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# MATERIALS EVALUATION AND CORROSION TEST NEEDS FOR A DIRECT-FIRED $SCO_2$ OXY-COMBUSTION PLANT

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## ABSTRACT

A significant amount of corrosion testing has been performed in recent years for high-temperature supercritical $CO_2$ power cycles, mostly in a high-purity $CO_2$ environment that is expected in cycles with indirect heating. Additional material corrosion considerations are required for oxy-combustion cycles, where the primary process fluid composition within the combustor and throughout the loop will include other elements including water, oxygen, and other intermediate species within the combustor. This paper presents a literature review and material test recommendations for a 10 MW high-temperature sCO2 oxy-combustion cycle application that is under development by KEPCO, Hanwha Power Systems, and SwRI. The review focuses on publications that provide corrosion test data for relevant materials and thermal barrier coatings up to 700-750 C or higher in an $sCO_2$ mixture with additional constituents that are expected for the cycle.

## LIST OF ACRONYMS

Ref.: reference number

MFSS: martensitic/ferritic stainless (includes also carbon steel and iron)

ASS: austenitic stainless steel

Al SS: alumina forming stainless steel

CrNi: chromium-nickel alloys

AlNi: alumina forming nickel alloys

T: temperature

P: pressure

Cont.: presence of contaminants

Coat: presence of coatings

Exp.: experiments performed

$\Delta M$: mass change

echem: electrochemistry

SEM: scanning electron microscopy

EDS: energy dispersive X-ray spectroscopy

XRD: X-ray diffraction

XPS: X-ray photoelectron spectroscopy

μH: micro-hardness

GC: Gas chromatography-mass spectroscopy

GD: Glow discharge optical emission spectroscopy

## APPLICATION OVERVIEW

Recently, oxy-combustion gas turbine systems have attracted significant attention due to the technology's potential for the production of electricity while reducing $CO_2$ gas emissions. In an oxy-combustion gas turbine, utilizing supercritical $CO_2$ as the working fluid can reduce the machinery footprint and enable highly efficient turbomachinery and cycle performance. Based on these potential advantages, KEPCO has formed a consortium with Hanwha Power System and SwRI, as well as academic institutions in both Korea and US to develop unique a oxy-combustion gas turbine power plant. To minimize turbine design complications at this stage, the turbine inlet conditions have been restricted to maximum values of 750°C and 300 bara. The fuel gas composition is supplied from a Natural Gas Terminal in the Korean Peninsula, while the oxidizer composition is derived from an ASU based on an IGCC plant in Korea.

Hanwha Power Systems is developing an axial high-efficiency robust turbine for the oxy-combustion application based on technologies and experiences accumulated from various gas turbine development projects. Unlike a conventional gas turbine, the oxy-combustion gas turbine will be operated at very high pressure conditions at high temperature and will operate with a supercritical fluid mixture (including $CO_2$, oxygen, argon, nitrogen, and water). These conditions require a very strict structural design criteria and a corrosion/erosion-resistant design. By the end of 2019, Hanwha Power Systems will optimize the aerodynamic and structural turbine design to satisfy the required efficiency and a lifetime.

The oxy-combustion gas turbine requires a novel combustor design that will be developed by SwRI to operate at supercritical oxy-combustion conditions. Extreme pressures and potentially locally high temperatures of oxygen-methane flames makes aspects of $sCO_2$ oxy-combustion similar to the thrust chambers of staged combustion liquid rocket engines. However, unlike rocket engines, the final exhaust of the combustor is heavily diluted with $CO_2$ to manage turbine inlet temperatures. This dilution is similar in principle to conventional air-breathing gas turbines but with $CO_2$ replacing nitrogen as the diluent. This is a crucial distinction, since $CO_2$ is chemically active and an effective radiator and its presence in high concentrations alters the combustion behavior. Because of these unique aspects and the relative newness of the application, combustor development for direct-fired $sCO_2$ systems is currently a clean sheet process.

The gas turbine and combustor for the oxy-combustion application operate in a high-temperature corrosive fluid mixture, and attainment of long design life for these components will require material selections that minimize corrosion. In order to minimize uncertainty, materials testing will be performed as part of the oxy-combustor plant development program. A literature review was performed as a first step to identify existing corrosion data for supercritical oxy-combustion mixtures and also promising alloys for testing. This paper presents an overview of the materials generally of interest for $sCO_2$, a literature review to identify significant variables and corrosion data specific to oxy-combustion mixtures, initial recommendations for materials for this application, and a summary of future materials testing work to be performed in the program.

