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REVIEW OF HAYNES® 282® ALLOY FOR SUPERCRITICAL CO_2 STRUCTURAL APPLICATIONS

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ABSTRACT
In this paper, HAYNES® 282® alloy (282® alloy) properties, microstructure, high temperature oxidation resistance, weldability, and American Society of Mechanical Engineers (ASME) code case highlights are reviewed. The long term performance of high temperature, high strength, creep resistant alloys is critical to the success of supercritical carbon dioxide equipment. Several modern power generation technologies require alloys that can operate continuously at or above 700ºC. 282® alloy is a precipitation strengthened nickel based super alloy that meets these requirements. The results of 282® alloy research reviewed in this paper include long-term cyclic oxidation behavior in air and sCO2, independent research and validation of 100k hour creep life, and successful welding of the alloy in the age hardened condition. The latter is critical for joining of hardened components (flanges, piping, heat exchanger internal, etc.) and field repair. Several highlights from the code case for this ASME-approved material are also presented.

INTRODUCTION
This paper presents a comprehensive overview of a nickel-based alloy that is qualified for long term, high temperature service in super critical carbon dioxide.

HAYNES® [1] 282® alloy was first available for commercial use in 2005. 282® alloy is a precipitation strengthened alloy whose primary alloying elements are Ni-Cr-Co-Mo-Ti-Al. Its primary commercial applications are in the aerospace, industrial gas turbine, and automotive industries. Heat treatments applied to the 282 alloy have the purpose of forming chromium-rich $M_{23}C_6$ carbides and of precipitating gamma-prime particles. Detailed information about the alloy's development, thermal stability, microstructure, and properties has been explained in a previous paper [1,2].

The operating conditions of supercrictical carbon dioxide (sCO2) power cycles and advanced supercritical steam cycles (A-USC) require high pressure, high temperature plant components to be manufactured from nickel-based superalloys. Research conducted by the U.S. Department of Energy (DoE) proved HAYNES® 282® alloy (UNS N07208), a Ni-Cr-Co-Mo-Ti-Al precipitation strengthened alloy was a leading choice for A-USC applications [3]. Research performed by the DoE and Haynes International, Inc. led to the production of required American Society of Mechanical Engineers (ASME) code case data. The data generated focused on a single step age hardening treatment, which is a four hour single step age hardening heat treatment at 800°C (1472°F) followed by air cooling (800°C

[1] HAYNES and 282 are registered trademarks at Haynes International, Inc.

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(1472°F)/4 hr/AC). The 282® alloy ASME code case is 3024 and the Code Case is applicable to Section I and Section VIII, Division 1 construction.

Research efforts parallel to DoE code case efforts [4-6] have been heavily support by Haynes International, Inc. through several pathways. One pathway included Haynes International, Inc. providing alloy product forms (bar, plate, forgings, cast stock, powder, pipe, and tube) to private and federally-funded research programs. The programs have produced many demonstrations of potential end use products for demonstration scale and laboratory scale 282® alloy components. These components include a forged rotor shaft, a cast turbine rotor casing, heat exchanger tube bundles, advanced manufactured microchannel heat exchangers, and micro turbine components with blades integrated with the rotor shaft to produce one-piece turbine internals. A second pathway is that Haynes International often provides internally-generated data to selected research programs and customer applications in support of their goals.

COMPOSITION AND MICROSTRUCTURE

Table 1 contains the ASME chemical composition of 282® alloy in weight percent.

Element	Nominal Composition, %
Ni	Remainder
Cr	18.5-20.5
Fe	1.5 max
Mn	0.3 max
Co	9.0 - 11.0
C	0.04 - 0.08
Si	0.15 max
S	0.015 max
P	0.015 max
Al	1.38-1.65
B	0.003-0.010
Cu	0.1 max
Mo	8.0-9.0
Ta	0.1 max
Ti	1.9-2.3
Nb	0.2 max
W	0.5 max
Zr	0.02 max

Table 1. Nominal alloy composition in HAYNES® 282® alloy. UNS N07208.

