



ECAR-6588 Chemical Compatibility of MARVEL Components

April 2021

Changing the World's Energy Future

Brandon L Moon



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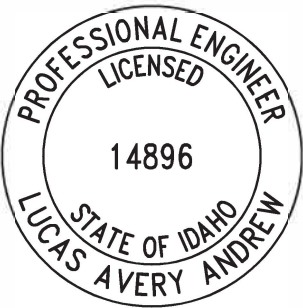
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Chemical Compatibility of MARVEL Components

Project # 33526



1. Effective Date	---- 10/02/23	Professional Engineer's Stamp 
2. Does this ECAR involve a Safety SSC (see def. LWP-10200)?	YES	
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4. SSC ID	n/a	
5. Project No.	33526	
6. Engineering Job (EJ) or Engineering Change (EC) No.	EC 1755	
7. Building	MFC	
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9. Objective / Purpose This ECAR serves to demonstrate the compatibility of MARVEL Reactor materials in contact with the two molten metal coolants, sodium potassium eutectic and lead. Operational requirements are determined, and recommendations for material treatment or replacement are presented.		Luke Andrew Walsh Engineering Services 2023.09.27 10:44:53-06'00'
10. If revision, please state the reason and list sections and/or page being affected.		
11. Conclusion / Recommendations This ECAR demonstrates the compatibility of the structural material (316H) with the two molten metal coolants Sodium Potassium Eutectic (NaK) and Lead. Though lead is no longer utilized within MARVEL as the secondary coolant. The information regarding the material compatibility of lead is retained in this ECAR for informational purposes. This ECAR shows that by maintaining oxygen within NaK to 10-25ppm and keeping carbon content within the fluid as below 30 ppm corrosion can be minimized within the system. It has been determined that all materials with direct interaction with NaK will be subject to little corrosion with no impact on the ability of the primary coolant system to perform its function, and fuel cladding will remain intact. Concerns have arisen regarding welds, and heat affected zones, as these areas appear to be the most likely in which corrosion and loss of coolant is possible. Haynes 230 and 208 are used for construction of the Stirling Engine heat exchanger tubes. They are high nickel alloy and likely incompatible with molten lead and thus should be replaced with 316L stainless steel. Oxygen content within the lead should be maintained		

between 10^{-6} wt% and 10^{-4} wt% to minimize corrosion of the Intermediate Heat Exchanger, and Stirling engine helium tubes. The oxygen content within the NaK should be maintained below 25 ppm to minimize formation of potentially hazardous oxides, such as potassium superoxide (KO_2). Further control of NaK oxygen content serves to minimize the risk of corrosion on the stainless-steel surfaces that will be exposed to NaK during operations.

This document demonstrates the importance of chemistry control within the MARVEL system to mitigate adverse effects to structural materials and components.

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1.0 PROJECT ROLES AND RESPONSIBILITIES

Project Role	Name	Organization	Pages Covered (if applicable)
Performer	Kade Fish	Walsh Engineering Services	See DCR 704008
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Independent Reviewer ^b	Drew Johnson	C610	See DCR 704008
CUI Reviewer ^c	Michael W. Patterson	C120	See DCR 704008
Manager ^d	Brandon Moon	U022	See DCR 704008
Requestor ^{ef}	Carl Bailly	U720	See DCR 704008
Nuclear Safety ^f	Doug Gerstner	H374	See DCR 704008
Document Owner ^f	Brandon Moon	U022	See DCR 704008
Reviewer ^f	N/A	N/A	N/A

Responsibilities:

- a. Confirmation of completeness, mathematical accuracy, and correctness of data and appropriateness of assumptions.
- b. Concurrence of method or approach. See definition, LWP-10106.
- c. Concurrence with the document's markings in accordance with LWP-11202.
- d. Concurrence of procedure compliance. Concurrence with method/approach and conclusion.
- e. Authorizes the commencement of work of the engineering deliverable.
- f. Concurrence with the document's assumptions and input information. See definition of Acceptance, LWP-10200.

NOTE: Delete or mark "N/A" for project roles not engaged. Include ALL personnel and their roles listed above in the DCR system. The list of the roles above is not all inclusive. If needed, the list can be extended or reduced.

