

PHASE TRANSFORMATIONS IN CREEP STRENGTH ENHANCED FERRITIC STEEL WELDS

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Abstract: Creep Strength Enhanced Ferritic (CSEF) steels are extensively used in the modern fossil power plants with supercritical steam parameters. The high creep strength of CSEF steels is based on a microstructure of tempered martensite with finely dispersed carbides, nitrides, and carbonitrides that is produced by tempering. Accurate determination of the A_1 temperature in CSEF steels is of critical importance for the development of appropriate tempering and post weld heat treatment (PWHT) procedures. A database of A_1 temperatures in CSEF steel is generated using advanced phase transformation analysis technique. The effect of exceeding the A_1 temperature during tempering on the microstructure in CSEF welds is also investigated. Model-based design of experiment (DoE) is applied to evaluate the effect of alloying elements on the A_1 temperature. A predictive formula for the A_1 temperature in CSEF steels is developed using measurement-based DoE. The results of these studies are applicable for materials selection and development of optimized PWHT procedures for CSEF steel welds.

Keywords: CREEP STRENGTH ENHANCED FERRITIC STEELS, WELDING, HEAT TREATMENT, PHASE TRANSFORMATIONS, MICROSTRUCTURE

1. Introduction

The Creep Strength Enhanced Ferritic (CSEF) steels (ASTM Grades P91, P92, P122) are high alloy steels that contain between 9% and 12% Cr, small amounts of Mo, V, Nb, and varying additions of W, Co, B, N, and Ni. Due to their excellent creep properties, CSEF steels are extensively used in the modern fossil power plants with supercritical steam parameters.

The microstructure of CSEF steels in the standard as-received condition is tempered martensite with finely dispersed carbides, nitrides, and carbonitrides that provide optimal combination of high creep strength and toughness [1]. However, during welding this microstructure is adversely altered by formation of fresh martensite in the weld metal and the heat affected zone (HAZ). Depending on the base metal and weld metal composition, formation of small amounts of delta ferrite and/or retained austenite is also possible. To restore the optimal microstructure and creep properties, CSEF steel welds should be subjected to a PWHT in a range of temperatures slightly below the A_1 temperature. Data for the A_1 temperatures in CSEF steels and weld metals is not readily available. An ASTM Boiler and Pressure Vessel Code specification that is based on the weld metal Mn+Ni content is currently used for determination of the maximum allowable PWHT temperatures in CSEF steel welds.

This paper summarizes the results from a series of industrially sponsored research projects on phase transformations in CSEF steel welds conducted at the Welding and Joining Metallurgy Laboratory of the Ohio State University. A database of measured A_1 temperature values in Grade P91 and P92 steels and their respective weld metals was developed by advanced phase transformation analysis techniques. Most of the weld metal A_1 temperatures within this data base were lower than the ASTM maximum allowable PWHT temperatures. The effects of exceeding the A_1 temperature during PWHT on the CSEF steel weld microstructure was investigated by phase transformation analysis and metallurgical characterization. Model-based design of experiment (DoE) was applied to evaluate the effect of alloying elements on the A_1 temperature. A predictive equation for the A_1 temperature in Grade P91 steels was developed using measurement based DoE. The results of these studies are applicable for materials selection and development of optimized PWHT procedures for CSEF steel welds.

2. Materials and Procedures

The A_1 temperature database developed in this study covered more than 70 Grade P91 and P92 steel base and weld metals. The model-based DoE and the measurement DoE were developed in the full composition range of Grade P91 steel. The ASTM A335-05 composition specifications for Grade P91 and P92 steels and the AWS A5.5:2006 specification for undiluted weld metal of Grade 91 shielded metal arc electrodes are shown in Table 1.

Table 1: Composition of ASTM Grade P91 and P92 steels and AWS Grade P91 shielded metal arc weld deposit (wt. %)

Element	Grade P91 Steel	Grade P92 Steel	Grade P91 Weld Metal
C	0.08-0.12	0.07-0.13	0.08-0.13
Mn	0.30-0.60	0.30-0.60	0.3-1.2
Si	0.20-0.50	0.50*	0.3
S	0.010	0.010	0.010
P	0.020	0.020	0.010
Cr	8.00-9.50	8.00-9.50	8-10.5
Ni	0.40	0.40	0.8
Mo	0.85-1.05	0.30-0.60	0.85-1.2
V	0.18-0.25	0.15-0.25	0.15-0.3
Nb	0.06-0.10	0.04-0.09	0.02-0.1
N	0.03-0.07	0.03-0.07	0.02-0.07
Al	0.040	0.040	0.04
Cu	-	-	0.25
W	-	1.5-2.00	-
B	-	0.001-0.006	-
Mn + Ni	1.0	1.0	< 1.5