282® alloy is supplied in the wrought, solution annealed condition; see Figure 1 for a representative micrograph of the anneal grain structure [7]. Some residual carbide stringers are evident in the micrograph. Figure 2 shows the location of carbides in a higher magnification micrograph. Figure 3 shows the intragrain structure of solution annealed 282® alloy prior to heat treatment; very fine nano-scale gamma prime particles are evident in the grains. Complete suppression of nano-scale precipitation of gamma prime upon cooling is practically impossible. This fact has little effect on the ability to cold work the alloy in the mill annealed condition, as the annealed hardness is often in the range of 90 Rockwell B.

The alloy mechanical properties depend on the formation of beneficial secondary phases in the microstructure, namely carbides and gamma prime. The carbides begin to precipitate upon cooling below 1120°C (~2050°F) after solution annealing in the range of 1121 to 1149°C (2050 to 2100°F). Carbides are primarily of the form $M_{23}C_6$ that are rich in chromium, although nickel, cobalt, and molybdenum substitution is often present. M_6C are also present; they are rich in molybdenum with nickel and chromium substitution possible.

A single step heat treatment at 800°C for four hours followed by air cooling, which is also the ASME code-approved heat treatment, creates chromium rich $M_{23}C_6$ carbides that are discrete globular blocks; see Figure 4. Figure 4 shows the grain boundary carbide structure after aging and preferential etching to highlight the carbides. Gamma prime is a coherent Ni_3Al intragranular precipitate that forms at temperatures below approximately 1000°C; see Figure 5. Figure 5 is a micrograph of heat-treated and etched 282® alloy. Gamma prime is evident in intragranular regions.

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The single step heat treatment co-precipitates carbide and gamma prime networks in one step. This is important because a single stage heat treatment, compared to a two stage heat treatment, can provide significant time and cost savings to equipment owners.

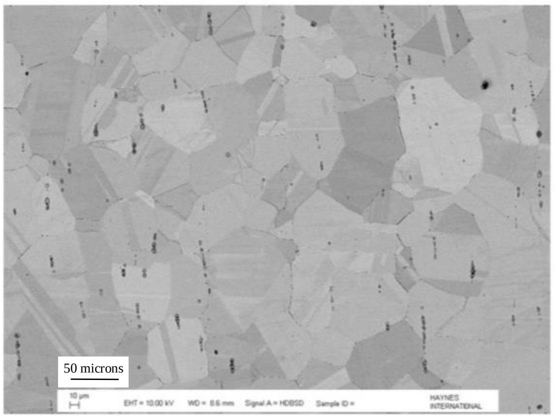

Figure 1. SEM image of mill annealed 282® alloy. Primary carbide stringers are evident in the microstructure.

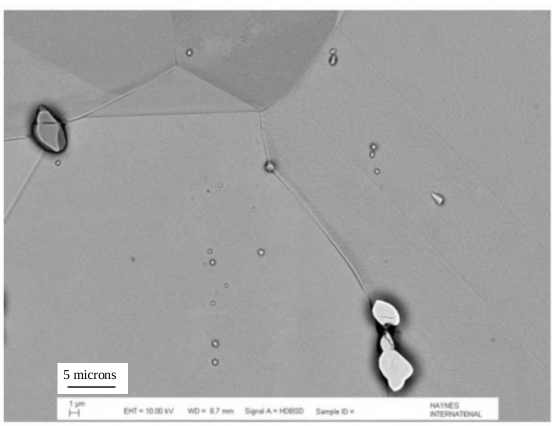

Figure 2. High magnification SEM image of mill annealed 282® alloy. Primary carbides are evident in the microstructure; dark carbides in the image are MC-type while bright carbides are M6C carbides.

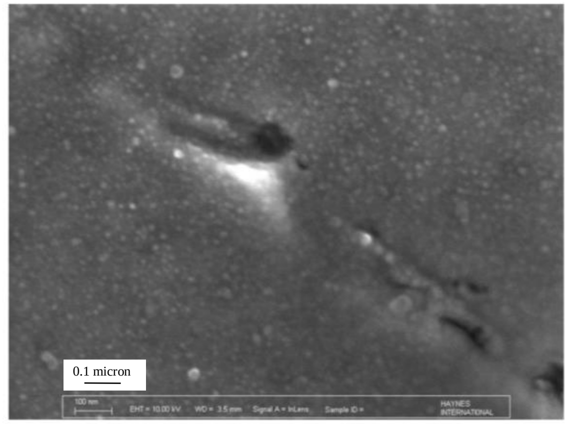

Figure 3. High magnification of mill annealed 282® alloy showing well dispersed very fine intragranular gamma prime particles. Particles sizes are typically less than 5 microns.

