



# ZBORNIK RADOVA CONFERENCE PROCEEDINGS

32. SAVETOVANJE SA MEĐUNARODNIM UČEŠĆEM  
32<sup>nd</sup> CONFERENCE WITH INTERNATIONAL PARTICIPATION

ZAVARIVANJE / WELDING 2022

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Društvo za unapređivanje zavarivanja-**DUZS**

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# ZAVARIVOST IZMEĐU ČELIKA TIPA 304H I ČELIKA TIPA P91 ZA PRIMENE NA VISOKIM TEMPERATURIMA

## WELDABILITY BETWEEN STEEL TYPE 304H AND STEEL TYPE P91 FOR HIGH TEMPERATURE APPLICATIONS

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**Rezime:** Ovaj rad predstavlja istraživanje zavarljivosti između dva različita čelika, martenzitnog čelika P91 i 304H austenitnog čelika. Oba materijala se preferiraju kao strukturalni materijali za primenu na višim temperaturama zbog svojih dobrih mehaničkih svojstva na visokim temperaturama. Mehanička svojstva na visokim temperaturama, kao što su zatezna čvrstoća i otpornost na puzanje, su veoma važni faktori koji obezbeđuju primenu materijala. P91 je modifikovani martenzitni Cr čelik sa većom količinom hroma koji poboljšava višu temperaturnu čvrstoću i molibdena koji povećava otpornost na puzanje. S druge strane, 304H predstavlja napredni austenitni nerđajući čelik sa kontrolisanim sadržajem ugljenika, što ga čini idealnim za aplikacije koje zahtevaju dobra mehanička svojstva na povišenim temperaturama. Sa povećanjem zahteva za visokom efikasnošću u industriji proizvodnje električne energije, aplikacije na visokim temperaturama obično zahtevaju spojeve između naprednih austenitnih nerđajućih čelika i nove klase martenzitnih nerđajućih čelika kako bi se postigao cilj sa povećanim parametrima pare. Stoga se ovaj rad fokusira na procenu zavarljivosti između ova dva različita čelika i karakteristike metala šava.

**Ključne reči:** P91, 304H, zavarljivost, različit zavareni spoj

**Abstract:** This paper presents research about weldability between two dissimilar steels, martensitic steel P91 and 304H austenitic steel. Both materials are being preferred as a structural material for higher temperature applications due to their good mechanical properties at high temperatures. The mechanical properties at high temperature, such as tensile strength and creep resistance, are very important factors that ensure the application of materials. The P91 is modified martensitic Cr steel with higher amount of chromium which improves the higher temperature strength and molybdenum that increases creep resistance. On the other hand, the 304H represents advance austenitic stainless steel with controlled carbon content, that makes it ideal for applications requiring good mechanical properties at elevated temperatures. With increasing the demand of high efficiency in the power generation industry the high temperature applications usually require joints between advanced austenitic stainless steels and new class martensitic stainless steels in order to achieve the goal with the increased steam parameters. Therefore, this paper focuses on the weldability assessment between these two different steels and the characteristics of the weld metal.

**Key words:** P91, 304H, weldability, dissimilar weld joint

## 1. INTRODUCTION

One of the reasons for using materials in high temperature applications are the ultra-super critical coal-fired power plants working with higher steam conditions. During electricity crises and the new methods for clean energy the use of coal needs to satisfy the environmental requirements and take care about the air pollutants [1]. Thus, the reduction of CO<sub>2</sub> emissions is by increasing the operating temperatures and pressure. The goal is to increase the efficiency and reduce the carbon footprint of new and existing fossil fired power plants.

The demand is being met with development of advanced materials that have enhanced high temperature mechanical properties, high temperature creep resistance and high temperature corrosion resistance. The utilization of the advanced materials in advanced power plant systems depends on their ability to be welded. Therefore, the weldability plays a significant role in the selection of materials.

The steel P91 is part of the group of heat-resistant steels and with its great mechanical properties: creep strength, thermal conductivity, high resistance to thermal fatigue, low coefficient of thermal expansion is suitable material for high temperature applications. The materials are used in new and revitalized power plants, for steam generators, fast breeder reactors and other heavy-duty applications [2,3].