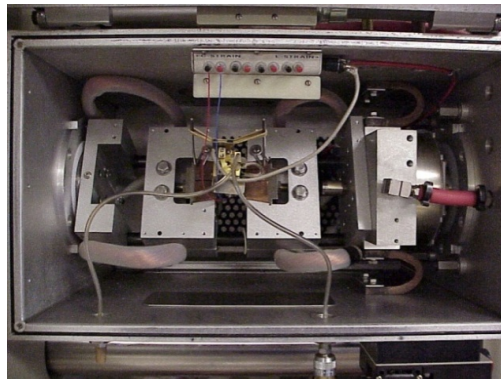
* Single values represent maximum content

The response of CSEF steel welds to improper PWHT was demonstrated in a submerged arc weld (SAW) of 0.75 in. thick P91 steel plate and in a non-diluted gas metal arc weld (GMAW) deposit of a P91 electrode wire (ER90S-B9). The chemical compositions of these welds are shown in Table 2.

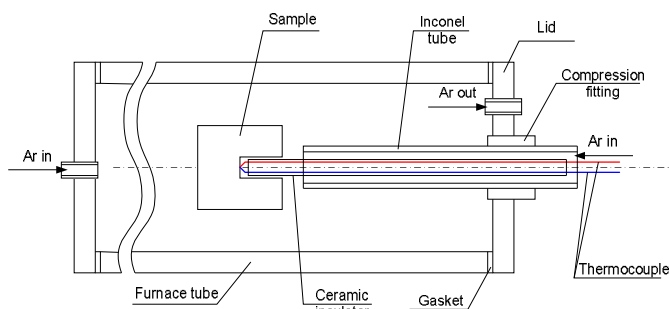
PWHT simulations were conducted using the Gleeble 3800TM thermal simulator and a conventional gas-shielded tube furnace. Dilatometry and Single Sensor Differential Thermal Analysis (SS DTA) were utilized for determination of the A_1 temperature and for phase transformation analysis during PWHT simulations. The A_1 temperature (close to equilibrium value of A_{c1}) was determined using the ASTM A1033-10 procedure [2] that utilizes a slow heating rate of 28 °C/hr. The dilatometry experimental setup in the GleebleTM thermo-mechanical simulator is shown in Figure 1.

Table 2: Weld metal compositions in the tested submerged and shielded metal arc welds (wt. %)

Element	Submerged Arc Weld	Gas-metal Arc Weld
C	0.116	0.07
Mn	0.60	0.55
P	0.007	0.009
S	0.001	0.001
Si	0.29	0.25
Cu	0.06	0.035
Ni	0.65	0.71
Cr	8.94	8.99
Mo	0.99	0.93
Al	0.006	0.012
Nb	0.06	0.06
V	0.194	0.18
N	0.037	0.037
Mn+Ni	1.25	1.27

**Fig.1** Dilatometry set-up in the Gleeble™ thermo-mechanical simulator

The SS DTA is a patented technique for phase transformation analysis that determines enthalpy changes in metallic alloys during continuous heating and cooling [3]. Compared to the classic DTA, the SS DTA technique utilizes a single thermocouple to acquire the thermal history of the tested material and software to generate a reference curve that is free of thermal effects of phase transformations. The use of a single thermocouple allows for in-situ application of SS DTA during thermal and thermo-mechanical processing of engineering materials. An example of SS DTA experimental set-up during heat treatment is shown in Figure 2.

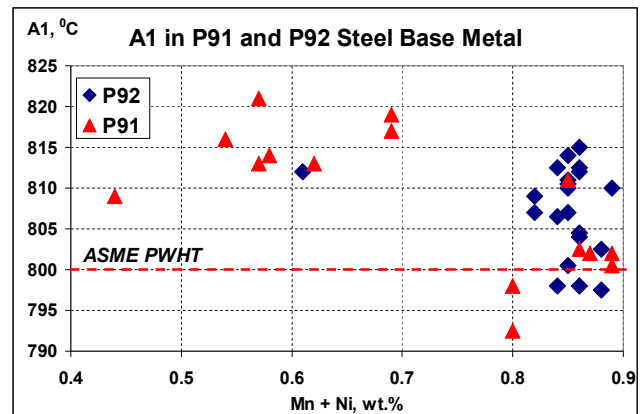
**Fig. 2** SS DTA experimental set-up for heat treatment.