## MATERIALS OVERVIEW

There are five different categories of alloys that have been considered to be used with high-temperature supercritical $CO_2$ (considered to be above 400°C) based on their corrosion properties: Martensitic stainless steels and ferritic stainless steels (MFSS, 10%-30% Cr for ferritic stainless steels, and 12%-17% Cr with 0.15 – 0.63% C for martensitic stainless steel), austenitic stainless steels (ASS, 16 to 30% chromium and 2 to 20% nickel), alumina austenitic stainless steels (Al SS), chromium-nickel alloys (CrNi), and alumina nickel alloys (AlNi). The main difference with regard to corrosion between those alloys is the type of oxide layers and their resistance to corrosion. The resistance to corrosion is linked to the composition of the material, and therefore, the composition and properties of the oxide layer. Throughout the literature, it has been found that the temperature is the most important variable when it comes to corrosion in $sCO_2$ and that the different types of alloys could be ranked based on the temperature, summarized in Table 1.[1] The corrosion is usually assessed by measuring the mass gain during the exposure of the test coupons to $sCO_2$.

**Table 1. Temperature Range of Different Type of Alloys Considered for Use in High-temperature Supercritical $CO_2$. The colors represent the temperature range within which the materials are considered to be acceptable (green) or not (red) based on their oxidation properties. The criterion being a combination of mass gain, oxide thickness, presence of crack, carburization, etc.**

| **Temperature (°C)** | **300** | **350** | **400** | **450** | **500** | **550** | **600** | **650** | **700** | **750** | **800** | **850** | **900** |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| **Type of alloy** | | | | | | | | | | | | | |
| **MFSS** | 🟩 | 🟩 | 🟩 | 🟩 | 🟥 | 🟥 | 🟥 | 🟥 | 🟥 | 🟥 | 🟥 | 🟥 | 🟥 |
| **ASS** | 🟩 | 🟩 | 🟩 | 🟩 | 🟩 | 🟩 | 🟩 | 🟩 | 🟥 | 🟥 | 🟥 | 🟥 | 🟥 |
| **Al SS** | 🟥 | 🟥 | 🟥 | 🟥 | 🟥 | 🟥 | 🟥 | 🟥 | 🟥 | 🟥 | 🟥 | 🟩 | 🟩 |
| **CrNi** | 🟩 | 🟩 | 🟩 | 🟩 | 🟩 | 🟩 | 🟩 | 🟩 | 🟩 | 🟩 | 🟥 | 🟥 | 🟥 |
| **AlNi** | 🟥 | 🟥 | 🟥 | 🟥 | 🟥 | 🟥 | 🟥 | 🟥 | 🟥 | 🟥 | 🟥 | 🟩 | 🟩 |

## LITERATURE REVIEW

Most of the literature covers testing performed at high pressure and temperature in pure $CO_2$. However, additional variables of interest have been covered, such as contaminants and coatings. Additional variables of interest that have not been studied have also been added.

### *Temperature*

Temperature has been found to be the most important variable for corrosion of the alloys used in $sCO_2$. Since the temperatures can vary greatly based on the design, it will affect the type of materials required. ASS can be used in locations where the temperature is below 650°C, while CrNi alloys will be required when temperatures reach 700°C. However, even nickel alloys have been found to have issues at higher temperature, e.g., inter-granular corrosion was observed on Inconel 718 and 738 at 700°C / 250 bara. [2]

The impact of temperature is observed on the thickness and type of oxide film layer on the materials. The duplex layer found on ASS can be detrimental to thermal conductivity. [3] Steels containing less than 9-12% Cr form a duplex scale comprising an outer layer of iron-rich oxide and an inner layer of Cr-Fe spinel. 9% Cr steels can form Cr-rich oxide in air but not in steam or $CO_2$. Ferritic steels containing greater than 20% Cr will form a single $Cr_2O_3$ oxide. Ferritic steels with a chromium content between 12 and 20% will form either a single layer of $Cr_2O_3$ or a duplex spinel oxide. [4] Depending on the gas composition, duplex scales can form on high Cr alloys.