The austenitic 304H stainless steel is characterized by high heat resistance in elevated temperatures. For boiler super heater tubes experiencing 630°C, austenitic stainless steels 304H, 316 or 347H are used and for steam headers is used P91 steel. The heater tubes needs to be welded with the steam headers, that is why these dissimilar welds become necessary.

## 2. MARTENSITIC MODIFIED STEEL P91

ASME Boiler and Pressure Vessel Code, Section IX, [4] defines the creep strength-enhanced ferritic steels as a family of ferritic steels whose creep strength is enhanced by the creation of a precise condition of microstructure, specifically martensite or bainite, which is stabilized during tempering by controlled precipitation of temper-resistant carbides, carbonitrides or other stable and/or meta-stable phases.

Martensite-ferritic steels modified with Cr, Mo, V and Nb are the new creep resisting steels used in applications for high temperature and pressure systems. In the 9-12% Cr steels family first was developed 12%Cr steel that have high carbon content resulting with formation of martensite with high carbon content causing problems during welding. The next modified steel was with reduction of chromium and carbon content and modification by adding niobium. The martensitic steel was modified by adding vanadium and niobium and was created the steel P91 (A335) with improved creep resistance. The amount of Nb and V added enables the formation of submicron MX type carbonitride (M=Nb, V; X=C, N) with particle size lower than 0.1µm and the presence of these particles improves the creep resistance of the steel [5]. According to EN 10216-2 the P91 steel is defined as X10CrMoVNb9-1.

The chemical composition of steel P91 according to specification ASTM A355 is given in table 1 and it produces a fully martensitic structure figure 1 [6]. The martensite start temperature (M<sub>s</sub>) is around 400°C and it finish at martensite temperature (M<sub>f</sub>) around 200°C. The as-tempered microstructure consists of a fine prior austenite grains containing a lath-like tempered martensite structure with a high dislocation density that is stabilized by M<sub>23</sub>C<sub>6</sub> carbides and MX (Nb, V) carbo-nitrides.

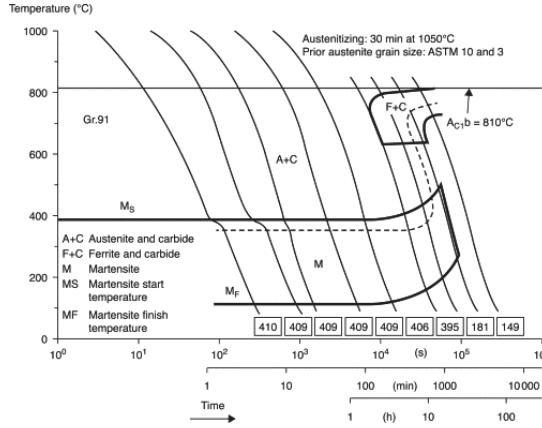


Fig 1: Continuous cooling transformation curves for P91 [6]

Table 1: Chemical composition of steel P91 (in wt.%) according to ASTM A355

C	Mn	Si	P	S	Cr	Ni	Mo	V	Al	Nb	N	Fe
0,08	0.30	0.20	max.	max.	8.00	max.	0.85	0.18	Max.	0.06	0.03	Bal.
÷	÷	÷		0.010	÷	0.40	÷	÷	0.04	÷	÷	
0.12	0.60	0.50			9.50		1.05	0.25		0.10	0.07	

On figure 2 [6] is presented illustration of grade P91, after normalizing and tempering [6]. Tempered martensitic structure is presented where M<sub>23</sub>C<sub>6</sub> carbides (M is rich in Cr) are shown as lath, block, packet and prior austenite grain boundaries. The carbonitrides (MX) are distributed in the matrix within lath and at the boundaries. The coexistence of subgrains of lath and block and fine precipitates are responsible for the high creep strength of steel P91.

