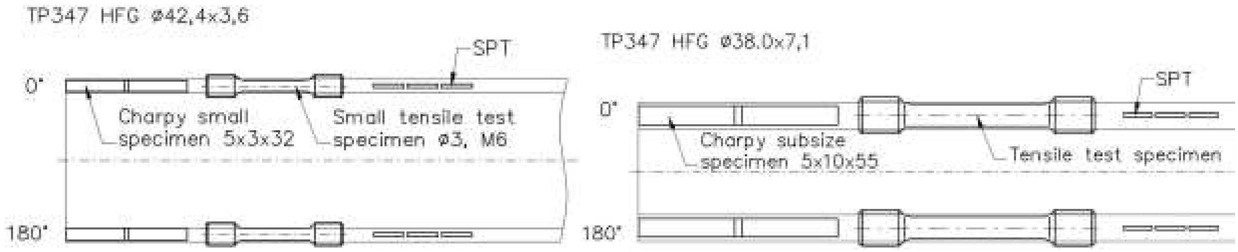


Fig. 1 Cutting plans for TP347H tubes a) thinner tubes; b) thicker tubes.

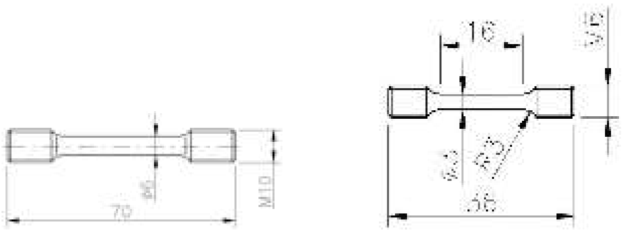
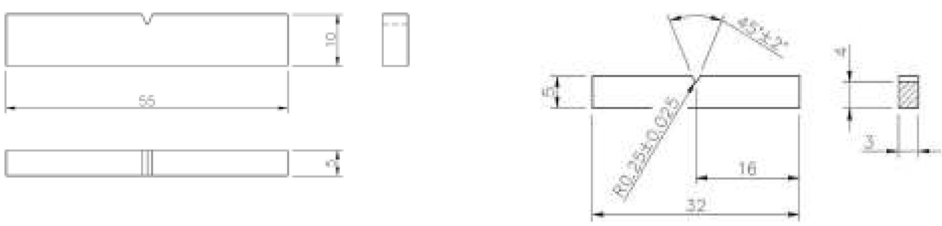


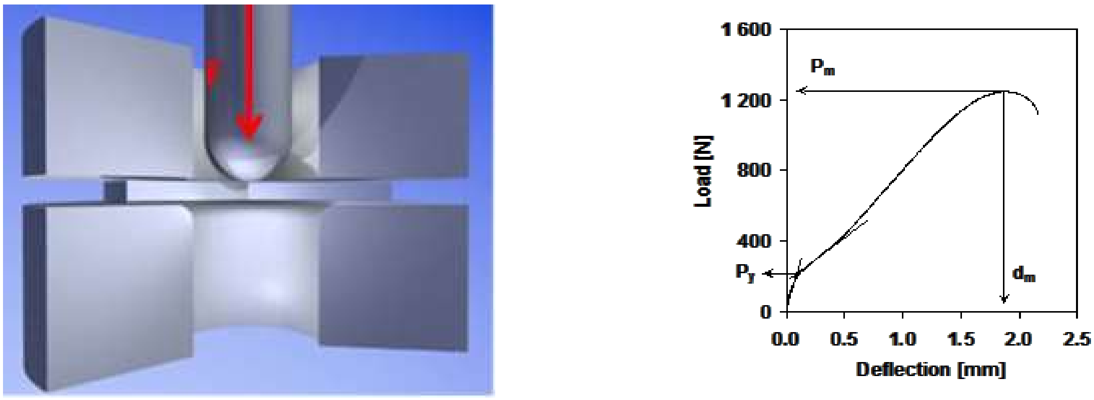
Fig. 2 Tensile test specimens



a)

b)

Fig. 3 a) Charpy subsize specimen; b) miniaturized Charpy specimen.



a) b)

Fig. 4 a) Principle of small punch test; b) Typical SPT record.

3. RESULTS

All samples were first investigated with LOM in order to get a general overview of the microstructural changes. ASTM Grain size [8] was also measured and has been found to be between G5 - G9 depends on components and conditions.