Carburization is a major issue that is linked to temperature. High Cr content in MFSS alloys promotes carburization by forming chromium carbide.[5] Such a difference might be attributed to the lower test temperature at which chromium carbide is more stable. Carburization can be observed by performing micro-hardness testing across the thickness of the oxide layer and the matrix underneath. High Cr+Ni content in ASS leads to carburization resistance. Higher mass gains can be measured as a result of the combination of faster oxide growth kinetics leading to thicker scale formation and carbon uptake from carburization.[5] Carburization underneath the oxide layers of ASS 316 appeared to promote oxide spallation at 650°C/200 bar.[6] Carburization did not seem to be an issue on some MFSS.[7] The carburization process has been found to be due to carbon penetrating the scales by grain boundary transport. The impact of carburization on the macro scale is also measured using tensile test. [8]

***Pressure***

Pressure has been widely assumed to play little to no role in the corrosion of all of the materials as long as carbon dioxide is supercritical. The impact of contaminants such as $O_2$ and $H_2O$ have been studied by exposing materials to a high-temperature $CO_2$ environment at a pressure of 1.0 bara.[9] The argument was made that the impact of pressure is minimum and that testing the contaminants at 1 bara, even below the critical point of $CO_2$, and therefore in vapor environment, should provide the same amount of corrosion than at 20 bara. [8] However, the impact of impurities at high pressure have yet to be studied.

However, the weight gain of the MFSS was also observed to increase with the pressure (450°C/9-200 bara). [10]

***Contamination of $sCO_2$***

There is a lack of information on the effect of contaminants (mainly $O_2$ and $H_2O$) at high pressure and temperature.

At low temperatures used in the transport of $sCO_2$ (below 200°C), it has been observed that no corrosion occurs in pure fluids but the water content is a key parameter. Temperature, water, and pollutants are the major factors leading to increasing the uniform or localized corrosion rates at those low temperatures.[1] The increase in contaminant water concentration also increases the corrosivity of $sCO_2$. [11,12]

*$O_2$*

It is unclear whether if $O_2$ is beneficial or detrimental. Adding 100 ppm of $O_2$ (650-750°C at 200 bar) increased the oxide thickness independently from temperature (650-750°C).[13] Addition of 10 and 100 ppm oxygen in $sCO_2$ accelerated oxidation with a thicker oxide layer developing on the surface and evidence of spallation (650-750°C /200 bara). For samples tested in environments containing oxygen impurity, thicker oxide layers were observed suggesting accelerated chromium diffusion. This also led to void formation beneath the oxide layer, which was dependent on both test temperature and oxygen impurity concentration. The void regions were found to contain a larger concentration of alumina and chromia, which could lead to better adherence of the oxide.[14]

Other work hypothesized that the presence of $O_2$ may promote more protective oxide scales (700°C / 200 bar).[15]

*Water*

High water vapor content may increase the probability of breakaway oxidation. [16] At low temperature water contamination has been found to accelerate corrosion in low-temperature $sCO_2$ (as used in pipeline transport and storage).[11,12]

*Combination of Contaminants*

500 hours cycles exposure were performed in several combined environments (at 1.0 bara): Ar–50% ($CO_2$–0.15 $O_2$), 100% $H_2O$ (no carrier gas), 50% $H_2O$–50% ($CO_2$–0.15 $O_2$), 50% $H_2O$–50% $CO_2$, 40% Ar–50% $H_2O$–10% ($CO_2$–0.15 $O_2$), and laboratory air. Higher levels of corrosion were observed in $CO_2$–0.15 $O_2$ than with 100% $H_2O$ based on the measured mass change after exposure performed between 550°C and 650°C. The addition of buffered $CO_2$ with $H_2O$ resulted in a faster oxidation rate. Varying the amount of $CO_2$ added or removing the $O_2$ buffer did not have a significant effect on the reaction rate or reaction product. All the exposure was performed at 1 bara and, therefore, not in supercritical conditions. The argument was made that the same effect of the contaminants should be expected below and above the critical point. [17]

### ***Welding***

Welding changes the local microstructure due to the high temperature in the vicinity of the weld. The chromium will diffuse to the grain boundaries and the chromium concentration in the matrix will drop significantly. Consequently, the corrosion resistance near the weld will drop. Since welding will likely be used in the manufacturing process, it is recommended to test coupons containing the heat affected zone near a weld. The extent of chromium depletion and its impact on the growth of an oxide film can be observed using SEM-EDS.

