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# High Effectiveness, Compact, High Pressure and Low Cost Super-Critical $CO_2$ Recuperator Performance, Bonding and Corrosion Resistance

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**ABSRACT**

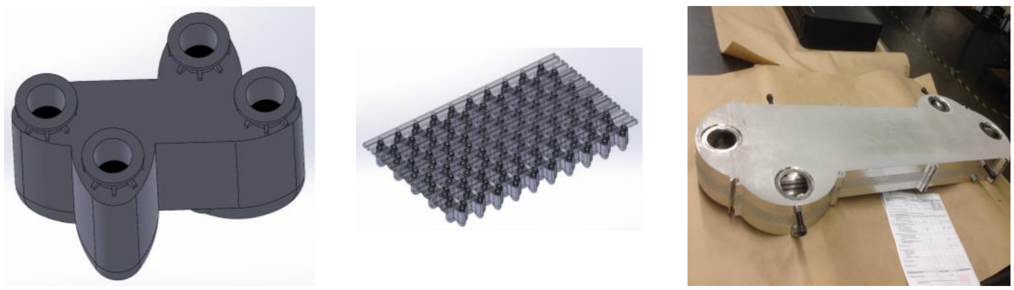
High-effectiveness, compact and high temperature recuperators play a major role in Supercritical $CO_2$ ($ScCO_2$) power cycle performance and economics. For compactness and low cost, these recuperative heat exchangers utilize many thousands of small channels to maximize heat transfer. To create this structure requires the bonding of thousands of heat exchanger components into a strong and durable structure that must last for decades under hot $CO_2$ fluid steady and cyclical conditions. These desirable characteristics must be achieved at low cost.

Altex is developing and testing a purpose-built heat exchanger that has novel inserts that create the small channels needed for high heat transfer rates in a compact configuration. Using experimentally determined heat transfer coefficients and friction factors, the heat transfer performance under expected Supercritical $CO_2$ operating conditions was predicted to be 15.6 kWt/UA for a 5,212 kWt capacity unit. To bond the heat exchanger components together, a load-assisted brazing process is utilized. Tests have shown that butt and peel-type joint strengths are 82% and 75% of the base 316 stainless steel material strength at room temperature, respectively. Also, at the higher operating temperatures, available data support that these joint strengths will exceed that of the base material. Besides providing needed joint strength, this brazing process can also be used to modify surface characteristics to yield corrosion resistance and lifetimes comparable to higher cost base construction materials. Using different braze formulations to fully coat 316 stainless steel base material, high temperature corrosion tests showed that the coated material had corrosion weight gains comparable to high nickel alloys costing many times that of 316 stainless steel.

**INTRODUCTION**

Given the required high base pressure of the Recompression Brayton $ScCO_2$ power system, the cycle pressure ratio is limited and recuperative heat exchangers are required to maximize cycle efficiency [1]. In the case of waste heat driven cycles, the recuperative heat duty is in the range of 100 % greater than the electrical power output, with fossil, concentrating solar and nuclear-based cycles needing 520% higher heat duties than the electrical power output. For a 400 MWe fossil fuel driven power plant, the recuperator capacity would then be 2,480 MWt that would have many millions of small diameter channels and a correspondingly large number of high strength recuperator component joints. Therefore, component base material tolerances and surface finishes and braze materials and processes must be at a high level to meet high temperature and pressure requirements. Furthermore, to optimize economic payoff, these expensive recuperators must last for 30 years, or more, without excessive corrosion and degradation.

To simultaneously achieve the objectives of high heat transfer and pressure drop performance, joint strength and corrosion resistance at low cost, Altex is developing and testing the High Effectiveness Low Cost (HELC) recuperative heat exchanger that is designed for a peak pressure of in the range of 3,500 psi. The unit uses materials, design, fabrication, bonding and coating processes that will result in lower cost at the compactness, performance strength and corrosion resistance needed to meet power cycle requirements over the long term. Figure 1 gives a picture of a 50 kWt HELC test article to the right and illustrations of a 50 MWt HELC module and an array of 50 modules with connecting pipes that yield the above-noted 2,500 MWt heat duty [2]. It should be noted that the footprint of the array is only 3.5% of a dry cooling condenser for a comparable 400 MWe capacity steam power plant. In this paper, the progress toward developing the HELC design for performance, integrity and corrosion resistance is described.