2.0 SCOPE AND BRIEF DESCRIPTION

The United States Department of Energy (DOE) is supporting the development of a new generation of nuclear reactors; under this support the Microreactor Applications Research Validation and Evaluation (MARVEL) reactor is being designed. This reactor will serve as a proof of concept, and testbed to facilitate the progression of microreactor technology for future commercial use. The MARVEL reactor will take advantage of molten metal coolants flowing under natural circulation. This ensures effective heat transfer, and inherent safety, as coolant flow is not dependent on the function of circulating pumps. However, the use of molten metal coolants presents challenges due to the high temperatures, and the corrosive nature of molten metal. The primary coolant subsystem utilizes sodium potassium eutectic (NaK) which has been used successfully in past nuclear reactors, namely EBR-1, and SNAP-8 providing basis for its use. The secondary coolant system will utilize eutectic Gallium Indium Tin (eGaInSn), its compatibility is documented in ECAR-6126. This document contains information regarding the previous secondary coolant, molten lead. The information regarding lead has been maintained within this document to record the compatibilities analyses performed, ensuring the information gathered through literature review is not lost.

3.0 DESIGN OR TECHNICAL PARAMETER INPUT AND SOURCES

N/A

4.0 RESULTS OF LITERATURE SEARCHES AND OTHER BACKGROUND DATA

Literature results and discussion on the relevance of literature findings are presented in section 7.0 Discussion/Analysis.

5.0 ASSUMPTIONS

All materials are manufactured to the reported specifications and qualities.

Phenomena associated with Sodium and Potassium individually applies to the eutectic compounds of the same.

Lead and Lead-Bismuth Eutectic (LBE) possess comparable chemical properties and behave with sufficient similarity that data for LBE can be used for estimation of behaviors in molten lead.[1]

Normal Operating Temperatures are assumed to be the only valid states for corrosion consideration.

NaK Normal Operation Temperatures: 477°C to 546°C

Lead Normal Operation Temperatures: 409°C to 434°C

Corrosion rates and operational conditions are bounded by operational temperatures. Corrosion rates and solubilities of key impurities have been shown to decrease with decreasing temperature[2-5].

6.0 COMPUTER CODE VALIDATION

- A. Computer type: N/A
- B. Operating System and Version: N/A
- C. Computer program name and revision: N/A
- D. Inputs (may refer to an appendix): N/A
- E. Outputs (may refer to an appendix): N/A
- F. Evidence of, or reference to, computer program validation: N/A
- G. Bases supporting application of the computer program to the specific physical problem: N/A

7.0 DISCUSSION/ANALYSIS

7.1 Introduction

Microreactor Applications Research Validation and Evaluation (MARVEL) is a U.S. Department of Energy project at the Idaho National Laboratory. The MARVEL project will serve as a demonstration test bed for microreactor technology development and operate 3 days a week for 2 years. It will use sodium potassium eutectic (NaK) and eGaInSn as primary and secondary coolants respectively. The reactor is primarily composed of 316H stainless steel, with Haynes alloy Stirling engines for electrical energy generation. These are both oxidation-corrosion-resistant materials well suited for service in extreme environments, which may be subjected to high pressure and heat. Materials that may encounter the primary coolant and the previous secondary coolant, lead, are identified, and their compatibility is determined.

7.2 Description of Materials and Fluids

7.2.1 Coolants

NaK has been selected as the primary coolant and will be supplied by Creative Engineers, Inc. Nominally 77.8 wt.% potassium and 22.2% sodium, the NaK will be in direct contact with reactor internals, including fuel rods, control rods, control drums, and monitoring equipment. NaK is a unique metal compound, is a liquid at temperatures above -12°C , has a high boiling point of 785°C and possesses desirable heat transfer properties, namely high thermal conductivity.

NaK retains many of the properties of its base alkali metals and must be handled carefully. Exposure of NaK to air and water must be minimized, as this can result in violent reactions, including fire and explosions.[6] NaK chemistry will be maintained through use of an inert argon cover gas system. Impurities in the cover gas are limited to those in Table 1: Properties of Fluids, to ensure that thermal, and physical properties are maintained, and the primary coolant boundary is not at risk.