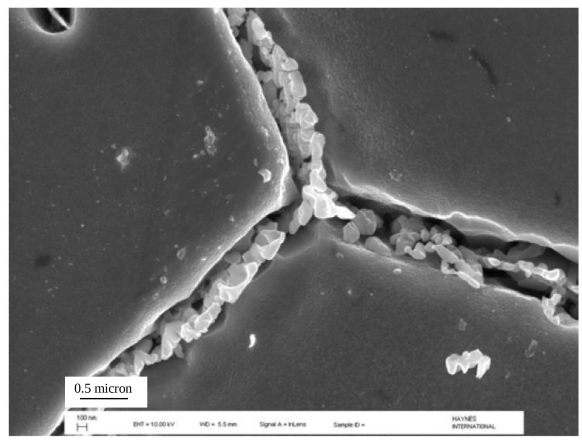

Figure 4. SEM images showing an etched triple point grain boundary in 4 hours single aged 282® alloy. Grain boundaries are decorated with globular carbide blocks.

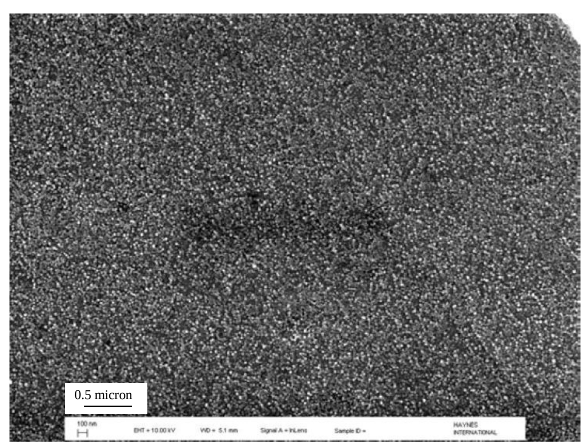

Figure 5. SEM image of etched 4 hours aged 282® alloy intragranular gamma prime precipitation. The typical gamma prime particle size is < 1 micron.

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MECHANICAL PROPERTIES

sCO_2 high temperature equipment requires an alloy with excellent high temperature strength, creep resistance, and elongation. The properties must be persistent following long-term thermal exposure. The average tensile properties from room temperature to 900°C are in Table 2. Tensile testing was conducted on precipitation strengthened 282® alloy plate from three heats of alloy.

Temperature (°C)	0.2% Yield Strength (MPa)	Ultimate Tensile Strength (MPa)	% Elongation
RT	733	1170	34
100	684	1123	34
200	655	1095	35
300	640	1060	35
400	639	1021	36
500	628	998	36
600	626	1002	32
700	620	952	23
800	577	745	16
900	406	480	30

Table 2. Tensile properties of HAYNES® 282® alloy from room temperature to 900°C

Retained tensile strength of 282 alloy is a key mechanical property that makes the alloy suitable for high temperature sCO2 applications. The data show that 282® alloy is very strong across a broad range of temperatures, and the ductility remains above 15% for all tests. It is important to note that the values in Table 2 are larger than the published ASME codes case data. The values are larger because the published code case data are often minimum values from multiple heats of testing, and sometimes an alloy owner (such as Haynes International, Inc.) requests that published values to be slightly lower than the actual minimums to impart conservatism. Figure 6 contains the ASME allowable stress for 282® alloy and other alloys often used in high temperature ASME applications; HAYNES® 230® alloy, HAYNES® 617 alloy, and 800HT alloy.

760°C is the target temperature for sCO2 applications and 282® alloy exceeds the creep life requirement to surpass 100,000 hours at 100 MPa (14.5 ksi) at 1400°F (760°C).

