PROPERTIES AND MICROSTRUCTURE OF WELDMENTS MADE OF NEW AUSTENITIC STEELS AFTER CREEP EXPOSURE

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Abstract

The newly developed grades of austenitic heat resistant steels (Super 304H, HR3C, TP 347 HFG) exhibit superior corrosion resistance in steam as well as creep strength thanks to their fine-grained microstructure, especially in case of Super 304H and TP 347 HFG. They are worldwide used in USC power plant boilers and substitute steels AISI 316, AISI 321 and/or AISI 347 formerly used in superheater and reheater tubes. On the other hand, the structural stability of these new steels is under examination, especially form the viewpoint of σ-phase precipitation which is known for its embrittlement effect.

The precipitation of σ-phase was already found in the mentioned steels after long-term annealing at working temperature in the base material of tubes as well as in the tube bends. However, it seems that the presence of applied stress (and/or deformation) significantly promotes the precipitation of this phase. Therefore, much more and coarser particles of σ-phase were detected in the weldments after creep exposure.

The paper presents the results of stress rupture tests of welded tubes made of steels Super 304H and HR3C, the assessment and prediction of long-term creep life and describes also the structural changes that appeared in these steels, especially precipitation of σ-phase, when significant difference in the amount of σ-phase between the both steels was revealed.

Keywords: Super 304H, HR3C, welded joint, creep strength, sigma phase

1. INTRODUCTION

In connection with the installations of USC boilers working with steam temperature above 593 °C and pressure 25 MPa, the attention was focused (besides low alloy steels for waterwalls and modified chromium steels for headers and pipelines) on austenitic steels for superheaters and/or reheaters. The new materials developed and implemented in USC boilers are upgraded austenitic heat resisting steel, which, in addition to increasing creep strength, show also better resistance to high temperature oxidation in the steam. This paper aims to evaluate the long-term creep properties of heat resistant steel for USC blocks and to investigate the formation of σ-phase and its effect on material properties of base metal and welded joint made of these steels.

2. NEW AUSTENITIC STEEL GRADES SUPER 304 H AND HR3C

Experience with the exfoliation of superheater tubes of austenitic steels AISI 304 (H) and AISI 316 (H) at temperatures over 650 °C led to efforts to increase the oxidation resistance in steam as well as creep strength at temperatures above 650 °C [1, 2], which resulted in the development of a new generation of austenitic heat-resistant steels for USC boilers, two of them known as Super 304 H (1.4907, X10CrNiCuNb18-9-3) and HR3C (1.4952, X6CrNiNbN 25-20. These steels have not been included in the European material standards yet and are used according to the German material sheets [3, 4] or according to ASTM A213 as TP310HCbN (HR3C) in the USA The steel Super 304 H is still produced according to ASME Code Case 2328 [5]. The comparison of creep rupture strength of several grades of chromium modified and austenitic stainless steels is shown in **Figure 1** [6].