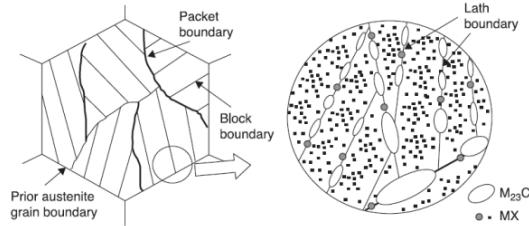
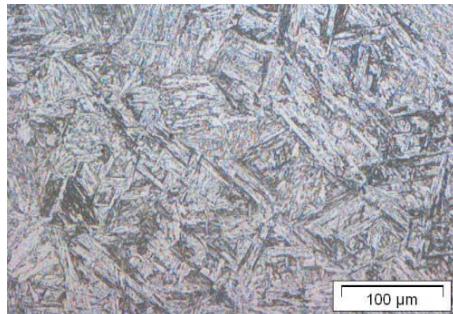


Fig 2: Illustrated tempered martensitic structure of grade P91 [6]

In order to exhibit a martensitic microstructure (figure 3), the chemical composition is balanced according to a formulation modified on the Chromium-Nickel Balance (CNB) where the elemental contents are in weight percent [7].

$$\text{CNB} = \text{Cr} + 6\text{Si} + 4\text{Mo} + 1.5\text{W} + 11\text{V} + 5\text{Nb} + 9\text{Ti} + 12\text{Al} - 40\text{C} - 30\text{N} - 4\text{Ni} - 2\text{Mn} - 1\text{Cu}$$



**Fig 3: Martensitic microstructure of P91 [8]**

Depending on the value of CNB there are different quantities of delta ferrite, CNB less than 10, delta ferrite is not present, between 10 and 12 is not easily present and for CNB above 12 significant quantities of delta ferrite are present.

The mechanical properties of P91 steel at 20°C according to ASTM A355 are given in table 2. The mechanical properties are corresponding to the correctly carried out heat treatment: normalization at temperatures of 1040-1060°C for 1 hour, cooling in still air and tempering at temperatures of 760-780°C.

Table 2: Mechanical properties of P91 steel at 20°C according to ASTM A355

Ultimate tensile strength, MPa	Yield stress, MPa	Charpy V notch impact strength, J	Brinell hardness	A <sub>5</sub> , %
585 min.	415 min.	40 min.	250 max.	17 min.

Due to its high creep resistance, comparable to 18-8 austenitic steel, P91 steel is qualified as low-alloy steel intended for service at elevated temperatures [2].

Brozda and Zeman [9] investigated the tendency of P91 steel to cracking as a result of heat treatment. Their investigation showed that the P91 steel is resistant to reheat cracking. It does not show any tendency to hot cracking and is resistant to reheat cracking in the coarse grain area of the HAZ. Their investigation was carried out on specimens subjected to the action of a simulated thermal cycle of maximum temperature  $T_{\max} = 1250^{\circ}\text{C}$ , each simulated thermal cycle was applied within the temperature range 450-650°C. The area reduction Z had a minimum value for each thermal cycle employed with test pieces treated in a thermal-strain simulator, lower than the permitted value of Z=20%.

### 3. AUSTENITIC STAINLESS STEEL 304H

Alloy 304H (1.4948) stainless steel is a modification of alloy 304 where the carbon content is controlled to a range of max. 0.08% due to improved high temperature strength to elements exposed to temperature above 700°C (table 3). Austenitic stainless steel, Super 304H, according to EN designation X6CrNi18-10, is intended for applications with super heater and reheater tubes due to its special properties: excellent heat resistance in raised temperatures. The chemical composition, mechanical properties, weldability and corrosion/oxidation resistance make the steel ideal for high temperature applications.

Table 3: Classification of creep resistant steels

<i>Heat-resistant steels and special materials</i>				
Bcc structure (body-centered cubic)				
Up to 400°C	Up to 500°C	500 to 600°C	600 to 650°C	Above 700°C
Unalloyed	Alloyed		High-alloyed	
Ferritic-pearlitic steels, fine-grain structural steels	Mo-legierte Stahle	Bainitic (martensitic) ferritic steels	Martensitic 9 to 12% chromium steels	Austenitic steels, Ni and Co-materials
P235GH	16Mo3	13CrMo4-5	X10CrMoVNb9-1	X8CrNiNb16-13
P355NH	18MnMo4-5	10CrMo9-10	X22CrMoV12-1	X8NiCr32-20
No extra proven methods; higher purity; fine grain	Tr-increase through molybdenum alloying	Carbide/nitride formation + tempering	Precipitation hardening + spec. heat treatment	Fcc structure with high crystal recovery temperature

In table 4 is given the chemical composition of super 304H steel. Due to its controlled carbon content to max. 0.08% provides improved high temperature strength and great creep strength when working in high temperature applications. It is used for applications up to 800°C for boilers, heat exchangers, pipelines, steam exhausts.