**50 MW Module      50 Module Array      50 kW Test Article**

**Figure 1 – HELC 50 MWt Module, 2,500 MWt Full-Scale 50 Module Array and HELC 50 kWt Test Article**

**RESULTS AND DISCUSSION**

As a purpose-built $ScCO_2$ recuperator, HELC needs to meet ASME pressure code requirements for operation at pressures of 3,500 psi with waste heat applications with a maximum temperature of 360 C and other applications with up to 700 C maximum temperature [3]. Given the temperature of the waste heat application, the entire HELC could be constructed of 316 stainless-steel material and meet the code requirement with a solidity of around 50**%,** considering a channel hydraulic diameter of 1.0 mm. For higher temperature applications, the hot end of the heat exchanger must utilize a more creep resistant, high nickel content alloy, such as Haynes 230. For the same pressure and temperature requirement, the solidity will be reduced. Besides having higher ASME Pressure Vessel Code allowable stress at high temperatures, high nickel content materials also have over an order of magnitude better corrosion resistance than stainless steel under high temperature $ScCO_2$ operating conditions [4]. This characteristic is important to lifetime and minimizing power system maintenance and replacement costs.

Relative to HELC heat transfer performance, tests have shown the ability of channel surface features to improve the heat transfer coefficient at good thermal efficiency (i.e. heat transfer versus the power required to drive the heat transfer). Tests have shown heat transfer enhancements of 350% with only a 15% reduction in thermal efficiency versus a smooth channel baseline case [5]. In contrast to these enhancements, typically used wavy channels enhance heat transfer by 218% versus a smooth channel, but the thermal efficiency is reduced by a substantial 53% [6]. To illustrate the impact of surface enhancements, Table 1 provides HELC performance predictions using a validated model with $ScCO_2$ properties with a design peak pressure and temperature of 3,000 psi and 311 F. These results are for a fixed core configuration with a channel hydraulic diameter of .033-in, of width 18-inches, height of 67-inches and a length of 25-inches. In addition to the fixed configuration, all of the entering $ScCO_2$ fluid conditions were fixed, and REFPROP properties and literature-based $ScCO_2$ heat transfer and pressure drop correlations were utilized [7]. As shown, the smooth channel case has the lowest heat transfer and pressure drop. Also, this case has the lowest effectiveness, which is important to cycle efficiency. Volume and weight metrics are also the highest for this case. In contrast, surface feature case 3 has over 8% higher heat transfer and a much higher effectiveness. This is achieved within pressure drop requirements. Volume and weight metrics for case 3 are the best of all cases. Lastly, all of case 3 performance parameters are better than the wavy channel case that is typically used in Printed Circuit Heat Exchangers (PCHE) [8]. These results illustrate the benefits of the case 3 surface features to heat exchanger performance.

**Table 1 – HELC Heat Transfer Performance for Different Surface Enhancement Features**

| Channel Surface Features | Smooth | 1 | 2 | 3 | Wavy |
|---|---|---|---|---|---|
| **Heat Transfer (kWt)** | **4,804** | **5,006** | **5,006** | **5,212** | **5,143** |
| **Hot Side Pressure Drop (Bar)** | **0.20** | **0.40** | **0.35** | **0.71** | **0.91** |
| **Cold Side Pressure Drop (Bar)** | **0.34** | **0.66** | **0.58** | **1.17** | **1.51** |
| **Effectiveness (%)** | **89.8%** | **93.6%** | **93.6%** | **97.4%** | **96.1%** |
| **Cubic Meter/UA** | **0.00191** | **0.00152** | **0.00152** | **0.00107** | **0.00123** |
| **Kilograms/UA** | **28.0** | **22.3** | **22.3** | **15.6** | **18.1** |

In order to contain the inserts that contribute to core structural strength and channel the fluids, the HELC design includes separation plates of the proper thickness and frames that also form the inlet and outlet manifolds. These plates and frames are constructed with the needed thicknesses to address both core and manifold pressure requirements at operating temperatures, with a completed test article included in Figure 1 [2].