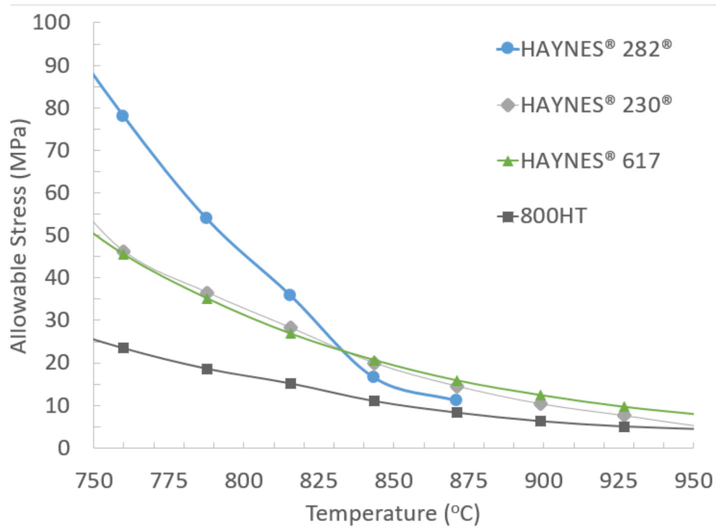

Figure 6. ASME allowable stress versus temperature for selected alloys, including HAYNES® 282® alloy.

In fact, 282® alloy is stronger [8] than it's closet peer in this alloy group, UNS N07740, and all of the ASME approved nickel based solid solution strengthened alloys for high temperature service. It is also notable that 282® alloy ASME maximum allowable temperature is 871°C, whilst UNS N07740 is 815°C.

The creep properties of 282® alloy demonstrate that the alloy is capable of long term service in high temperature sCO2 applications up to 871°C. A Larson Miller Parameter (LMP) plot is presented in Figure 7. The LMP plot (C=16.6) in Figure 7 contains data generated by ORNL [9] on single step aged 0.5" plate. These data also were used for a portion of the ASME code case. The plot clearly shows that across multiple heats, 282® alloy delivers very consistent long term creep properties in the single aged wrought condition.

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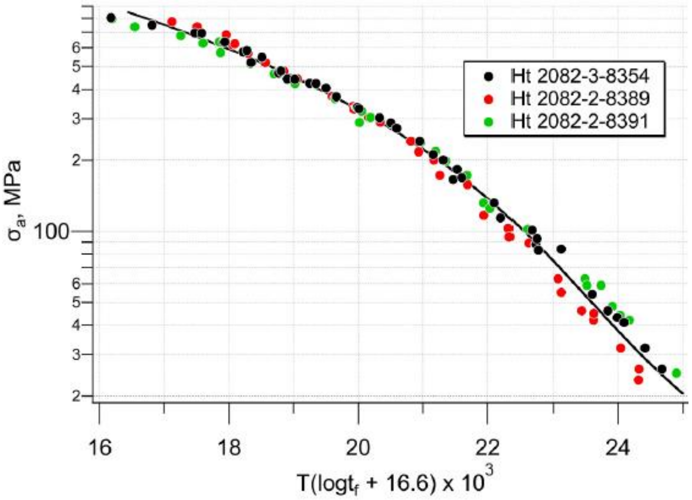

Figure 7. Larson Miller Parameter plot versus applied stress for HAYNES® 282® alloy. Data courtesy of Oak Ridge National Laboratory in support of 282® alloy ASME code case 3024.

Table 3 contains stress rupture data for 282® alloy from 649°C to 927°C and stress rupture times of 100 hours and 1,000 hours [10]. Data are presented for single step precipitation strengthened base metal and all weld metal. Welded 282® alloy properties are explored more fully in the next section.

Property	Test Temperature		282 Alloy Base ksi (MPa)	282 Alloy Weld ksi (MPa)
	°F	°C		
Stress-to-Produce Rupture, in 100 h ksi (MPa)	1200	649	104 (715)	101 (693)
	1300	704	80 (550)	76 (522)
	1400	760	58 (401)	54 (375)
	1500	816	41 (280)	37 (253)
	1600	871	26 (179)	23 (156)
	1700	927	14 (97)	13 (87)
Stress-to-Produce Rupture, in 1000 h ksi (MPa)	1200	649	86 (591)	101 (693)
	1300	704	62 (428)	76 (522)
	1400	760	43 (298)	54 (375)
	1500	816	27 (189)	37 (253)
	1600	871	15 (102)	23 (157)
	1700	927	7 (51)	13 (87)

Table 3. Comparative average creep-rupture properties of single step age hardened HAYNES® 282® alloy base metal and weld metal. Weld metal data comprised of GMAW and GTAW data.