3. Database of A_1 temperatures in CSEF Steels

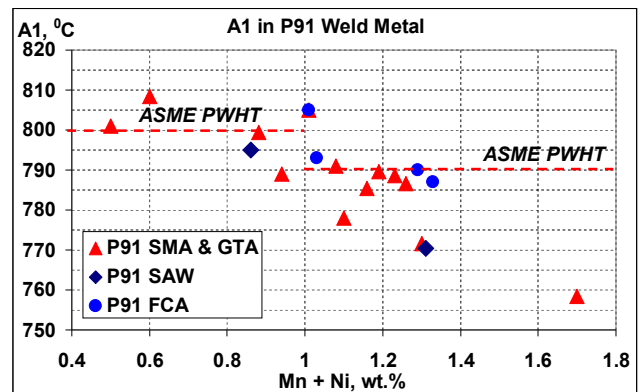
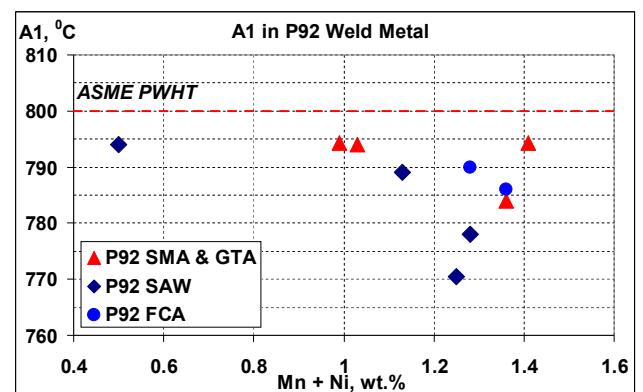
A database of A_1 temperature values in more than 70 commercial Grade P91 and P92 steels and undiluted deposits of P91 and P92 welding consumables was generated using dilatometry and SS DTA measurements. The A_1 temperatures determined in this study are presented in Figures 3, 4, and 5 as a function of the Mn + Ni content, and summarized in Table 3.

As the austenite stabilizers with most variable content in CSEF steels, manganese and nickel have been considered the main factors controlling the A_1 temperature. The ASME Boiler and Pressure Vessel Code specifies the maximum allowable PWHT temperatures in P91 steel welds as a function of the weld metal Mn + Ni content as follows [4]: 800 °C if Mn + Ni is below 1 wt.%; 790 °C if Mn +

Ni is between 1.0 and 1.5 wt.%; and 775 °C if Mn + Ni content is unknown. For P92 welds, the maximum allowable PWHT temperature is 800 °C. The maximum ASME allowable PWHT temperature is shown in Figures 3, 4, and 5 for each of the tested base metal and weld metal steel grades.

**Fig. 3** A_1 temperature in Grades P91 and P92 steels determined using dilatometry.

The results from this study show that the A_1 temperature in the tested alloys is not controlled only by the Mn + Ni content. A_1 temperature variations of up to 20 °C were found for alloys with equal or similar Mn + Ni content, Figures 3, 4, 5. Based on these results it can be concluded that the A_1 temperature is affected by the total balance of austenite and ferrite stabilizers in the alloy composition. It could be expected that the initial base metal microstructure (tempered martensite in as delivered condition and fresh martensite in weld heat affected zone), and the microstructural inhomogeneity in multipass welds would also affect the A_1 temperature in CSEF alloys.

**Fig. 4** A_1 temperatures in P91 weld metal determined using SS DTA.**Fig. 5** A_1 temperatures in P92 weld metal determined using SS DTA.

Some of the tested base metals (Figure 3), more than 75% of the tested Grade P91 weld metals (Figure 4), and all tested Grade P92 weld metals (Figure 5) have A_1 temperatures that are below or at the ASME code allowable maximum PWHT temperature. This result has a significant practical implication. Performing PWHT below or

at the ASME maximum allowed temperature can result in exceeding the base metal and/or weld metal A_1 temperature, leading to the formation of alpha ferrite and fresh martensite that are detrimental to the weld metal creep strength and toughness.