3.1 Microscopy investigations of sigma phase formation

The LOM investigations revealed the presence of sigma phase in the majority of the samples investigated. Sigma phase was found in greater amounts in position 0°, which is facing directly to the furnace and thereby meets the hottest flue gas – see Fig.5. A sigma phase free band of about 300 – 400 μm at the surface on the flue gas side was observed. The greatest concentration of sigma phase was in the mid-thickness of the tubes and its content was decreasing towards the steamside of the tubes. Small amounts of sigma phase were observed also in position 180° that is facing away from the furnace and is partially shielded from the hot flue gas by surrounding tubes. Sigma phase content in position 0° and 180° varies between 0,2 and 5,5 %.

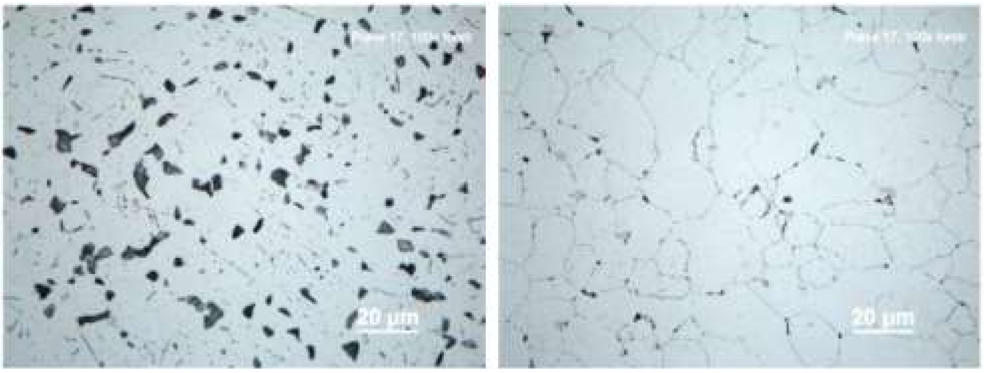


Fig.5 LOM image of sample 17 a) 0° - 5,5% of sigma phase, b) 180 ° - 0,6ˇof sigma phase

3.2 Mechanical testing

Tensile tests. The sigma phase is known to influence the mechanical properties, especially toughness, of materials at lower temperatures. Several test methods were used in order to find the most suitable and sensitive test method for evaluation of the influence of sigma phase on mechanical and fracture properties of TP347H and TP347HFG. The performed tensile tests did not show a significant difference in results due to the presence of sigma phase in the structure especially with respect to yield strength and tensile strength, see Table 1. Tensile strength seemed to be at the same level for all tubes at the side with sigma phase and at the side without sigma phase. Decrease of yield strength at the side with sigma phase appeared just in tubes with great amounts of sigma phase (tube 17 and 19 – 5,5% and 2,2 % of sigma phase) and in tube 13, which contains rather small amount of sigma phase (1,1%), but was operated at the higher temperature (585°C).

Table 1 Tensile properties of the tubes with maximum amount of sigma phase

Specimen ID	Tensile strength	Upper yield strength	Elongation	Reduction of area
Tube 17	**[MPa]**		**[%]**	
position 180°	675	357	48,0	64,0
	684	389	43,3	59,6
position 0°	676	277	38,7	45,9
	678	286	38,7	45,5

Plastic properties such as elongation and reduction in area showed a significant response where the affect of sigma phase resulted in a higher loss of reduction of area. The measured values of elongation and reduction of area can be directly related to toughness of steel as sigma phase appears to change of fracture properties. All investigated tubes showed decrease of elongation and reduction of area (of 8 – 25% depending on the content of sigma phase) compared to tubes without sigma phase.

Charpy V tests. Data of absorbed energy were plotted in two graphs (see Fig. 6) depending on the wall thickness and type of specimens used for testing. This was compared with results of steel TP347HFG in as received condition that were previously tested [7]. Drop of impact energy at the side with sigma phase happened at all tested tubes with the exception of tube 14, where the difference between the side with and without sigma phase is very small. Tube 14 has the smallest amount of sigma phase of all fine-grained tubes. Tube 17, with the highest amount of sigma phase, appears to suffer the biggest drop of impact energy. A significant drop of impact energy at the side with sigma phase was also observed for samples from coarse-grained tubes 13, 18 and 19. Level of impact energy of the coarse-grained tubes is generally higher than of the fine-grained tubes.