Lead was selected as the secondary coolant this has been replaced with eGaInSn and documented in ECAR-6126. The information regarding lead as a secondary coolant is presented below for reference but is no longer applicable to the MARVEL design. The secondary coolant system utilizes “pots” which are placed inside the NaK circulating loops. This allows for complete isolation of the primary coolant from both the secondary coolant and the electrical generating equipment. Lead possesses high thermal conductivity, making it a favorable heat transfer medium. Lead’s high melting point (328°C) makes it operationally difficult to maintain above its melting point during service. Lead identified as “corroding” has been determined to be of sufficient purity ,99.99% lead. It contains minimal impurities that may activate to form volatile products, such as polonium-210, resulting in minimization of safety concerns and cost. This grade of lead meets or exceeds impurities allowances provided by ASTM B29-79. The cover gas will be helium to ensure oxygen content is properly controlled in the secondary coolant system.

Table 1: Properties of Fluids

Name	Nominal Composition	Reported Purity	Limiting Requirements	Operational Temperature Range ($^{\circ}\text{C}$)
NaK	77.8 wt.% K, 22.2 wt% Na	Nuclear Grade supplied by CEI	10-25ppm Oxygen <30ppm Carbon <30ppm Halogens	477-546[7]
Lead	100% Pb	99.99	Meets or exceeds ASTM B29-79 Bi 1ppm	409-434[7]

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Argon (NaK)	100% Ar	99.998	6ppm H ₂ O 5ppm O ₂ 2ppm H ₂ 15ppm N ₂ 5ppm C 0.3ppm Kr 0.02ppm Xe 6ppm Ne	
Helium (Stirling Engine)	100% He	99.997	5ppm O ₂ 3ppm H ₂ O (High Purity He Air gas)	
Helium (Lead)	98% He 2% H ₂	TBD	TBD	

Materials selected for chemical compatibility study were determined based upon what components the coolants may be exposed to during normal operation and during credible failure scenarios. Materials that are expected to interact with coolant materials are identified in Table 2.

Table 2: Materials in Contact with Coolant

Material	Fluid	Contact Type	Description
SS316H	NaK/Pb	Continuous	Vessel
SS304	NaK	Continuous	Fuel Cladding/Rod Material
SS316L	NaK	Continuous	Neutron Source Canister
Beryllium	NaK	Continuous	Internal Reflector
Zirconium Hydride	NaK	Accident	Fuel Rod material (Breach of Cladding)
Graphite	NaK	Accident	Fuel Rod Reflector. (Breach of Cladding)
Chromium Carbide	NaK/Pb	Continuous	Weld Contaminant
SiO	NaK	Accident	Dielectric in Cable
BNi-5 Braze	NaK	Continuous	Thermocouple
Nicrosil/Nisil	NaK/Pb	Accident	Thermocouple Wires
SS316H	NaK/Pb	Continuous	Thermocouple Sheath
UNS NO6230 (Haynes 230)	Pb	Continuous	Stirling Engine
UNS NO7208 (Haynes 282)	Pb	Continuous	Stirling Engine
Lead	Pb	Continuous	Stirling Engine
Helium	NaK	Accident	Primary Coolant Boundary Breach
Helium	Pb	Accident	Stirling Engine Breach

7.2.2 316H Stainless Steel Properties

Type 316H is a high carbon variant of 316 making the steel suitable for use in applications where elevated temperatures are present. The increased carbon content delivers a greater tensile and yield strength. The austenitic structure of the material also gives this grade excellent toughness, even down to cryogenic temperatures. Type 316 stainless steel has good oxygen resistance in intermittent service up to 1600°F (871°C) and continuous service to 1700°F (927°C). Continuous use of Alloy 316 in the 850°F (454.4°C) to 1550°F (843.3°C) temperature range is not recommended, due to possible carbide precipitation. Alloy 316 performs well at temperatures below and above this range. The steel lends itself well for use in the petrochemical, gas, and chemical industry.

Benefits of using Type 316H Stainless Steel

1. Increased carbon content results in improved heat resistant qualities
2. Greater tensile yield strength
3. Greater short- and long-term creep strength

Stainless steels corrode when exposed to damaging chemicals, saline, grease, moisture, or heat for prolonged periods of time. Rusting is an oxidation process which can occur when iron is exposed to oxygen, whether it is alone or alloyed. Other constituents can increase the reaction's speed, for example, water and salt act as catalysts to the process. Rusting is a degradative process which can lead to increased friction, reduced product quality, decreased magnetic properties, and decreased electrical conduction.

It is expected that components that contain iron will corrode unless preventative measures are taken. Stainless steel's protection against corrosion is largely dependent on the amount of chromium present. Stainless steels contain chromium (>11%) which forms an oxide layer (Cr_2O_3). This oxide acts as a passivation layer and gives stainless steel its anti-rust property and a surface that does not stain or tarnish. Table 3 shows the nominal chemical composition of 316H stainless steel.