Table 3: A_1 temperatures in Grade P91 and P92 steel base and weld metals

Grade	P91 BM	P91 WM	P92 BM	P92 WM
Heats tested	15	19	21	16
Mn + Ni, wt. %	0.62 - 0.89	0.5 - 1.31	0.61 - 0.89	0.61 - 1.41
A_1 , °C	788 - 813	770 - 801	795 - 817	759 - 800
max $A_1(\text{BM}) - A_1(\text{WM})$, °C	43		58	

The results summarized in Table 3 have practical importance in terms of materials selection. Combining CSEF steels and weld filler metals with unknown A_1 temperatures may result in up to 60 °C difference in the base and weld metal A_1 temperatures of a particular weld. Insufficient tempering, over tempering, and/or exceeding the A_1 temperature can be expected in the base metal, HAZ and/or weld metal during the PWHT of such welds.

4. Response of CSEF Steels to Improper PWHT

The response of CSEF steel weld metal to improper PWHT was studied by performing heat treatments slightly below and above the A_1 temperature using the Gleeble™ and a conventional gas shielded convection furnace. The PWHT parameters for both the submerged and the gas-metal arc welds are shown in Table 4. The phase transformations determined during the PWHT of the test samples are shown in Figures 6 and 7. The final microstructure after PWHT in the GMAW weld is also shown in Figure 7.

Table 4: PWHT parameters of submerged arc and gas-metal arc welds.

Weld	Heating rate, °C/hr	Holding / A_1 temperatures, °C	Holding time, hr	Cooling rate, °C/hr
SAW 1	204	765 / 767	2	204
SAW 2	204	780 / 767	2	204
GMAW	600	800 / 787	2	144

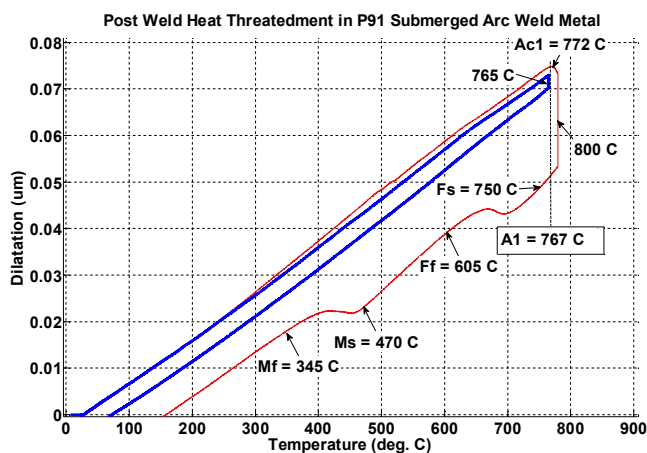


Fig. 6 Dilation curves in P91 submerged arc weld samples heat treated for 2 hrs at 765 °C and at 780 °C (A_1 temperature 767 °C).

The dilation curve in Figure 6 shows that the weld metal heat treated below the A_1 temperature does not undergo any phase transformations during cooling after tempering (blue curve). Exceeding the A_1 temperature during PWHT results in partial transformation of the as-welded martensitic microstructure to austenite. This transformation is noted on Figure 6 (red curve) as a sharp volume reduction during holding at 800 °C. During cooling, the austenite decomposes to ferrite and fresh martensite.

The SS DTA curve on Figure 7 shows two enthalpy change events (exothermic reactions) related to formation of ferrite during cooling in the GMAW weld that was tempered above the A_1 temperature. Islands of soft alpha ferrite (147 HVN) surrounded by tempered martensite (252 HVN) were identified in the microstructure of this weld.

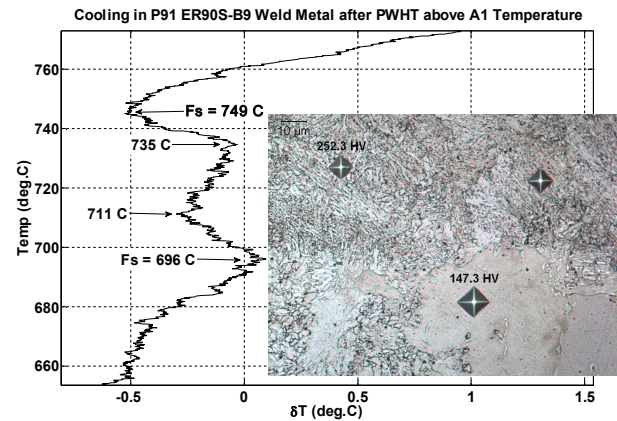


Fig. 7 SS DTA processed cooling curve and microstructure in ER90S-B9 gas-metal arc weld deposit heat treated at 800 °C for 2 hrs ($A_1 = 787$ °C).