Table 4: Chemical composition of super 304H steel (in wt.%)

C	Mn	Si	P	S	Cr	Ni	N	Fe
0,04 ÷ 0,08	max. 2.00	max. 1.00	max. 0.035	max. 0.015	17.00 ÷ 19.00	8.00 ÷ 11.00	max. 0.11	Bal.

Minimum mechanical properties required by ASTM A213 & ASME SA-213 are given in table 5:

Table 5: Mechanical Properties of 304H steel at 20°C according to ASTM A213 &amp; ASME SA-213

Ultimate tensile strength, MPa	Yield stress, MPa	Modulus of elasticity kN/mm <sup>2</sup>	Brinell hardness	A <sub>5</sub> , %
515 min.	205 min	200	201 max.	40 min.

#### 4. TYPE IV CRACKING IN STEEL P91

The type IV cracking represent creep cracking and occurs during service in the heat affected zone of ferritic steel weldments. The new creep strength enhanced materials require special attention during welding so that they can retain their high temperature properties.

In Figure 4 are presented the different regions of heat affected zone with creep failure locations [10]. The welds of P91 steel are subjected to Type IV cracking even though it possesses good strength because of carbide precipitation. It occurs during service and it is located in the FG-HAZ (fine-grain) or IC-HAZ (intercritical grain). A Type-IV cracking in

intercritical or fine grain HAZ was seen predominant in high temperature creep testing of this material resulting in pre-mature failure of the weld joints [10].

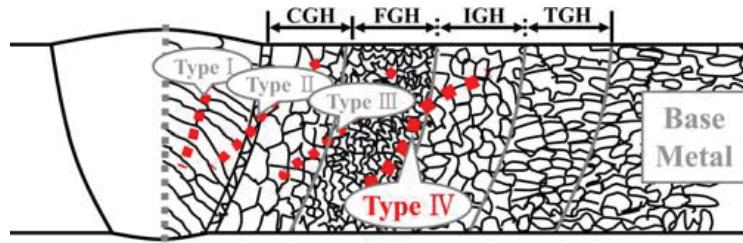


Fig 4: Different damage type of heat affected zone with creep failure locations [10]

To mitigate the type IV cracking research is carried out by Swaminathan et al. [11] by modification of alloy composition by addition of boron. Boron with controlled nitrogen added in P91 steel in the temperature range of 600-650°C has provided a better resistance to Type IV cracking in the material.

## 5. WELDING BETWEEN P91 AND 304H

With the composition, microstructure, properties and process parameters is often determined the weldability of material. The American welding society handbook defines weldability as “the capacity of a material to be welded under the imposed fabrication conditions into a specific, suitable designed structure and to perform satisfactorily in the intended service [12]”.

On figure 5 is presented schematic diagram of subzones in HAZ of P91 corresponding to the calculated equilibrium phase diagram [13].

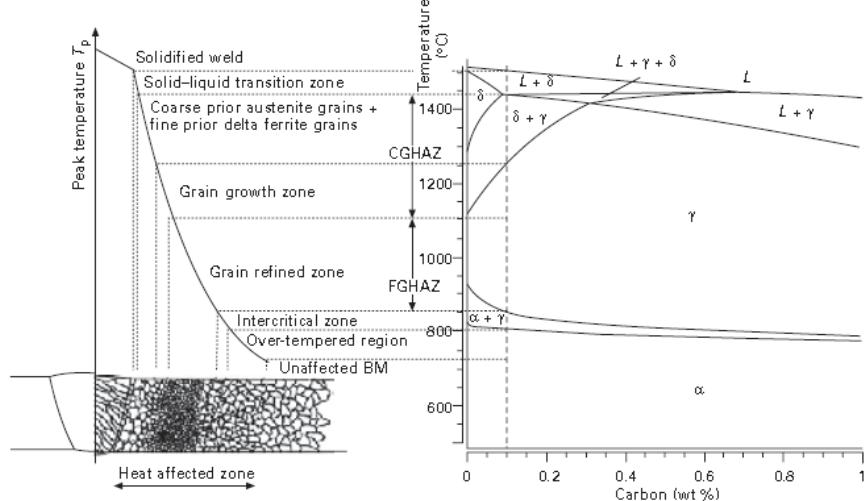
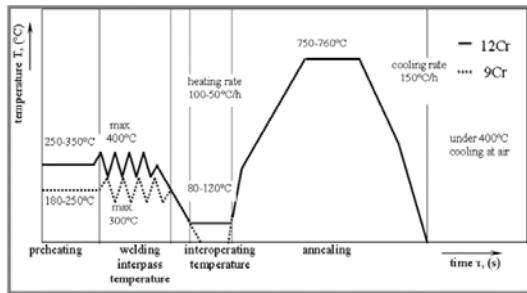