Grade 316 is an austenitic grade steel which is second only to 304 grades in commercial importance. Type 316 H is an austenitic stainless steel and has a high nickel content (10-14%) while combining other elements like chromium, nitrogen, and molybdenum. The presence of molybdenum and elevated chromium levels greatly improves the corrosion resistance of 316H, particularly reducing the risk of pitting and intergranular corrosion.

Table 3: Chemical Composition of 316H[8]

UNS No	S31603 (wt.%)
--------	---------------

EN	1.4401
AISI	316H
Carbon (C)	0.04-0.10
Silicon (Si)	0.75
Manganese (Mn)	2.00
Phosphorus (P)	0.045
Sulphur (S)	0.030
Chromium (Cr)	16.00 – 18.00
Molybdenum (Mo)	2.00-3.00
Nickel (Ni)	10.00 – 14.00
Nitrogen (N)	NA

7.2.3 316H and 316L Stainless Steels:

The key difference between 316H and 316L stainless steel is the carbon content. While 316H has a maximum carbon content of 0.10%, 316L has a maximum carbon content of only 0.03%. SS 316L, the low carbon version of SS 316, is immune from sensitization (grain boundary carbide precipitation). SS 316H, with its higher carbon content has application at elevated temperatures, same as SS 316Ti which is a Titanium stabilized grade. Table 4 describes the chemical composition of 316H and 316L stainless steel. Containing less carbon than 316 and 316H, 316L has better intergranular corrosion resistance, reducing susceptibility to carbide precipitation during welding. However, 316H is advantageous for increasing carbon content which increases hardness and strength and improves hardenability and creep resistance. Furthermore, 316H is required by ASME BPVC Section III Division 5 for use at High Temperatures and Pressures. As part of ASME BPVC Section III Division 5, restrictions are recommended to be imposed on 316SS to be used in compliance with the code. These include chemical composition and grain size. Chemical composition is restricted to those in Table 3, with the addition of a grain size limitation of ASTM 3-6 Table HBB-U-1 of ASME BPVC Section III Division 5 [9]. The additional carbon content of 316H requires additional attention to the welds, such as limitations on heat

input, weld contamination prevention and that proper post weld heat treatment has been conducted to reduce carbide precipitation.

Table 4: Chemical Composition of 316 Stainless Steels

SS	316 (wt.%)	316H (wt.%)	316L (wt.%)
Ni	10 – 14	10 – 14	10 – 14
Fe	Bal	Bal	Bal
Cr	16 – 18	16 – 18	16 – 18
Mo	2 – 3	2 – 3	2 – 3
C	0.08 max	0.10 max	0.03 max
Si	0.75 max	0.75 max	0.75 max
Mn	2 max	2 max	2 max
P	0.045 max	0.045 max	0.045 max
S	0.030 max	0.030 max	0.030 max
N	0.1 max		0.1 max

7.3 Acceptance Criteria

- Lead: for temperature range 400-700 °C it is recommended that oxygen content within the lead be maintained at 10^{-6} - 10^{-4} wt% [3, 10]. This ensures proper formation of a protective oxide layer on the surface of stainless steel exposed to lead, while mitigating the formation of lead oxides which may negatively impact coolant flow and heat transfer. Type 316 stainless steels have historically been recommended for use with molten lead.[11] Attributed rates of corrosion are unknown. Based on lower grade stainless steels, namely 302, corrosion may prove significant up to 0.12-0.42 inches per year (3.05-10.67 mm per year) which would exceed the thickness of the intermediate heat exchanger and Stirling Engine Tubes, which is 0.1341 inches (3.406 mm), and 0.031 inches (0.787mm) respectively. As such monitoring of surfaces exposed to lead for corrosion and degradation should be conducted by non-destructive testing. Though lead is no longer being utilized as the secondary coolant. The above criteria are applicable for systems operating with similar materials and temperature.
- NaK: acceptable so long as oxygen is kept between 10-25ppm, and carbon and halogens are at or below 30ppm within the NaK system for temperatures up to 1000°F (537.78°C) [2, 12]. Stainless steels of grades 304, 316 and 347 are considered to have near unlimited life in NaK systems at these conditions [2].
- 316H Stainless Steel: Acceptable so long as chemical composition falls within values proposed by Table 3, and maintains an ASTM grain size of 3-6.