The results of this study demonstrate that exceeding the A_1 temperature during PWHT of CSEF steel welds results in the formation of detrimental microconstituents for the creep properties (ferrite) and toughness (fresh martensite). The products of austenite decomposition in CSEF welds are determined by the level of inhomogeneity in their microstructure. The as-welded microstructure in multipass CSEF welds consists of fresh martensite and partly tempered martensite. The latter is produced by reheating during the sequential bead deposition in multipass welds. It is expected that upon exceeding the A_1 temperature the fresh martensite and the partly tempered martensite in would transform to austenite that has varying alloying content and homogeneity. During cooling, the austenite containing higher amounts of undissolved precipitates (carbides and carbonitrides) is less stable and would decompose to ferrite, while higher alloyed homogeneous austenite would form fresh martensite.

5. Effect of Alloy Composition on A_1 Temperature in CSEF Steels

The results presented in Sections 3 and 4 of this paper have shown the importance of A_1 temperature for the proper selection of welding consumables and PWHT temperatures for CSEF steel welds. A_1 temperature data for CSEF steels and welding consumables is not readily available. Experimental determination of the A_1 temperature is time consuming and requires specialized equipment. This motivated the development of a composition-based predictive equation for the A_1 temperature in CSEF steels.

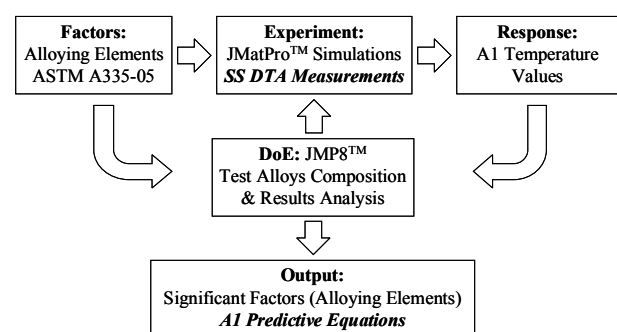


Fig. 8 Flow chart of the Model-Based DoE (JMatPro™) and the Measurement Based DoE (SS DTA).

A model-based and a measurement-based design of experiments (DoE) were developed to study the effect of alloying elements on the A_1 temperature in Grade P91 steels. The model-based DoE utilized the thermodynamic software JMatPro™ to predict the A_1 temperature. The measurement-based DoE utilized the SS DTA technique to experimentally determine the A_1 temperature. Three level partial factorial experiments were developed in the DoE software JMP8™ within the alloy composition specified by ASTM (Table 1). Figure 8 shows the flow chart of the two DoE procedures.

The output from the model-based DoE identified the alloying elements with the strongest influence on the A_1 temperature, Figure 9. These alloying elements were then varied in the measurement-based DoE to develop a predictive equation for the A_1 temperature in Grade P91 steel. Copper was also added to the measurement-based DoE, although it was not included in the ASTM specification (Table 2). Previous experience had shown that copper has a significant effect on the A_1 temperature in Grade P91 steel.

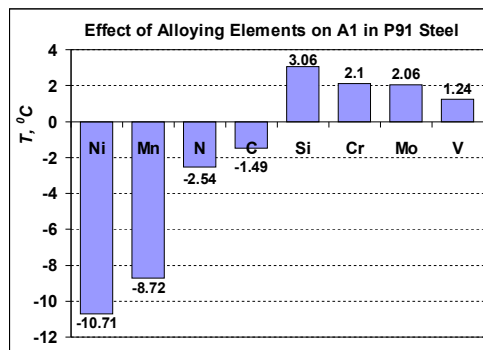


Fig. 9 Effect of the alloying elements on the A_1 temperature in Grade P91 steel predicted by the model-based DoE (JMatPro™).

Test sample compositions for the measurement-based DoE were designed by the JMP8™ software. These samples were produced utilizing gas-tungsten arc melting and casting in shielding atmosphere of argon. The samples were further processed to reproduce the rolled microstructure in Grade P91 plates. The processing included: 1) homogenization at 1050 °C for 4 hrs; 2) hot rolling at 1000 °C in three steps to a total thickness reduction of 34%; 3) normalization at 1050 °C for 0.5 hrs; 4) tempering at 750 °C for 2 hrs.