Fig 5: Equilibrium phase diagram of steel P91 [13]

To maintain and assure quality welds special attention should be dedicated to temperature time cycle of steel P91 as shown in figure 6 [14]. All heat treatment operations are a key factor when welding P91 steel for obtaining the required toughness and creep resistance.



**Fig 6: Temperature time cycle during welding of martensitic 9 or 12% chromium steels [14]**

Joining of austenitic and martensitic steel structural heterogeneities may occur on the line of fusion of the welded joint at the points of their joining or during the operation at elevated temperatures [15]. Due to the mismatch between the coefficients of thermal expansion (CTE) and carbon migration, failures have been reported in these welds for many high temperature tubular applications [16].

When martensitic steel is welded with austenitic steel it is commonly used filler materials based on nickel. Filler materials based on nickel provide transition in coefficients of thermal expansion (CTE) and efficient for stopping the carbon diffusion from the low Cr material into high Cr material compared with conventional austenitic base material [16,17]. When welding martensitic P91 steel with austenitic stainless 304H steel, the best way is to create a buffer layer on the low alloyed side of the joint. First the P91 steel needs to be buffered with nickel based alloy and followed by a heat treatment. Buffered and after heat treatment the P91 steel can be welded with the austenitic stainless 304H steel using filler materials with nickel based alloy without any further pre-heating and heat treatment after welding. Also, on the 304H steel is not performed any buffering to avoid transformation of austenite structure with cracks.

There are other several ways to perform the joining of dissimilar metals. One of them is rotary friction welding which does not involve melting and widens the choice of interlayer materials and also the ability to employ multiple interlayers to ensure a smoother change in CTE (coefficient of thermal expansion) between the two base materials [18]. And laser gas metal arc (hybrid) welding which together with FSW are presenting low heat input processes, with reduction in residual stresses and distortion and potential elimination of type IV cracking.

## 6. CREEP STRENGTH OF DISSIMILAR METAL WELDS

The creep phenomenon which occurs at elevated temperatures plays a major role in failure of welded joints. In ASME Section II, at elevated-temperature creep regions, the allowable stress is determined by several factors, such as 100% of the average stress to produce a creep rate of 0.01%1000h, 67% of the average stress and 80% of the minimum stress to cause rupture at the end of 100 000h [19].

In dissimilar weld between P91 steel and austenitic stainless steel, the creep was seen occurring on the P91 steel side. The joints are usually tested at temperature range of 550-700°C and it was observed that creep life of such joints is of P91 [20].

According to Zielinski at all [15], after 105 000h service of dissimilar welded joint at maximum working temperature of approximately 540°C there where revealed insignificant degree of degradation of the microstructure of base material and HAZ on the austenitic material side. The most degraded area was HAZ on the martensite steel side. The changes in the microstructure due to production of material, welding and heat treatment of the welded joint, contribute to accelerate damage during service and results in type IV cracking.

## 7. CONCLUSION

A very little research work is being carried out on base metal and weld metal between P91 steel and 304H austenitic stainless steel. In ultra-super critical power plants this type of joints are with an increasing demand because of their better performance. Therefore, for the accurate prediction of weld joints, its accuracy in service life is essential.

Zielinski at all [15] considered on the possibility of applying the PWHT of P91 steel in the lower acceptable range of annealing temperature due to the occurrence of degraded microstructure of the dissimilar welded joint within HAZ on the P91 steel side.

To achieve good microstructural welded joint between martensitic P91 steel and austenitic 304H steel, it is necessary to respect all the recommendations and parameters for welding, post weld heat treatment and the use of a suitable nickel-based filler material.

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