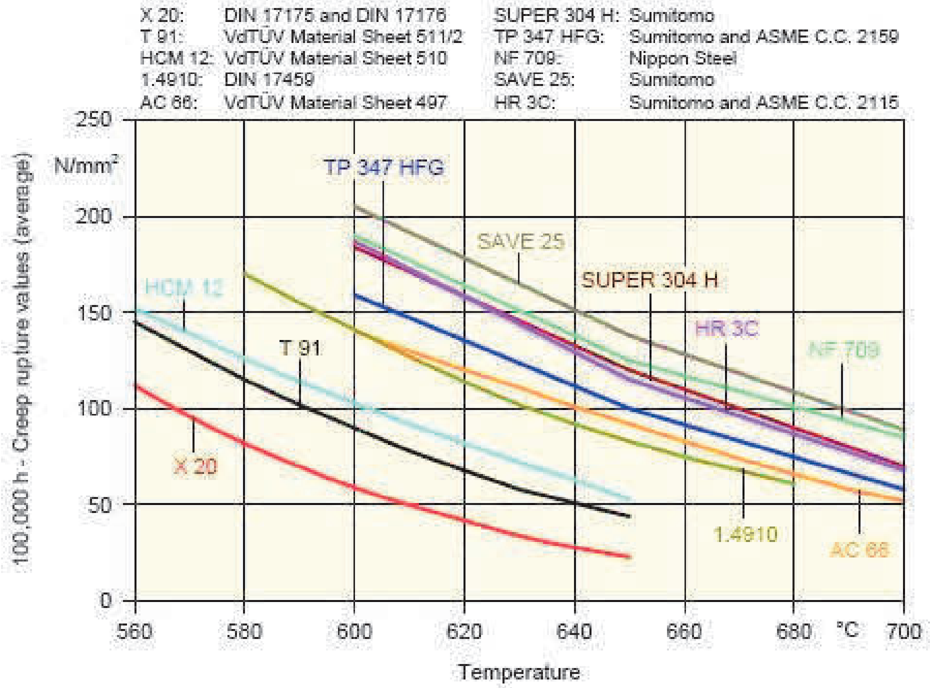


Figure 1 Comparison of creep rupture strength of various creep resistant steels [6]

The most significant change in chemical composition of steel Super 304 H compared to AISI 304 grade is an addition of 3 % Cu and alloying by niobium and nitrogen. Copper forms particles of ε-phase in the matrix, i.e. small spherical precipitates which significantly reinforce the matrix. Steel HR3C, developed form the steel grade AISI 310, then has optimized and balanced nitrogen and niobium contents, which should increase creep resistance and also reduce the susceptibility to the formation of undesirable hard and brittle σ-phase [7].

3. EXPERIMENTAL MATERIAL AND ITS PROPERTIES

Tubes ø 38 x 6.3 mm made from steels Super 304 H and HR3C were used as an experimental material for the evaluation of creep properties of the base material of tubes (BM) and their welded joints (W). The exact chemical composition and mechanical properties are shown in **Tables 1** and **2**. The weldments were made by orbital GTAW with the THERMANIT 304HCu wire with ø 0.8 mm in the case of Super 304 H steel and Thermanit 617 (or UTP A 6170 Co) for HR3C tubes. Details of the welding process were stated in [8].

Table 1 Chemical composition of tubes made of Super 304 H and HR3C steel [wt. %]

Steel	C	Si	Mn	P	S	Cr	Ni	Nb	N	Cu	B	Al
Super 304 H	0.08	0.25	0.81	0.030	0.001	18.3	9.0	0.49	0.11	3.07	0.004	0.005
HR3C	0.06	0.41	1.19	0.016	0.000	24.9	19.9	0.44	0.26	-	-	-

Table 2 Mechanical properties of tubes made of Super 304 H and HR3C steel

Steel	$R_{p0.2}$, [MPa]	R_m, [MPa]	A, [%]	$R_{p0.2}$ (600°C), [MPa]	KV (10x2.5 mm), [J]
Super 304 H	326	627	43	239	30
HR3C	363	740	49	186	40

4. RESULTS OF CREEP TESTS OF BASE MATERIAL AND WELD JOINTS

Creep tests were performed at temperatures 650, 700 and 750 °C. The calculated values of creep rupture strength in 10 000 and 100 000 hours ($R_{u/T/10^4}$ and $R_{u/T/10^5}$) are stated in **Table 3** and compared with the mean values given in the material sheets [4, 5]. Seifert parametric equation was used for the calculation [9]:

$$\log R_{uT} = A_0 + A_1 P + A_2 P^2, \qquad P = \left[T \cdot (C + \log t_r) \cdot 10^{-4}\right] \tag{1}$$

where T is temperature in K, t_r is time to fracture in hours, A_1, A_2, ... A_k and C are material constants.

Recalculation of experimental results into the value of Larson-Miller parameter P_{LM} was used to compare the evaluated creep resistance of the base metal and welded joint by using the Eq. (2) [10]:

$$P_{LM} = T \cdot \left[\log(t) + C\right] \tag{2}$$

Constant C equals to 20.8 and 16.6 for Super 304 H and H3C steels, respectively, which are the values calculated by the method of least squares from data stated in the material sheets [4, 5].