Small punch test is a method which sensitively responds to the structure of steel. Fig. 7 shows comparison of test records of the SPT specimens from both sides of the Tube 17 with the highest amount of sigma phase. From Fig. 7, differences between the side with and without sigma phase can be clearly seen. It was recognized that sigma phase affects SPT fracture energy significantly. The drop in fracture energy is about 50 %. SPT results were compared with "as received" data of Ø 38,0 x 6,3 mm tube made of TP347HFG steel that was investigated at MMV earlier [7]. The results are also shown graphically in Fig. 7 right, where the test results are supplemented by values of TP347HFG grade steel in as received conditions [7]. In this way it was possible to compare both the effect of sigma phase and the effect of operation conditions on fracture behaviour of the steel under investigation. It was assumed that the side without sigma phase was degraded just due to operation and the side with sigma phase was degraded due to operation and presence of sigma phase.

4. DISCUSSION

Specimens which had been exposed at Nordjyllandsværket were assessed with respect to microstructure evolution. Surprisingly sigma phase was revealed on the TP347HFG and TP347H type steel. Sigma phase is a Cr rich intermetallic which is a brittle phase which will increase the likelihood of a brittle fracture at ambient temperature. The microstructure of TP347H is austenitic strengthened with primary Nb-rich precipitates of MX type. Precipitation of secondary MX, $M_{23}C_6$ and sigma phase takes place during service at elevated temperatures. In the present work only NbC and sigma phase were detected after 100,000h of service. Minami's [1] long term aging experiments of austenitic steels also show presence of NbC and sigma phase at temperatures below 650°C. These observations are in a good agreement with MatCalc calculations that predicts MX and sigma phase as the equilibrium phases in TP347H. The analysed sigma phase contained on average, 38%Cr. 1% Si, 2%Mn and 4% Ni and was preferentially observed on grain boundaries. The presence of this phase on grain boundaries will affect significantly both the mechanical properties and the corrosion properties.