### ***Impact on Mechanical Properties***

Some mechanical testing (tensile test) has been performed on the nickel alloys and austenitic stainless steel after exposure to $sCO_2$. It was found that the mechanical properties of austenitic stainless steel were diminished after exposure to $sCO_2$ (unlike the nickel alloys). The ultimate tensile strength (UTS) of alloy 800HT increased from 560 MPa in as received condition to 750 MPa after exposure in $sCO_2$ at 650°C. The heat treatment alone was found to affect the UTS, but exposure to $sCO_2$ further increased the UTS. Consequently, it would be recommended to expose tensile test specimens of the stainless steels chosen for the lower temperature range.[18]

Tensile properties of Alloy 800 HT and Alloy 625 showed hardening and loss of ductility after exposure at 550-650°C / 200 bar. The increase of temperature also resulted in an increase of UTS, from 550 to 725 MPa (as-received vs. 650°C) for 800HT and from 950 MPa to 1,250 MPa for 625. Meanwhile, for SS 310S, SS 347H, Alloy 600, and Alloy 690, tensile property changes were relatively small (±25 MPa) after exposure at 550-650°C / 200 bar. [19]

Tensile test performed on specimens exposed did not indicate any degradation of the tensile properties for Ni-based alloys after the exposure to $sCO_2$ at temperatures up to 650°C at 200 bara for 1,000 hr. [18] The same was observed on a variety of MFSS, ASS, CrNi, and AlNi. [7]

### ***Stress Corrosion Cracking***

Stress corrosion cracking is a mode of failure that results from the combined effect of applied stresses and corrosive environment leading to accelerated crack growth of a susceptible material due to its microstructure. The lower temperature range materials are likely to be under the highest amount of tensile stress if used as a pressure boundary. Therefore, it may be interesting to have loaded C-rings of the most promising materials for the low-temperature range.

Exposure of C-rings (at 75%, 85%, 95% of rupture stress) of a variety of MFSS, ASS, CrNi, and AlNi was performed at 750°C and 200 bar, in pure $sCO_2$ for 500 hours. No evidence of cracking was observed on any of the C-ring samples. [20]

### ***Galvanic Corrosion***

Galvanic corrosion occurs when two materials with different electrochemical potentials are in contact with a corrosive environment. As a result, the more noble metal does not corrode while the more active metal corrodes at a faster rate than without a galvanic couple existing. There is usually very little change in corrosion rates when materials with similar composition are in contact. However, there may be some issue in the case of nickel alloys/stainless steel couples that would exist in the combustor test loop. It has also been suggested in the literature that galvanic corrosion may not be an issue because $sCO_2$ is not considered an electrolyte. However, it may be of interest to electrically couple two samples of different material (stainless steel and nickel alloy) and measure the weight change of each sample individually after exposure to assess galvanic corrosion.

### ***Coatings***

Thermal barrier coating (TBC) has been considered as a way to protect materials against corrosion since they are already in use in turbines. Two types of TBC materials have been tested at 0.1 MPa, $CO_2$ + 10% $H_2O$ (a) diffusion bond coatings (Pt diffusion or simple or Pt-modified aluminide) with commercially vapor-deposited yttria-stabilized zirconia (YSZ) top coatings and (b) high-velocity oxygen fuel (HVOF) sprayed MCrAlYHfSi bond coatings with air-plasma sprayed YSZ top coatings. [21]

Other TBC of interest is composed of the ceramic top coat ($ZrO_2$ stabilized with $Y_2O_3$, applied with air plasma spraying or electron-beam physical vapor deposition) and a metallic bond coat (usually Al rich to create an alumina oxide layer). The effect of $CO_2$-10% $H_2O$ cycling environment at

1,150°C was investigated. Replacing air with $CO_2$ did not show any negative effects, and in fact greatly increased the lifetime, from 1,447 1-hr cycles to 2,260 1-hr cycles . The combination of air and $H_2O$ resulted in a lifetime of up to 1,339 1-hr cycles. Damages were either intrinsic (oxide growth, internal stresses leading to cracking and failure) or extrinsic (erosion, local damages due to impact or particles melting, diffusing, and hardening the top coat leading to potential failure). However, it is important to take not that those experiments were performed at low temperatures and that it may reflect the behavior of the coatings at higher pressure. [22]