7.4 Safety

7.4.1 Safety Functions (Ref: ECAR-6440 Rev 0)

Chemical compatibility between structural materials and coolants is essential in ensuring that MARVEL is a safe functional reactor. This compatibility ensures that containment and cooling capabilities of the MARVEL reactor system are maintained during its operation. A primary safety function that is ensured by proper chemical compatibility is the preservation of the primary coolant boundary. The primary coolant boundary ensures that NaK is not exposed to air or water, which would result in fire, small explosions, release of caustic fumes, or damage to TREAT facility structures. Further, preservation of the primary coolant boundary ensures that any evolved radionuclides are confined.

Related to the maintenance of the primary coolant boundary is core cool ability. This is assured in the design of the reactors primary coolant system and guard vessel structure. This system has been designed to ensure that even in the case of a leak of the primary coolant into the guard vessel, the core will remain covered by the NaK. More information regarding how the core will remain covered can be found in ECAR-6586.

There are multiple systems within the MARVEL design that will experience high pressures and temperatures. As such, they are designed to ASME Boiler Pressure Vessel Code (BPVC), which ensures that systems, such as the primary and secondary coolant system, can withstand the temperatures and pressures they will be exposed to during normal and anticipated abnormal conditions. If no preventative measures are taken, exposure to the molten metal coolants may result in deterioration of base materials or welds. This may result in failure due to temperature and pressure fluctuations during normal operations, and shutdown cycles.

Of primary concern, due to the high pressures involved, is the chemical compatibility of the Stirling engines with the molten lead. The operating fluid within the Stirling engines is high pressure helium 754 psig at 20°C. Corrosion of the Stirling engine tubes may result in the release of helium into the secondary coolant system. In the case of helium release, the bellow seal around the secondary coolant system will release, due to its design release pressure of 5 psig. In the event of helium release, lead splashing, and aerosolization is expected resulting in molten lead contamination of the subsequent area. This contamination will be contained, and both personnel and TREAT facilities will be protected by the upper confinement boundary which contains the upper plenum of the MARVEL reactor system.

The use of inert gases presents a suffocation hazard in the event of a leak. Argon, which is denser than air, will displace air resulting in stratification of the local atmosphere. This

can lead to regions around the reactor or in the reactor pit that are deficient in oxygen, resulting in a safety hazard to personnel that may need to enter these areas. Proper leak detection, and atmosphere monitoring should be used to ensure that personnel can perform their tasks safely. In the event of inert gas leaking, proper PPE, and associated procedures to identify leak location and resolve the leak shall be utilized.

7.4.2 Phenomena and Failure Mode

7.4.2.1 *Welding Related Issues*

Carbide precipitation within the heat affected zone (HAZ) is common in austenitic steel, and is especially prevalent in high carbon steels, such as 316H. Carbide precipitation results in localized chromium depletion which increases the region susceptibility to corrosion. This phenomenon is known as sensitization, as the chromium depleted region is more sensitive to corrosion attack. Solution heat treatment (heating and quenching to unify grain structure), the use of stabilized steels, or low carbon steels allows for minimization of carbide precipitation, in turn reducing the risk of sensitization due to welding [8]. Low carbon steels are not allowed by ASME section III division 5, thus the applicability of low carbon steels to alleviate weld sensitization is limited for MARVEL. Homogenous carbide distribution in the steel matrix results in improved dislocation and sub-boundary hardening which in turn improves creep resistance [14] which is why high carbon steels are required for high temperature applications. Since the welding process localizes carbides around the weld, a negative impact to creep properties is expected. The negative impact has not been quantified in literature; however, remediation is identical to those utilized for decreasing sensitization. The only code approved mechanism for alleviating carbide precipitation in welds is through solution annealing, this allows for the bulk material properties to be restored to the native properties of 316H (ASME BPVC Section III Division 5 HBB-4212 [9]).

It is recommended that all welds anticipated to be exposed to elevated temperatures should undergo post weld heat treatment (PWHT) (Appendix A). In the case of 316H, this is accomplished by solution annealing per ASME BPVC Section III Division 5 [9]. However, the code does not require PWHT, rather solution annealing is required for the material to be used for fabrication. Due to the complex geometry of MARVEL, severe deformation is expected to occur if the entire PCS undergoes PWHT at the same time. As such, PWHT has been applied specific weldments anticipated to experience the greatest stress, this is shown on MARVEL drawings 1014606 and 1014609.