Table 3 shows that the alloy stress-to-produce rupture values at 871°C are 179 MPa for 100 hours, 102 MPa in a 1,000 hour test. The stress-to-produce rupture in 10,000 hours is 55MPa and the ASME allowable stress at the same temperature is 11MPa for 100khr service. The weld data show that although the wrought metallurgy was changed by welding, the stress-to-produce rupture at 100 and 1,000 hours are not negatively affected. In fact, there is little change in the alloy performance when comparing wrought creep properties to the properties in the as welded condition.

OXIDATION

282® alloy can resist oxidation in sCO2 at time scales relevant to long-term operation of high temperature equipment. Several research programs focused on alloy oxidation in sCO2 environments conducted over approximately the past fifteen years. Short-term oxidation tests were commonly near 500 hours and long-term tests were over 10,000 hours. The range of the testing pressures were one bar to 400 bar and temperatures ranged from 650°C to 900°C. Figures 8 through 10 are oxidation data generated by Oak Ridge National Laboratory [6] with support of Haynes International for 282® alloy. HAYNES® 625 alloy and HAYNES® 230® alloy are also included for context. The plots include oxidation kinetics using the parabolic rate constant versus inverse temperature (Figure 8), oxidation rate as mass gain versus time (Figure 9), and oxidation mass gain at 750°C and 800°C versus alloy aluminum and titanium composition (Figure 10). As mentioned earlier, 282® alloy is an ASME code approved alloy, but the code does not require oxidation rates be specificed. The impact of oxidation on creep life is incorporated, in a sense, into the short and long term creep tests (in air). Long-term oxidation study of 282 alloy showed minimal metal loss, or thickness reduction, over 10kh exposure. Accordingly, 282 alloy could provide long-term oxidation resistant performance of a component operating near 760°C.

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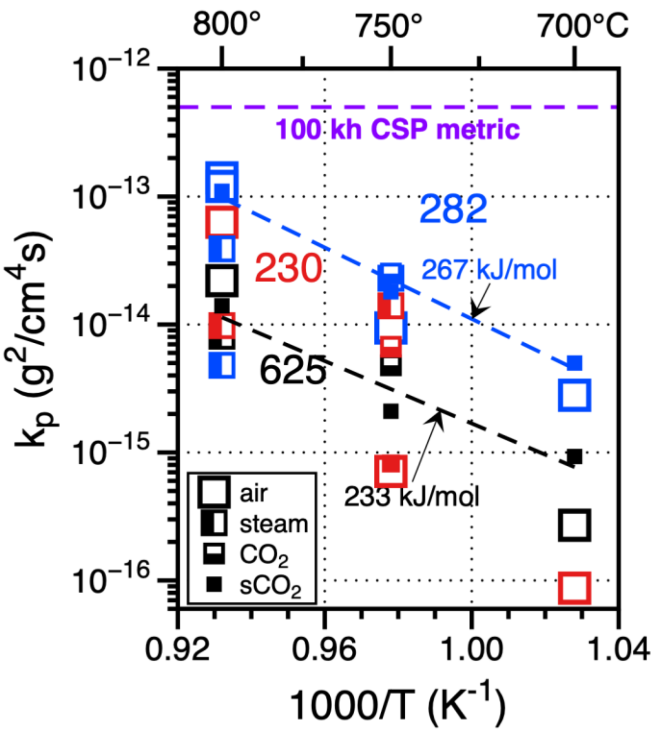

Figure 8. Plot of oxidation rate constant, k_p, versus inverse temperature. The 100khr metric line from the advanced ultra supercritical program is also included for reference.

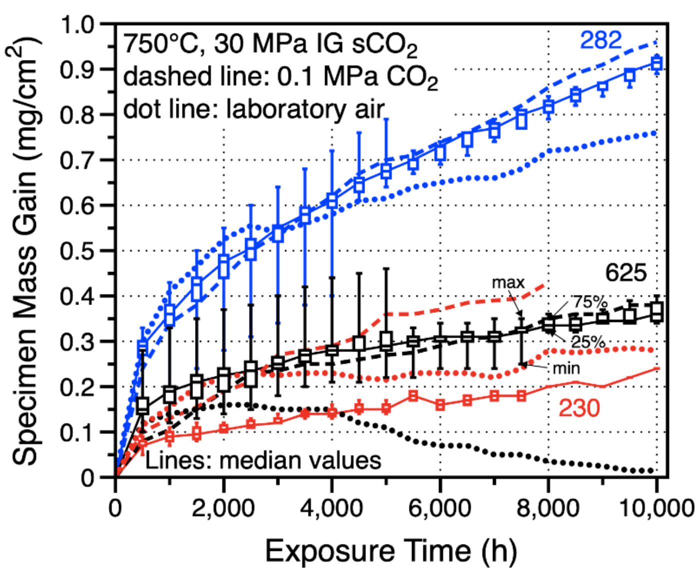

Figure 9. Oxidation mass gain versus time for selected alloys including HAYNES® 282® alloy.