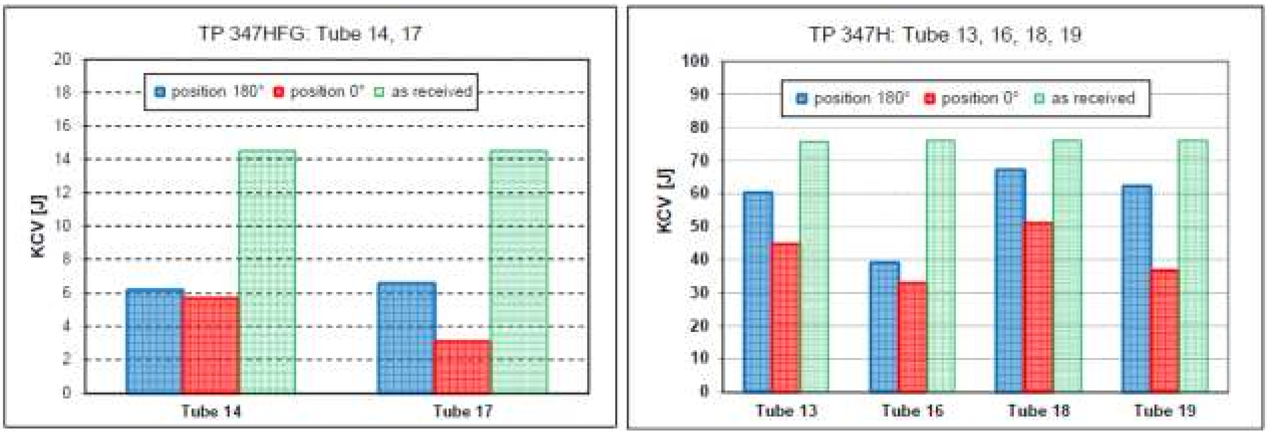


Fig.6 Results of impact tests

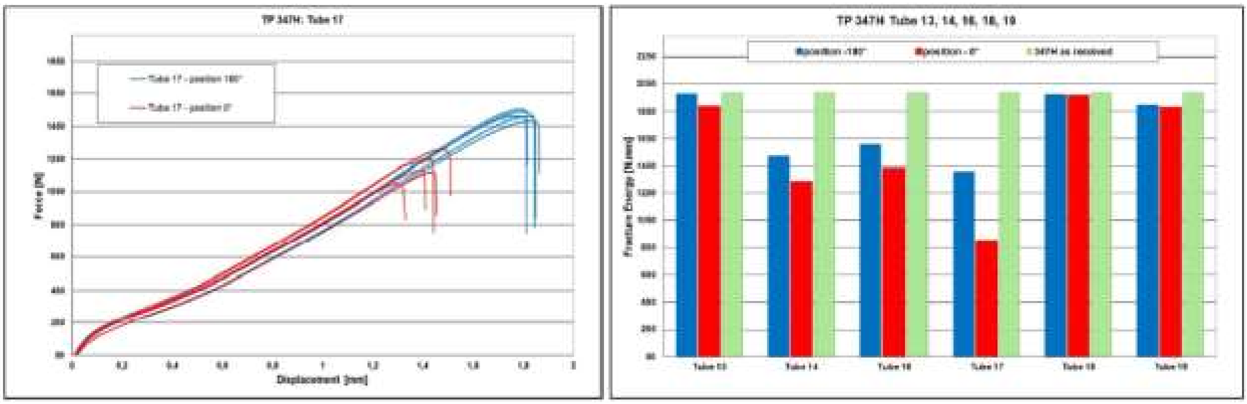


Fig.7 Results of SPT

The formation of sigma phase is dependent on C, Nb and Cr content in the material [9]. Thermodynamic calculations of the effect on C on formation of sigma phase, show the rapid decrease of the content of sigma phase when C content increases to 0.1 wt% [10]. According to [9] sigma phase will form when C content is below a critical level and Cr equivalent is greater than 18 wt%. The critical C content can be reached by precipitation of Nb carbides, thus the Nb/C ratio is an important factor for sigma phase formation.

The power plant needed to know if the localised presence of sigma phase would compromise the structural performance of the superheaters. However since the tubes in question had a small wall thickness (some as small as 3.6 mm) and sigma phase was only localised on one side of the tube, it was not possible to undertake conventional mechanical material testing. However with the use of miniature specimens and small punch test, it was feasible to undertake mechanical testing in localised areas.

The conventional tensile testing seems not to be sensitive enough to quantify the effect of sigma phase on the strength of TP347H, but a small effect could be detected on the plastic properties (elongation and reduction of area). With either the more sensitive dynamic test methods (impact testing) or more localized SPT, a drop in fracture energy clearly could identified the presence of brittle phase in the structure. In addition electron microscopy revealed more brittle fracture contra the ductile fracture where there was no sigma phase. Since sigma phase is stable at higher operating temperatures (550 - 620°C), and after 100,000 hours had nucleated preferentially at grain boundaries, it could be feared that the sigma phase content in the specimens with lesser visible sigma phase would increase after longer exposures, thereby making other components more susceptible to fracture. Whilst sigma phase does not promote fracture at operating temperatures but only at temperature below 200°C, care must be taken during outages when servicing the components. Very important is the fact, that SPT method can be successfully used not only for evaluation of the effect of sigma phase but also for evaluation of degradation level due to operation. As the SPT requires only a very small volume of testing material this method can be used as a useful tool for monitoring and residual lifetime assessment of materials exploited in service.

CONCLUSIONS

Based on experimental results, the following important facts can be concluded:

1) Detailed microstructural analyses and material properties evaluation have been carried out on tubes taken from the Danish coal-fired Ultra Super Critical (USC) plant after 100,000 operation hours.
2) Sigma phase was detected on side facing to the furnace. The portion of sigma phase varied between 1 and 5.5 % on the side facing the furnace and about zero on the side facing away the furnace.
3) Several testing methods were used for evaluation and quantification of effect of sigma phase on material properties. Static test methods were not so sensitive to show this effect as more suitable seem to be impact testing and also small punch testing.
4) Drop in absorbed energy in both types of Charpy specimens were identified due to presence of various amount of sigma phase in the structure, for the worst tube with about 5 % is a drop in absorbed energy about 50% compare to virgin state of TP347 HFG steel. A brittle fracture was observed where there was more sigma phase.
5) Effect of sigma phase were also studied using small punch test method, results shows significant changes in force – displacement record as well as in fracture energy of SPT

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