***Summary***

**Table 2. Literature Review Summary**

| Ref | MFSS alloy | ASS alloy | Al SS alloy | CrNi alloy | AlNi alloy | T (°C) | P range | Time (hours) | Cont. | Coat. | Exp. |
|---|---|---|---|---|---|---|---|---|---|---|---|
| 1 | Mild steel | 304L, 316L, 904L | | 625, 690 | | Review | | | | | |
| 2 | | 316 | | 718, 738 | | 550-700 | 150 bara<br>250 bara | 3,000 | No | No | M |
| 3 | T91 | 31603 (316L), S30815,N08800 | | | | 550 | 250 bara | 310 | No | No | GD, SEM, XRD |
| 4 | | | | | | Review | | | | | |
| 5 | Gr91, VM12, Crofer 22H | 304H, HR3C | | 617, 740H | | 650-750 | 200 bara | 1,000 | $O_2$, $H_2O$ | No | M, SEM, EDS, H |
| 6 | | 316, 310, 800H | | | | 650 | 200 bara | 3,000 | No | No | M, SEM, XRD, XPS |
| 7 | Gr91, Save12, 410SS, Ebrite, AL294C | 201SS, 347HFG, 304H+SP, 310HCbN, NF709, 800H, HR120 | AFA OC4 49.1, Ohm40, APMT, PM2000, IN718 18.8 | Hastelloy X, 625, HR230, CCA617, HR282, 740 | HR224, HR214, NM105, 713LC, CM247, PWA1483, NiCrAlYHf | 650°C-750°C | 200 bara | 500 | No | No | M, tensile |
| 8 | Gr91 | Ebrite, 347HFG, 310HCbN | APMT | 625, 230, CCA617, 282 | 214, 247 | 750°C | 1-300 bara | 500 | 0.15% $O_2$, 10% $H_2O$ | No | M, H, tensile |
| 9 | | | | 6178, Hastelloy X, 625, 230, CCA617, 282, 740 | 224, 214, 105, 713LC, 247, 1483, NiCrAlYHf | 650°C-750°C | 1 bara (cont.)<br>200 bara ($sCO_2$) | 500 | Air, $CO_2$+$O_2$, $CO_2$+ $H_2O$ | No | M |
| 10 | NF616, HCM12A | 347 | AFA OC6 | | | 450°C | 92.74-200 bara | 400 | No | No | GC, M, SEM, EDS. |

| Ref | MFSS alloy | ASS alloy | Al SS alloy | CrNi alloy | AlNi alloy | T (°C) | P range | Time (hours) | Cont. | Coat. | Exp. |
|---|---|---|---|---|---|---|---|---|---|---|---|
| 13 | | | | Haynes 230, Haynes 625 | | 650°C-750°C | 3,000 psi/200 bara | 1,000 | 100 ppm $O_2$ | No | M, SEM, EDS, XRD |
| 14 | | | | Haynes 230 | | 650°C-750°C | 200 bara | 1,000 | 10-100 ppm $O_2$ | No | M, Raman, XRD, SEM, EDS |
| 15 | Gr91 | 304H | | 740H | | 700°C | 200 bara | 300 | $O_2$, $H_2O$ | No | M, H |
| 16 | T23 | Super 304H, Sanicro 28, Kanthal APM | | Sanicro 63, C276 | | 570°C-630°C | 1 bara | 287 | $H_2O$, $O_2$, $SO_2$ | No | SEM, XRD |
| 17 | Gr22, Gr315, Gr91, Gr92, Gr122, SAVE12, 410SS | Fe-15Cr, Fe-20Cr, Fe-25Cr, Fe-30Cr, 347HFG, Super304H, SAVE 25, 310HCbN | | HR120, 617, 740 | | 550°C-650°C | 1 bara | 500 | $O_2$, $H_2O$, synth. ash | No | M |
| 18 | | 800HT | | 600, 690 | | 450°C-650°C | 200 bara | 1,000 | No | No | M, SEM, EDS, tensile |
| 19 | G91 | 310S, 316H, 316LN, 347H, 800HT | | 600, 625, 690 | | 550°C-650°C | 200 bara | 1,000 | No | No | M, tensile |
| 20 | | HK40, HK50, DAFA30, A286 | CAFA7 | 282, Waspaloy, 720, 718, Rene 41, CMSX-8, PWA1483, Rene N4, CMSX-4 | | 750°C | 200 bara | 500 | No | No | M, C-ring, microstructure |
| 21 | | | | | N5, N515, X4, 1483, MCrAlYHF | 1,000°C-1,050°C | 1 bara | 1 | $H_2O$ | TBC | M, SEM |
| 22 | | | | | | Review | | | | | |
| 23 | UNS G15130 CS | | | | | 35°C | 80 bara | 48 | $O_2$, $SO_2$, $H_2O$ | No | M |
| 24 | Fe, 1080CS | 304, 316 | | | | 265°C | 165 bara | 9177 | $H_2O$, $CH_4$ | No | M, model, echem |
| 25 | | | | | | 65°C | 1 bara | 350 | $SO_2$, $H_2O$ | No | |
| 26 | | | | 617 | | Review | | | | | |