Commercially available PCHEs have been successfully used as recuperators for $ScCO_2$ power cycle test units. These units are constructed by diffusion bonding stacks of metal plates that have chemically etched channels for the $ScCO_2$ fluid. The stack diffusion bonding process requires high quality surface flatness and cleanliness, with substantial solidity supporting the high compression loads needed for good diffusion bonding within the vacuum furnace [8]. Furthermore, for the large heat duties needed for $ScCO_2$ power cycles, the PCHE modules can be very large, requiring careful control of platen loading to ensure even pressure over the large article during bonding. In addition, with the high temperature required for diffusion bonding and the large articles, the heat up and temperature uniformity must be carefully controlled to produce high quality bonds throughout the article. In contrast, HELC applies a Load-Assisted Brazing (LAB) process that uses high nickel content braze filler material to address surface flatness imperfections and any tolerance mismatch between plate, frame and insert components [2]. While the LAB bonding approach has surface preparation, stack loading and associated cost advantages over diffusion bonding, it must produce very strong joints at the high operating pressures and temperatures. To evaluate joint bonding strength, small coupons that used the LAB bonding process and simulated sections of the HELC core were constructed and, after LAB bonding, segments were cut from the coupons and tensioned to failure in an Instron machine [9]. HELC joint designs tested include those in simple tension (i.e. butt joints) and those where some bending and tension stresses develop (i.e. peel type joints). These types of joints covered all possible joints used in HELC. To bond the core components, two different braze compounds were utilized, NiCr 33 and NiCr 152. The compositions of these compounds are given in Table 2, which show that they contain silicon and phosphorous that is used to suppress the melt temperature of the mostly nickel-based braze material [10]. In addition, heat exchanger base component high nickel (HR230, HR282, IN740, HR214, CM247) and high iron (Gr.91 and 316SS) materials are included for comparison.

**Table 2 – Base Metal and Braze Compound Compositions**

| Alloy | Fe | Ni | Cr | Al | Mo | Mn | Si | W | Co | Ti | Nb | Ta | Hf | P | Trace Elements |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| Gr. 91 | 89.7 | 0.1 | 8.3 | | 1 | 0.3 | 0.1 | | | | | | | | |
| HR230 | 1.5 | 60.5 | 22.6 | 0.3 | 1.4 | 0.5 | 0.4 | 12.3 | | | | | | | |
| HR282 | 0.2 | 58 | 19.3 | 1.5 | 8.3 | 0.1 | 0.06 | | 10.3 | 2.2 | | | | | |
| IN740 | 1.9 | 48.2 | 23.4 | 0.8 | | 0.3 | 0.5 | | 20.2 | 2 | 2.1 | | | | |
| HR214 | 3.5 | 75.9 | 15.6 | 4.3 | | 0.2 | 0.1 | | | | | | | | .02 Zr |
| CM247 | 0.07 | 59.5 | 8.5 | 5.7 | 0.7 | | | 9.9 | 9.8 | 1 | | 3.1 | 1.4 | | |
| NiCr 31 | | 71.5 | 22 | | | | 6.5 | | | | | | | 4.5 | |
| NiCr 33 | | 64.5 | 29 | | | | 6.5 | | | | | | | 6 | |
| NiCr 152 | | 66 | 30 | | | | 4 | | | | | | | 6 | |
| 316SS | 65.705 | 12 | 17 | | 2.5 | 2 | 0.75 | | | | | | | 0.045 | 0.08 C, 0.03 S, 0.1 N |

The braze material also includes chromium that creates a strongly adhering surface oxide layer that is a barrier to further oxygen diffusion into the material, and thereby reduces the rate of corrosion. In addition, the silicon oxidizes and also forms a barrier to further limit oxygen diffusion and corrosion. These braze materials were applied to the joint areas between the plates and inserts. The coupons were then placed horizontally in the vacuum furnace, loaded to the needed pressure and taken through the recommended braze temperature-time history. The temperature ramp-up, hold and cooldown were scheduled to produce a uniform thermal condition at the braze melt point and to maximize joint strength. Following cooldown, the six-inch coupons were cut into multiple segments that were tension tested to failure using an Instron machine. Figure 2 shows the stress at failure in tension for NiCr 33 and NiCr 152 for the pure tension butt and peel type joints. These samples were tested at room temperature. As shown, joints formed with NiCr 33 have less strength than those formed with NB 152, for both the butt and peel type joints. Also, the butt joints are stronger than the peel joints, as expected. With the peel joints, stress concentrations are expected to develop at the peel point, which will then result in the earlier failure of the peel type joints compared to butt joints. Also given in Figure 2 is the tension failure stress for the 316-stainless steel material used to construct the heat exchanger components. As shown, the higher strength NiCr 152 joints were 82% and 75% of the base material strength for butt and peel joints, respectively, at room temperature [9]. When the material is heated to operating temperatures, the joint strength will be reduced. However, the 316-stainless steel base material strength will be reduced even more, resulting in the joint and base material strength becoming even closer in magnitude. This is supported by supplier data that shows that the braze material joint strength for NiCr is 85% at room temperature but is 101% of 316L stainless steel strength at 1670F.