Table 3 Creep properties of tube and weldment made of Super 304 H and HR3C steels

Temp.	Super 304H						HR3C					
	$R_{u/T/10^4}$ [MPa]			$R_{u/T/10^5}$ [MPa]			$R_{u/T/10^4}$ [MPa]			$R_{u/T/10^5}$ [MPa]		
	Tube	Weld	[4]	Tube	Weld	[4]	Tube	Weld	[5]	Tube	Weld	[5]
650 °C	174	158	160	102	88	116	168	141	171	102	92	114
700 °C	104	89	101	57	43	68	104	99	108	58	63	66
750 °C	60	47	61	31	19	37	62	70	64	32	44	39

The comparison of creep tests of base metal (BM) and welded joint (W) is for both steels shown in **Figure 2**. Fulfilled points represent the ruptured specimens, while empty points are still running tests. The solid lines labelled WB 550 and WB 546 represent the mean creep strength of both steels according to [4, 5] and the dashed line the lower 20% tolerance limit. The results confirm good creep resistance of the tested tubes as well as their welded joints, when base materials oscillate around the mean values and welded joints are very close to or even inside the lower 20% tolerance limit, even though they have lower tolerance limit 40 %.

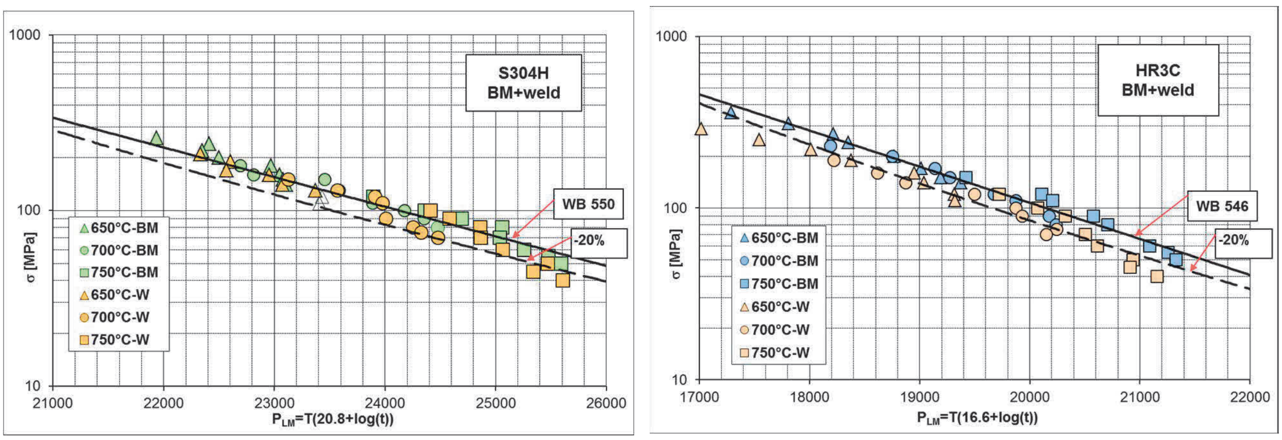


Figure 2 Creep strength as a function of Larson-Miller parameter for both steels and weldments

Although the creep strength of both steels does not look to be affected significantly by structural changes appearing during creep exposure and characterized principally by σ-phase formation, plasticity, i.e. elongation and mainly reduction of area falls rapidly with increasing time to rupture. This effect is more pronounced in

HR3C steel and weldment but the same tendency especially for higher temperatures can be seen in Super 304 H steel, too, see **Figure 3**.