| Ref | MFSS alloy | ASS alloy | Al SS alloy | CrNi alloy | AlNi alloy | T (°C) | P range | Time (hours) | Cont. | Coat. | Exp. |
|---|---|---|---|---|---|---|---|---|---|---|---|
| 27 | T91 | AL-6XN, 310, 316, 800H | | HA230, HA242, In625, PE16 | | 200°C - 500°C | n/a | 200 | No | No | SEM, EDS |
| 28 | | | PM2000 ODS | | | 650°C | 200 bara | 3,000 | No | No | ΔM, SEM, XRD |
| 29 | 12Cr-steel | 316FR | | | | 400°C - 600°C | 200 bara | 2,000 | No | No | ΔM |
| 30 | | | | | | 450°C - 650°C | 200 bara | 1,000 | No | No | ΔM |
| 31 | | 316 | | C276 | | 650°C - 750°C | 200 bara | 1,000 | No | No | ΔM |
| 32 | AGr22, Gr91, 12CrCoW, 410SS, 201SS | Fe25Cr, FeCrMo, 304H, 347HFG, 709, 310+Nb | | 800H, 718, 282, mod 617, 625, NiCrW, 740 | 214 | 400°C - 750°C | | | No | No | |

## MATERIALS OF INTEREST

This section provides an identification of promising materials that may be useful for the oxy-combustion power cycle application. This selection is based on available data that are very scarce, and additional testing will be performed under the program before any final selection. If the final combustor concept utilizes a liner as currently anticipated, the pressure vessel will be at a relatively low temperature (400°C-500°C) due to the bypass/dilution $CO_2$ mixture temperature and the liner/injector/transition piece will be at a higher temperature of 650°C-750°C. The materials were initially selected based on corrosion resistance results reported in the literature, and the initial list was reduced based on published creep and yield strengths at maximum temperature. For combustor casing materials that will see the lower temperature range of 400°C-500°C, the maximum temperature and allowable stress criteria in the ASME Boil & Pressure Vessel Code, Sec. I or VIII Div 1 and Div II are shown. Higher-temperature materials may be used for injector/liner components and do not need to be code-qualified. The final material selection will also consider the forming process of the parts and if the materials need to be wrought or cast. Materials of interest are organized into two temperature ranges corresponding to the combustor inlet and exit temperatures.

### *Temperature Range: 400°C-500°C (Combustor Inlet & Pressure Vessel)*

The safest choice of material to use in $sCO_2$ at 400°C-500°C are austenitic stainless steel and some martensitic ferritic stainless steels. The nickel alloys would work well but are a very expensive choice. The “top picks” for this temperature range are presented in Table 3.

**Table 3. Top Picks within the Temperature Range of 400°C-500°C**

| Trade Name | UNS | Standard Specification | Notes | Max Temperature Limit [C] (BPV Code Section) | Allowable Stress at 500 C [MPa] |
|---|---|---|---|---|---|
| Gr91 | K90901 | ASTM A387 Grade 91 Class 2 | Most commonly tested MFSS and may be of interest for this study. | 649 (VIII-2) | 204 |
| 800H | N08800 | ASTM B407 | | 816 (VIII-2) | 138 |
| 310 | S31000 | ASTM A965 | | 816 (VIII-2) | 116 |
| 347H/347HFG | S34709 | ASTM A965 | | 816 (VIII-2) | 125 |

The above alloys have all shown great behavior in previous studies and are the most highly recommended for this work based on the literature currently available. Gr91 performs best at the low-temperature range of 400-450°C[32] and is expected to provide a cost advantage compared to austenitic stainless steels. If the uncertainty in a component or cycle design/performance may result in temperatures above this range then it would be best to exclude it.

The alternative alloys presented in Table 4 have not been the subject of multiple studies in the literature, but no significant issues have been reported below 500°C and therefore may be viable alternatives that would also require testing.

**Table 4. Alternative Choices Within the Temperature Range of 400°C-500°C**

| Trade Name | UNS | Standard Specification | Max Temperature Limit [C] (BPV Code Section) | Allowable Stress at 500 C [MPa] |
|---|---|---|---|---|
| 625 | N06625 | ASTM B443 | 593 (I) or 649 (VIII-1) | 192 |
| HK40 | J94204 | ASTM A351 | - | - |
| HK50 | J94224 | ASTM A297 | - | - |
| 310HCbN/HR3C | S31042 | ASTM A959 | 732 (I) | 117-158 |
| NF709 | S31025 | ASTM A213 | - | - |
| HR120 | N08120 | ASTM B515 | 899 (VIII-1) | 113-153 |

Other ASS have shown issues, such as 304H, which displayed deep carburization, and 316 that suffered from inter-granular corrosion.[15, 27]

***Temperature Range: 650°C-750°C (Combustor Exit and Liner)***

Nickel alloys with a chromium-based oxide film are recommended for this application. Stainless steels oxide films are very thick at these higher temperatures and are not recommended.