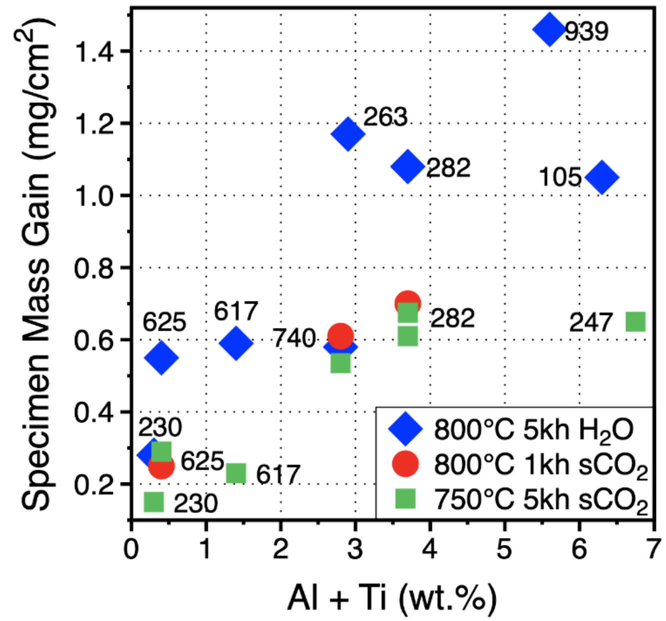

Figure 10. Oxidation mass gain versus alloying content of aluminum plus titanium. At 705ºC and 800ºC in sCO2 and water for various exposure times.

WELDING 282® alloy

282® alloy is easily fabricated and welded. The alloy's high level of creep strength is attained at a relatively low volume fraction of the strengthening gamma-prime phase, resulting in outstanding resistance to strain-age cracking. Additionally, slow gamma-prime precipitation kinetics allow for the alloy to have excellent ductility in the solution annealed condition. The preferred welding processes are gas tungsten arc (GTAW or TIG) and gas metal arc (GMAW or MIG), using 282 alloy bare filler wire. Preheating of HAYNES® 282® alloy is not required, as long as the base metal to be welded is above 32°F (0°C). Interpass temperatures should be less than 200°F (93°C).

After welding, 282® alloy should be age-hardened. The use of a full solution anneal (typically at 2075°F/1135°C) after welding and prior to age-hardening treatment is neither required nor prohibited. For heavy section weldments, or complex weldments with high residual stress, a full solution anneal prior to the age-hardening treatment may be advisable to minimize the threat of cracking.

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282® alloy weldability has been explored by several companies and organizations (United States Department of Energy, the Electric power Research Institute(EPRI), nickel alloy fabricators such as Babcock and Wilcox, Haynes International, Inc, several universities. It has been demonstrated that wrought product can be welded in thick sections up to 3.3 inches (84mm) [11].

Figure 11 is a micrograph of a welded cross section of a gas tungsten arc welded (GTAW) specimen. Two 19 mm (0.75”) thick plates in the solution-annealed condition were welded together and then aged at 800ºC for four hours. The sample was polished, electrolytically etched in HCl – oxalic acid, and subjected to Rockwell C hardness testing. A hardness profile was collected across the sample; the locations of the measurements are identify in red numbers (1 through 11) in the figure. The hardness data are in Table 4.