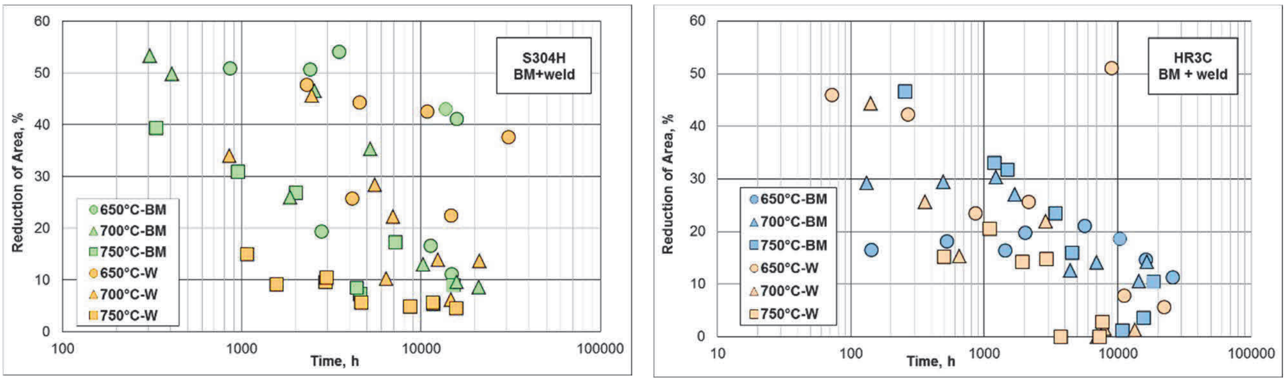


Figure 3 Reduction of area as a function of time to rupture and temperature

5. RESULTS OF METALLOGRAPHIC ANALYSIS OF BASE MATERIAL AND WELD JOINTS

In order to find the reason for rapid drop of plasticity with increasing time to rupture, the ruptured specimens were longitudinally cut and prepared for metallographic analysis and comparison with the as-welded state. The detailed information about these creep tests (temperature, stress, time to rupture, reduction of area and location of fracture are stated in **Table 4** and show that in case of HR3C steel the reduction of area dropped form more than 40 % at 650 °C down to less than 3 % at 750 °C at similar time to rupture.

Table 4 Parameters of analyzed creep tests

Weld	Specimen	T, [°C]	σ, [MPa]	t_r, [h]	Z, [%]	Fracture at
Super 304 H - Super 304 H	DP 99	650	140	14 632	22.4	BM
HR3C - HR3C	DP 03	650	160	8 968	51.1	BM
HR3C - HR3C	DP 20	750	50	7 704	2.8	CG HAZ

The examples of microstructure of creep tests of weldments after creep exposure at 650 °C of both tested steels with the dark particles of σ-phase precipitated on grain boundaries are shown in **Figure 4**. The rupture locality was in both cases base material.

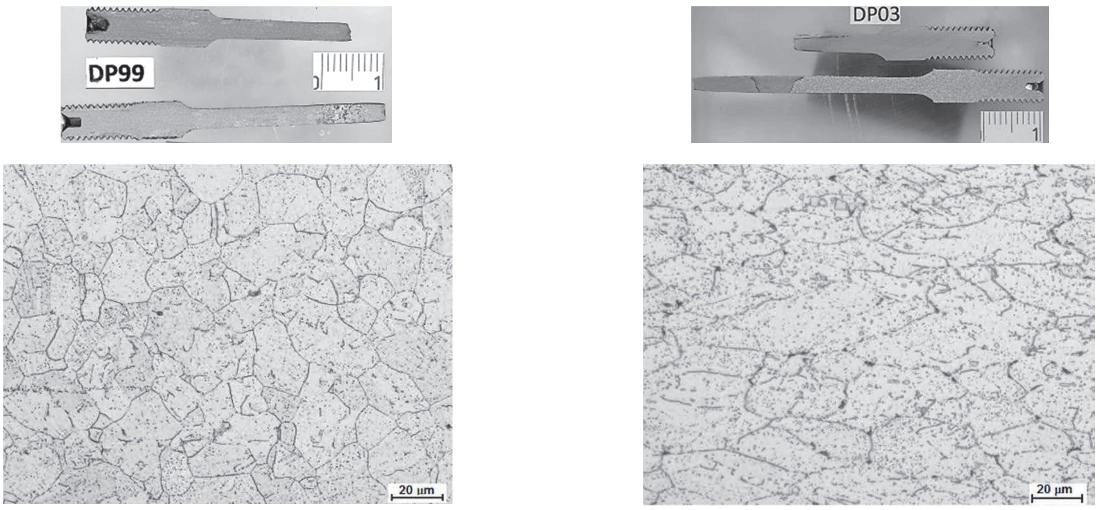
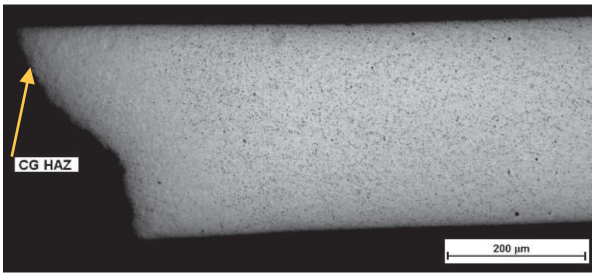
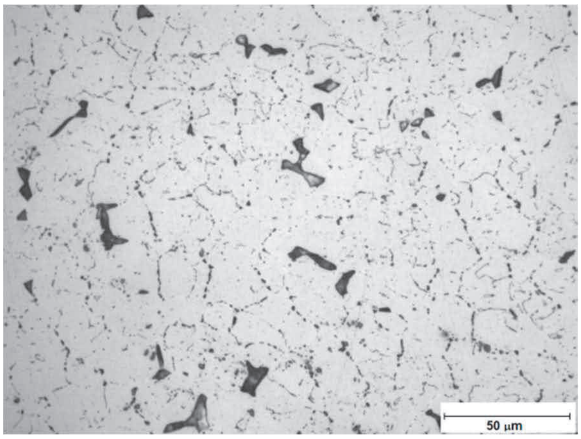