Stress corrosion cracking is common in austenitic stainless steels as the nickel concentration within these steels is nominally between 8-12 wt% Ni. This nickel content results in an increased susceptibility to stress corrosion cracking, which is most common in aggressive environments such as those containing chlorine or sodium hydroxides [13]. Delta ferrite concentration in welds is specified by ASME BPVC Section III Division 5. This code requirement ensures that risk of welds experiencing stress corrosion is minimized. Stress corrosion has not been reported in liquid metal; however, it is known to occur in regions where chromium carbide precipitation has occurred. Thus, likely locations for this to occur within the MARVEL reactor system is near welds within the HAZ [15].

7.4.2.2 *Corrosion of 316H under Molten Pb*

Properties that are responsible for the many uses of elemental lead include its ductility, ease of welding, low melting point, high density, and ability to absorb gamma and X-ray radiation. Molten lead (Melting point: 327.5 °C (621.5 °F), Density: 11.29 gram/cm³ at 20 °C (68 °F), Boiling point: 1,744 °C (3,171.2 °F)) is an excellent solvent and collector for elemental silver and gold.[16]

Advanced nuclear reactor design has, in recent years, focused increasingly on the use of heavy liquid-metal coolants, such as lead and lead-bismuth eutectic. Similarly, programs on accelerator-based transmutation systems have also considered the use of such coolants. Russian experience with heavy-metal coolants for nuclear reactors has provided credibility to the validity of this approach. The significant concern is the compatibility of structural materials with these coolants.[17]

A report by Argonne National Laboratory concerning iron-based alloys exposed to molten lead-bismuth under a temperature gradient was essential in evaluating material transport. [17] The temperature in the hot leg of the convection harp was ~ 550°C and the temperature in the cold leg was ~350-425°C. The Argon report proves AISI S-5 (silico-manganese shock resisting steel) alloy steels are attacked by molten lead-bismuth due to the silicon content present in the alloy composition. It was observed, after 4500 hours, that the depth of intergranular penetration ranged up to 0.04 mm in the hot leg and up to 0.005mm in the cold leg. Their report indicates that AISI S-5 would not be suitable as a structural material for nuclear reactors using lead-based alloy coolants. However, it was found that HT-9 steel (High-Cr martensitic steel) is not attacked by the molten lead-bismuth. The samples appear to have been protected by a stable, adherent, Cr₂O₃ or FeCr₂O₄-type spinel layer which only forms at an oxygen pressure higher than ~1 x 10⁻³⁹ atm. Close control of oxygen activity was not necessary to form the protective spinel. If the oxygen activity is well below that needed to form PbO (~1 x 10⁻³³ atm) and above

that needed to form the spinel, sample freedom exists to form a protective layer on HT-9.

The comparison of AISI S-5 and HT-9 corrosion behavior under molten lead-bismuth clearly demonstrates the important role of chromium in the passivation of HT-9 and AISI S-5 alloys exposed to molten Pb-Bi [17]. Thus, since our MARVEL system has 316H stainless steel with a high chromium content, (16-18%) there will be limited attack by molten lead coolant unless the oxygen pressure is uncontrolled.

The 316 stainless steels have historically been recommended for use with molten lead [11]. Corrosion rates associated with this recommendation were not published. Other stainless steels, 302, 410 and 430, did have published rates which may result in corrosion rates of 0.12-0.42 inches per year (3.05-10.67 mm per year), and was tested at 327°C [11]. This is significant corrosion that could result in Intermediate Heat Exchanger, 0.1341 inches (3.406mm) thick, being compromised leading to a primary coolant boundary failure.