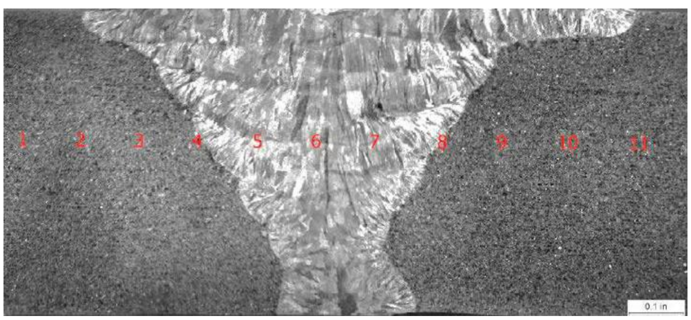

Figure 11. Micrograph of welded HAYNES® 282® alloy plate. Cross section is polished and etched; red labels are hardness measurement locations.

GTAW Specimen	
Location	Hardness (HRC)
1	34.9
2	35.8
3	36.8
4	37.6
5	36.5
6	37.0
7	36.1
8	38.6
9	36.9
10	36.9
11	35.1

Table 4. Hardness profile data of 282 alloy weldment.

The hardness profile data show that the welding and precipitation hardening treatment has little effect on the cross-weld hardness. There is some indication that the weld is at most 3.7 HRC point higher than the parent alloy, although the regions near the weld line indicated by numbers 4 and 8 were hardest. The fusion zone was at most 2.1 HRC higher compared to the lowest base metal hardness measurement of 34.9.

It is important to note that large power generation components and piping may not be able to be heat treated in the as welded, fully fabricated condition. This can be due to system size, the requirement to fabricate on site, and parts with complex geometries. To address this need, Haynes developed guidelines to weld precipitation hardened 282® alloy parts. Once welded, the local welded area can be heat treated on site in accordance with the single step heat treatment.

ASME code case activities also included bend testing of wrought and welded 282® alloy plate. Each specimen was precipitation strengthened prior to welding and no post weld heat treatment was performed before bend testing. The weld processes were GTAW and gas metal arc welding (GMAW). A 4T radius mandrel (mandrel radius is equal to 4X the plate thickness) and the wrap-around test method (ASME Boiler and Pressure Vessel Section IX, figure QW-466.3) were recommended for qualification purposes. Figure 12 is a photograph of representative welded bend specimens. The face side, root side, and side bend orientations are shown. No cracking was evident in any specimen.

Figure 12. Photograph of bend test specimens. No cracks were evident in the single step heat treated HAYNES® 282® alloy specimens.

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Another important parameter within ASME code is the Weld Strength Reduction Factor (WSRF), which needs to be applied when calculating design stresses and pressure boundary thicknesses. The WSRF methodology in STP-PT-077 acknowledges that WSRFs can be calculated by comparing the time-temperature-strengths relationships from data generated using all base metal specimens, welded specimens, and all weld metal specimens where:

$$WSRF = \frac{Rupture\ Stress\ (weld)}{Rupture\ Stress\ (base\ metal)}$$

282® alloy creep test results show that WSRFs depend on temperature. The WSRF for 282® alloy are in Table 5. It is worth noting that the WRSF for UNS N07740 is 0.7 for all temperature ranges up to its maximum allowable temperature in accordance with ASME, which is 815ºC (1500ºF). Also, Table 5 includes WSRF up to 927°C (1700ºF), the ASME Code Case only specifies WSRF up to 871ºC (1600ºF), which is the maximum use temperature for 282® alloy.

Temperature (ºC)	Weld strength reduction factor
593 - 620	0.99
621 - 815	0.93
816 - 870	0.86
871 - 927	0.84

Table 5: WSRF for HAYNES® 282® alloy.

Figure 13 is a plot of 282 LMP data for base alloy and weld alloy creep rupture data [12] collected over a temperature range of 593°C – 927°C (1100°F – 1700°F). The plot shows the base alloy performance and weld alloy performance are very similar, which is crucial for the alloy performance in sCO2 power generation applications.

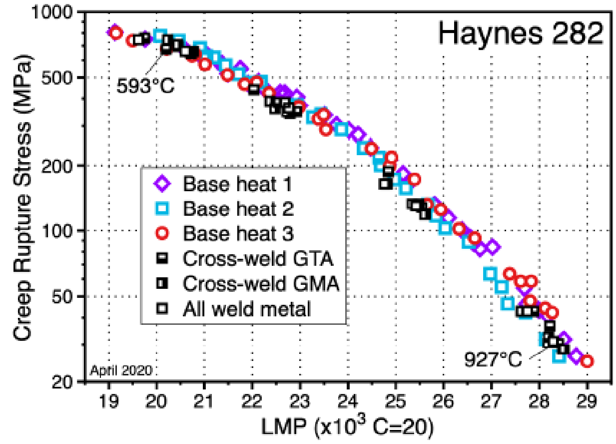

Figure 7. Larson-Miller parameter plot of the creep data.