A typical SS DTA curve exemplifying the determination of A_1 temperature in the model-based DoE is shown in Figure 10. The predictive formula for the A_1 temperature in Grade P91 steel derived from the measurement-based DoE is given in Equation 1. This formula is valid for the whole composition range of ASTM Grade P91 steel (Table 2) and for copper content between 0.12 and 0.40 wt.%. It was assumed that copper content below 0.12 wt.% does not have a significant effect on the A_1 temperature.

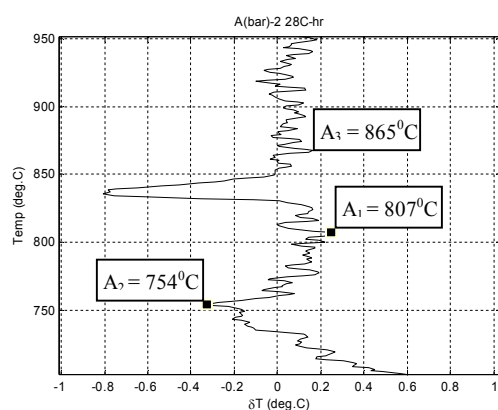


Fig. 10 Critical temperatures in measurement-based DoE test sample determined using SS DTA.

$$A_1 (°C) = 2113 - 243 \cdot C - 174 \cdot N + 87.5 \cdot Si - 24.4 \cdot Mn + 16.676 \cdot Cr^2 - 288.49 \cdot Cr - 365.45 \cdot Ni^2 + 153.05 \cdot Ni + 164 \cdot Mo^2 - 299.2 \cdot Mo + 1320 \cdot V^2 - 570 \cdot V - 194.3 \cdot Cu^2 + 83.9 \cdot Cu \quad (1)$$

The newly developed predictive formula was validated by dilatometry measurements of the A_1 temperature in ten commercial heats of Grade P91 steel with Mn + Ni content between 0.44 and 0.89 wt.%, Figure 11. The deviation of the predicted A_1 values from the measured ones was in the range of range ± 3 °C. Most of the A_1 values predicted using the JMat-Pro™ software were 5 to 10 °C lower than the measured ones. A_1 temperature values predicted by a

neural network-based equation developed by Santella [5] also gave significant deviations of the measured A_1 values.

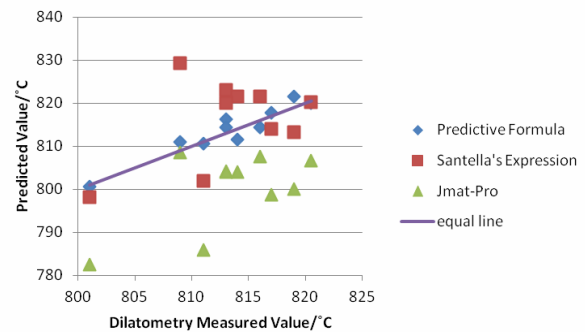


Fig. 10 Predicted vs. measured values in ASTM Grade P91 steels.

Conclusions

1. A database of measured A_1 temperatures in more than 70 Grade P91 and P92 steel base and weld metals has been developed. Some of the steels and most of the weld metals in this database have A_1 temperature lower than the ASME allowable maximum PWHT temperature. The maximum difference between the base metal and weld metal A_1 temperatures in this database is 58 °C.
2. Exceeding the A_1 temperature during PWHT in CSEF welds results in formation of alpha ferrite and/or fresh martensite in the final weld microstructure that are known to be detrimental for the creep strength and toughness.
3. Selection of welding consumables and PWHT temperatures that does not consider the actual A_1 temperatures can result in insufficient tempering, over tempering, and/or formation of ferrite and fresh martensite during PWHT of CSEF welds.
4. The A_1 temperature in CSEF steels is a complex function of the alloy composition and microstructure. Although the Mn + Ni content has a very strong effect, it can not be considered as single determining factor for the A_1 temperature.
5. A predictive equation for the A_1 temperature in Grade P91 steels is developed utilizing measurement-based DoE. This equation accurately predicts the A_1 temperature in the ASTM Grade P91 steel composition range and can be used for materials selection and determination of PWHT temperatures.

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