Figure 4 Macrostructure of creep specimen and microstructure of BM of Super 304 H (left) and HR3C (right)

On the other hand, at 750 °C the rupture locality shifted to the coarse-grained part of heat affected zone (CG HAZ), see **Figure 5**. When microstructure of CG HAZ and base material is compared it is clear that precipitated in the CG HAZ formed of chains along grain boundaries, while in the base material these particles are distributed more randomly. Precipitation of σ-phase on the grain boundaries is also accompanied by the local depletion of chromium content, which can further lower their strength.





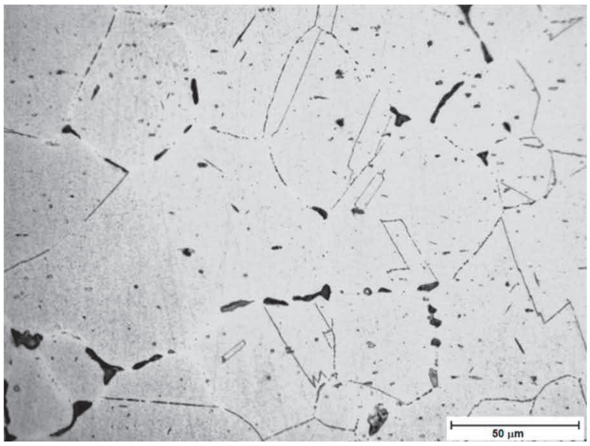


Figure 5 Creep test DP 20:
above left: rupture line in CG HAZ
above: chains of σ-phase particles along brain boundaries in CG HAZ
left: distribution of σ-phase particles in base metal

6. DISCUSSION

It was observed that in creep resistant stainless steels, σ-phase has a detrimental effect on creep properties when precipitated on grain boundaries, but little effect when it precipitates intragranularly. It precipitates first on triple points and then on grain faces. After long-term ageing at high temperature, it also forms on incoherent twin boundaries and intragranular inclusions.σ-phase was found in most of the grades of austenitic stainless steels. However, it forms after different times and its formation is faster in stabilized grades than in other grades, which correlates with the fact that σ-phase forms when the carbon content falls below a critical value and the chromium equivalent is higher than 18 wt. %. [11] The precipitation of $M_{23}C_6$ lowers the carbon and chromium concentration in the solid solution and then retards its precipitation. Elements like Cr, Nb, Ti, W or Mo are known to promote the formation of σ-phase, silicon promotes and accelerates its formation, while carbon, nitrogen and boron inhibits it. In general, formation of σ-phase in ferrite is about 100 times faster than in austenite, which means that also the presence of δ-ferrite accelerates σ-phase precipitation. [12] The formation range of σ-phase is from 600 to 900 °C and the presence of ferrite, which is higher in Cr than austenite, significantly accelerates σ-phase formation. Therefore, weld metals containing retained ferrite are most susceptible to σ-phase embrittlement. Cold work also accelerates the nucleation of σ-phase [13] and the same is true for high temperature creep exposure. The presence of σ-phase itself does not necessarily mean a problem; in order to cause significant losses in toughness and ductility, the particles must be continuously or nearly continuously distributed in the microstructure. CG HAZ where grain size is much coarser than in the base material is then the ideal location where continuous films of σ-phase can develop.

7. CONCLUSIONS

The evaluation of creep resistance of superheater tubes and their weld joints made of steels Super 304 H and HR3C confirmed that the creep rupture strength should lie within the permissible scatter band around the mean values, which gave a very good prospect for their long-life operational work. On the other hand, precipitation of brittle σ-phase appearing during creep exposure in the structure and mainly the formation of chains of this phase in the heat affected zone of weldments can result in extremely low plasticity especially of coarse grained part of HAZ.

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