Figure 13. Larson Miller Parameter plot for base alloy and welded HAYNES® 282® alloy specimens.

SUMMARY

282® alloy is precipitation hardenable alloy whose primary alloying elements are Ni-Cr-Co-Mo-Ti-Al. Heat treatments applied to the 282 alloy have the purpose of forming chromium-rich $M_{23}C_6$ carbides and of precipitating gamma-prime particles.

The operating conditions of supercrictical carbon dioxide (sCO2) power cycles and advanced supercritical steam cycles (A-USC) require high pressure, high temperature plant components to be manufactured from nickel-based superalloys. Research conducted by the U.S. Department of Energy proved HAYNES® 282® alloy (UNS N07208) is a leading choice for sCO2 applications. Research performed by the DoE and Haynes International, Inc. led to the production of required American Society of Mechanical Engineers (ASME) code case data. The data generated focused on a single step age hardening treatment, which is a four hour single step age hardening heat treatment at 800°C (1472°F) followed by air cooling (800°C (1472°F)/4 hr/AC). The 282® alloy ASME code case is 3024.

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REFERENCES

[1] Pike, Lee. *100+ Years of Wrought Alloy Development at Haynes International. 8th International Symposium on Superalloy 718 and Derivatives.*

[2] L.M. Pike, "Development of a Fabricable Gamma-Prime (ɣ') Strengthened Superalloy," (Paper presented at *Superalloys* 2008, Champion, PA, September 14-18, 2008) 191-200.

[3] Srivastava, S.K. & Caron, J.L. & Pike, L.M.. (2014). Recent developments in the characteristics of HAYNES 282 alloy for use in A-USC applications. pp. 120-130, Advances in Materials Technology for Fossil Power Plants, Proceedings from the Seventh International Conference October 22-25, 2013, Waikoloa, Hawaii, USA

[4] D.L. Klarstrom and L.M. Pike, "Material Solutions for Advanced Steam Power Plants," *Advances in Materials Technology for Fossil Power Plants, Proc. Fifth Int. Conf.*, October 2007, pp.107-118, EPRI 2008.

[5] V. P. Deodeshmukh and B. A. Pint, "Long-Term Performance of High Temperature Alloys in Oxidizing Environments and Supercritical CO2," in Proceedings of the Joint EPRI – 123HiMAT International Conference on Advances in High Temperature Materials,

[6] Pint, B.A. (2018). Performance of Wrought Superalloys in Extreme Environments. In: , et al. Proceedings of the 9th International Symposium on Superalloy 718 & Derivatives: Energy, Aerospace, and Industrial Applications. The Minerals, Metals & Materials Series.

[7] Robertson, JR. "Continued Developments in the Characteristics of HAYNES® 282® Alloy for Use in A-USC Applications." *Proceedings of the ASME 2018 Symposium on Elevated Temperature Application of Materials for Fossil, Nuclear, and Petrochemical Industries*. *ASME 2018 Symposium on Elevated Temperature Application of Materials for Fossil, Nuclear, and Petrochemical Industries*. Seattle, Washington, USA. April 3–5, 2018. V001T01A007. ASME.

[8] ASME Boiler and pressure vessel code Section VIII Division 1.

[9] Michael L. Santella, Peter F. Tortorelli, Mark Render, Bruce Pint, Hong Wang, Vito Cedro, Xiang (Frank) Chen, Effects of applied stress and grain size on creep-rupture lifetime prediction for Haynes 282 alloy, Materials Science and Engineering: A, Volume 838, 2022

[10] Haynes International, Inc. data submitted in part to support ASME Code Case 3024.

[11] A-USC Report on thick section Welding of Haynes® 282® alloy.

[12] Pint, Bruce A., Wang, Hong, Hawkins, Charles Shane, and Unocic, Kinga A. Technical Qualification of New Materials for High Efficiency Coal-Fired Boilers and Other Advanced FE Concepts: Haynes® 282® ASME Boiler and Pressure Vessel Code Case. United States: N. p., 2020. Web. doi:10.2172/1649169.

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