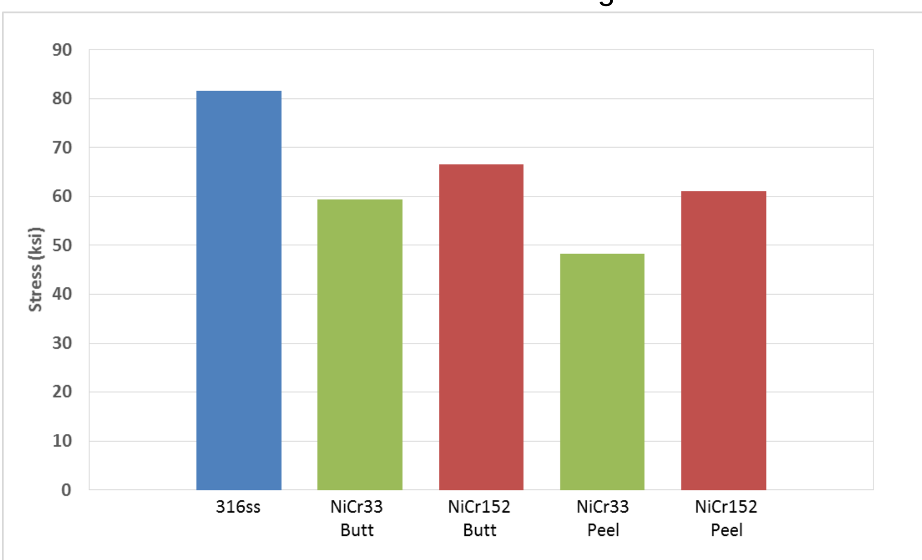



**Figure 2 – Comparison of Braze Joint and Base Material Stress at Failure**

The bond strength tests show that the braze layer strongly adheres to the base material and that, even when it is just applied to joints, flows over a portion of the base material. This is illustrated in Figure 3, which is a butt joint coupon cut to expose the side of an insert that shows an uncoated portion in the middle of the insert [10]. The braze has migrated out of the joints shown at the top and bottom of the picture, but a portion in the middle is still uncoated. This suggests that the entire surface of the components, rather than just the joints, must be coated with braze to maximize potential corrosion resistance.

Given the high nickel content of the braze material, and the adherence, flowability and coating capabilities of this material, it has potential to modify the surface characteristics of the base material to reduce corrosion potential. Furthermore, braze compounds can incorporate chromium, silicon and aluminum additives that will form strongly adhering thin oxide layers, which then reduces oxygen diffusion and further oxidation and corrosion of the underlying material.