Alumina oxide film forming material (stainless steels and nickel-based) is not recommended either because it appears that the protective alumina film does not form at the lower end of the temperature range. Furthermore, it would seem that those alloys are still at the development stage and are not commercially available.

The most recommended alloys are listed in Table 5, based on the multiple data published in the literature. Alloy 282 is not currently code-qualified, but estimated maximum temperature and allowable stresses are provided.[33]

**Table 5. Top Picks Within the Temperature Range of 650°C-750°C**

| Trade Name | UNS | Standard Specification | Max Temperature Limit [C] (BPV Code Section) | Allowable Stress at 750 C [MPa] | Yield Strength at 750-760 C [MPa] | Creep Rupture Strength at 750 C [MPa] (hr) |
|---|---|---|---|---|---|---|
| 740H | N07740 | ASTM B983 | 800 (I) | 84.1 | 596 | 200 (10k) |
| 282 | N07208 | ASTM B637-12 | 800 (est.) | 105 (est.) | 612 | 186 (10k) |
| 230 | N06230 | ASTM B572-06 | 982 (VIII-1) | 50.8 | 323 | 91-98 (10k) |

Table 6 presents other nickel alloys that did not show any issues in the published literature, however, they were not widely investigated and very little information in $sCO_2$ is available.

**Table 6. Alternative Choices Within the Temperature Range of 650°C-750°C**

| Trade Name | UNS | Standard Specification | Max Temperature Limit [C] (BPV Code Section) | Allowable Stress at 750 C [MPa] | Yield Strength at 750 - 760 C [MPa] | Creep Rupture Strength near 750 C [MPa] (hr) |
|---|---|---|---|---|---|---|
| Waspaloy | N07001 | ASTM B637 | - | - | 706 | 290 (1k) |
| Udimet 720 | N07720 | n/a | - | - | 770 | 480 (1k) |
| Rene 41 | N07041 | SAE AS7469B | - | - | 938 | 276 (1k) |
| 617 | N06617 | ASTM B167 | 982 (VIII-1) | 50.4 | 872 | 140 (1k) |
| MA 754 | N07754 | n/a | - | - | 275 | - |
| Hastelloy X | N06002 | ASTM B572-06 | 482 (VIII-2) | - | 218 | 107 (1k) |

## FUTURE WORK

Autoclave testing will be performed at KAIST for the most promising material samples in a $CO_2/H_2O/O_2$ mixture and pressures/temperatures representative of cycle conditions. The test plan includes weight gain testing of base material samples and (for some materials) samples with thermal barrier coatings. Micro-tensile, c-ring, and welded specimens will also be included in the autoclave test campaign for evaluating the variables discussed in the Literature Review portion of this paper. After autoclave testing, SEM/EDS inspection of the specimen cross sections will be performed to identify the composition and measure the depth of the oxide film is recommended. Finally, tensile and micro-hardness testing will also be performed in order to measure the mechanical properties and depth of carburization of the material, respectively.

## REFERENCES

1. S. Sarrade et al., *J. Supercrit. Fluids*, **120**, 335–344 (2017).

2. H. Saari, R. Petrusenko, K. Zanganeh, C. Parks, and B. Maybee, in *Proceedings of the 4th International Symposium on Supercritical CO2 Power Cycles.*,, Pittsburgh, Pennsylvania (2014) http://citeseerx.ist.psu.edu/viewdoc/download?doi=10.1.1.705.2497&rep=rep1&type=pdf.

3. F. Rouillard, F. Charton, and G. Moine, *CORROSION*, **67**, 095001-095001-7 (2011).

4. R. Moore and T. Conboy, *Metal Corrosion in a Supercritical Carbon Dioxide - Liquid Sodium Power Cycle*, Sandia National Laboratories, (2012).

5. S. C. Kung, J. P. Shingledecker, I. G. Wright, and B. M. Tossey, in *Corrosion 2017*,, NACE International (2017) https://www.onepetro.org/conference-paper/NACE-2017-9006.

6. G. Cao, V. Firouzdor, K. Sridharan, M. Anderson, and T. R. Allen, *Corros. Sci.*, **60**, 246–255 (2012).

7. B. A. Pint, R. G. Brese, and J. R. Keiser, in *Proceedings of the 5th International Symposium on Supercritical CO2 Power Cycles.*,, San Antonio, TX (2016).

8. B. A. Pint, R. G. Brese, and J. R. Keiser, *Mater. Corros.*, **68**, 151–158 (2017).

9. B. A. Pint and J. R. Keiser, *JOM*, **67**, 2615–2620 (2015).

10. J. J. Jelinek et al., in *Corrosion 2012*,, NACE International (2012) https://www.onepetro.org/conference-paper/NACE-2012-1428.

11. S. Sim, F. Bocher, I. S. Cole, X. B. Chen, and N. Birbilis, *Corrosion*, **70**, 185–195 (2013).

12. S. Sim et al., *Int. J. Greenh. Gas Control*, **17**, 534–541 (2013).

13. J. Mahaffey, M. Anderson, D. Adam, and K. Sridharan, in *Proceedings of the 5th International Symposium on Supercritical CO2 Power Cycles.*,, San Antonio, TX (2016) http://sco2symposium.com/www2/sco2/papers2016/Materials/009paper.pdf.

14. J. Mahaffey, D. Adam, A. Brittan, M. Anderson, and K. Sridharan, *Oxid. Met.*, **86**, 567–580 (2016).

15. S. C. Kung et al., in *Proceedings of the 5th International Symposium on Supercritical CO2 Power Cycles.*,, San Antonio, TX (2016) http://sco2symposium.com/www2/sco2/papers2016/Materials/009paper.pdf.

16. M. Montgomery et al., *Mater. Corros.*, **66**, 257–269 (2015).

17. B. A. Pint and J. K. Thomson, *Mater. Corros.*, **65**, 132–140 (2014).

18. H. J. Lee, H. Kim, S. H. Kim, and C. Jang, *Corros. Sci.*, **99**, 227–239 (2015).

19. H. J. Lee, C. Jang, and H. Kim, in *Proceedings of the 4th International Symposium on Supercritical CO2 Power Cycles.*,, Pittsburgh, Pennsylvania (2014) https://scholar.google.com/scholar?hl=en&as_sdt=0%2C44&q=Compatibility+of+candidate+structural+materials+in+high-+temperature+s-CO2+environment.+In%3A+&btnG=.

20. J. R. Keiser, M. McDowell, and D. N. Leonard, in *Corrosion 2017*,, NACE International (2017) https://www.onepetro.org/conference-paper/NACE-2017-9532.

21. B. A. Pint, K. A. Unocic, and J. A. Haynes, in *Proceedings from the Seventh International Conference Advances in Materials Technology for Fossil Power Plants*,, Waikoloa, Hawaii (2014).

22. B. Gleeson, *J. Propuls. Power*, **22**, 375–383 (2006).

23. Y. Hua, R. Barker, and A. Neville, *CORROSION*, **71**, 667–683 (2014).

24. A. W. Propp et al., *Corrosion in Supercritical Fluids*, Idaho National Engineering Laboratory, (1996).

25. G. Stein-Brzozowska, J. Maier, and G. Scheffknecht, *Energy Procedia*, **4**, 2035–2042 (2011).

26. P. S. Korinko, *High Temperature Environmental Interactions of Inconel 617: A Paper Study for the TEF*, Savannah River Site (United States). Funding organisation: US Department of Energy (United States), (2000) http://inis.iaea.org/Search/search.aspx?orig_q=RN:32032845.

27. D. Fleming and A. Kruizenga, *Identified Corrosion and Erosion Mechanisms in SCO2 Brayton Cycles.*, Sandia National Laboratories, (2014) http://prod.sandia.gov/techlib/access-control.cgi/2014/1415546.pdf.

28. V. Firouzdor, G. P. Cao, K. Sridharan, M. Anderson, and T. R. Allen, *Mater. Corros.*, **66**, 137–142 (2015).

29. T. Furukawa, Y. Inagaki, and M. Aritomi, *J. Power Energy Syst.*, **4**, 252 (2010).

30. L.-F. He et al., *Corros. Sci.*, **82**, 67–76 (2014).

31. R. Olivares, D. Young, P. Marvig, and W. Stein, *Oxid. Met.*, **84**, 22p (2015).

32. B. A. Pint, R. G. Brese, and J. R. Keiser, in *Corrosion 2016*,, NACE International (2016) https://www.onepetro.org/conference-paper/NACE-2016-7747.

33. Brun, K., Friedman, P., and Dennis, R. (2017), *Fundamentals and Applications of Supercritical Carbon Dioxide (sCO2) Based Power Cycles*, Woodhead Publishing, 2017.

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