**Figure 3 – Braze Flow from Joints on Vertical-Oriented Face of Insert**

To demonstrate the corrosion resistance potential of high nickel braze material, 316 stainless steel coupons were coated with NiCr 33, NiCr 152 and NiCr 31, which have the compositions given in Table 2. As shown in the table, these braze materials have a high chromium content, similar to that of the high nickel alloy HR 230 and IN740. As shown in Table 2, the 316-stainless steel has a high iron content, which at high temperature with $ScCO_2$ forms a weakly adhering oxide layer that can flake from the surface, leading to high rates of corrosion [9]. By fully coating the 316 stainless steel coupons with the braze compound, this rapid base material oxidation can be avoided, yielding a material that has the low cost of a stainless steel but the corrosion resistance of a high nickel alloy. To support this speculation, the coated coupons were taken through the same braze cycle as the heat exchanger core coupons. These coupons were then placed in the high pressure and temperature corrosion test apparatus shown in Figure 4. The unit was operated with a small flow of industrial grade $CO_2$ at a pressure of 200 bar and a temperature of 700 C to 750 C for 400 hours. Figure 5 gives the weight gain of NiCr 33, NiCr 152, NiCr 31 braze coated 316 stainless steel coupons versus well known high nickel alloys, including HR 230, IN 740 and HR 282. As shown in Table 2, these braze compounds and nickel-based alloys have high levels of nickel and chromium, with the braze having higher levels of silicon than the alloys. The high level of silicon in the braze reduces the melt temperature to have good braze flow without distorting the base material, but the silicon can also oxidize near the surface and act as another barrier to further oxygen diffusion and oxidation. Also, aluminum can oxidize near the surface and act as a barrier [4]. As shown in Table 2, the high nickel alloys have some aluminum content where this component is absent from the selected braze compounds. In addition to the silicon melt temperature depressant, the selected braze compounds also included phosphorous melt depressant. As shown in Figure 5, the braze-coated coupons have comparable weight gain to the high nickel braze alloys confirming that the high nickel base material alloys, besides having good joint strength, can also provide corrosion resistance for lower cost base materials. In contrast, uncoated 316 stainless steel coupons will have over an order of magnitude higher weight gain and corrosion than the coated coupons. It should be noted that an uncoated HR 282 coupon was tested by Altex and the results in Figure 5 are similar to the results in Reference 4, supporting the validity of the comparisons. With these good braze coating corrosion resistance results at 400 hours of continuous testing, work is planned to test other braze formulations and base material combinations for longer exposure times.

**Figure 4 – High Pressure and Temperature $ScCO_2$ Test Apparatus**

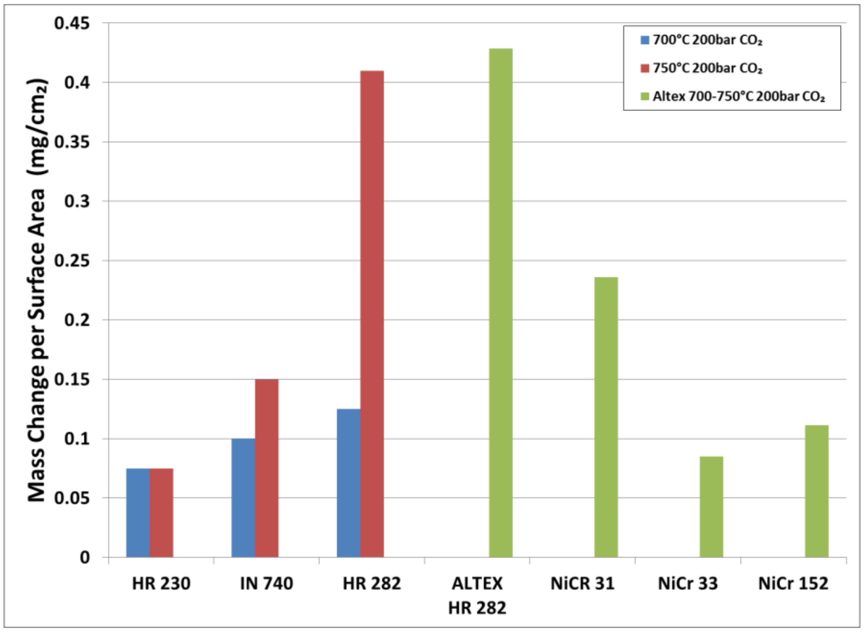



**Figure 5 – Comparison of High Nickel Braze Compound Coated Stainless Steel Coupons and High Nickel Alloy Corrosion Weight Gains**

## CONCLUSIONS

HELC performance predictions show that the Altex Case 3 surface feature enhancements have the best overall performance metrics relative to smooth and wavy channel features applied in PCHEs. Using high nickel content braze compounds and the LAB process to bond HEX components together it was found that butt and peel type joints had 82% and 75% of the base 316 stainless-steel material strength at room temperature. Furthermore, at operating temperatures, the high nickel content joints are expected to close the strength gap with the base material. In either case, the joints are easily designed so that the failure will occur in the base material. Besides providing strong joints, the braze compounds have compositions that are similar to high nickel alloys that have good corrosion resistance at high temperature $ScCO_2$ operating conditions. Tests of 316 stainless steel high nickel braze coated coupons showed that corrosion weight gains were comparable to the much more expensive high nickel corrosion resistant alloys. These results support that the LAB braze alloys can provide both good joint strength and corrosion resistance with the lower cost of a 316-stainless steel type component base material. Based on the encouraging results to date, more development and test work are planned to optimize both HELC heat exchanger strength and corrosion resistance using the LAB-CB process.

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