The formation of an oxide film on an alloy surface is determined by temperature, oxide stability and oxygen activity in the system. The oxygen partial pressure in our MARVEL system can be roughly estimated from the measured moisture content and the hydrogen concentration in the He-H₂ cover gas. From the known Gibbs energy of formation of water, the estimated PO₂ in the system at 550°C will be much larger than needed to form Cr₂O₃ or FeCr₂O₄, but lower than that needed to form PbO. Clearly, the existing oxygen partial pressure (oxygen pressure higher than $\sim 1 \times 10^{-39}$ atm) in the system permits formation of the Cr-containing oxides but not PbO.[17]

7.4.2.3 *Secondary Materials Interactions with Molten Pb*

NaK:

Capacitive pressure difference transducers that utilize a coupling medium have been successfully used in lead-bismuth systems. The use of a coupling medium is to protect the transducer medium, which is temperature restricted to below that of the lead-bismuth operating temperature. NaK has been used successfully as this coupling medium,[3] indicating that there will be no reaction should NaK and lead interact. The secondary coolant system is designed to be maintained at -10 psig, while the primary coolant system is designed to be maintained at 55 psig, resulting in a net maximum pressure differential of 65 psig. In the case of a primary coolant boundary breach via a leak in the secondary coolant system, NaK will infiltrate the secondary coolant system until hydrostatic equilibrium is reached. Depending on the volume of NaK that infiltrates the secondary

coolant system, the intermediate heat exchanger could overflow resulting in contamination of the upper confinement. This will contaminate any filters utilized in the cover gas system, may damage electrical cables near the Stirling engines, and may result in fuming, fire, or explosions. Any gaseous products released by NaK being introduced to the secondary coolant system are contained by the Upper Confinement Boundary which minimizes the possibility of personnel exposure.

If lead enters the primary coolant boundary, it must flow down the downcomer within the primary coolant system. This may result in lead freezing inside of the primary coolant system, resulting in decreased flow through the affected downcomer. If the entire volume from a single intermediate heat exchanger is lost into the primary coolant system, it will result in the covering of the base of all four of the downcomers' exits. This may result in a complete loss of flow, or channel flow, through the lead, which will result in the reduction of energy conversion into the Stirling engines. However, the MARVEL reactor is designed to remain coolable even in instances where the natural circulation of the NaK coolant is disrupted or ceased. Sufficient heat transfer is allowed through the coolant, guard vessel, and into the walls of the reactor pit, ensuring temperature within the MARVEL system is within design specifications at all postulated states.

Haynes:

UNS NO6230 and UNS NO7208 are also known as Haynes 230 (UNS NO6230) and Haynes 208 (UNS NO7208) which are nickel-chromium-tungsten-molybdenum alloys that combine excellent high-temperature strength, long-term thermal stability, and resistance to oxidizing environments up to 2100°F (1149°C) for prolonged exposures in harsh environments. These two variants of Haynes are used in the Stirling Engines for the construction of the tubes and dome shown in Figure 1. However, owing to the high nickel percent present in the alloys, compatibility with molten lead is questionable.[1] Additionally, Haynes's compatibility in NaK coolant is also being closely examined in case there are impurities present in the alloys.[18] Reports show that the higher the nickel content, the more rapidly the solid metal dissolves in the molten metal system. As a ROUGH rule of thumb, where contact with low melting metals is concerned, the lower nickel alloys, or even the ferritic stainless steels, are preferred. High nickel alloys, such as RA600 (76%Ni) tend to be attacked more severely. Literature data indicate that material behavior is quite similar in Pb and LBE. Zhang[19] pointed out the higher solubility of the main elements of the alloy in LBE than in liquid Pb, although this effect could be more evident even in austenitic steel with high nickel dissolution.

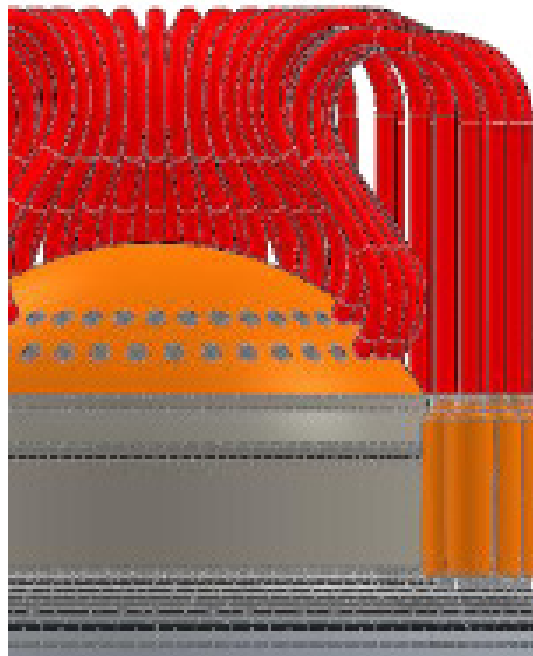


Figure 1: Stirling Engine Hot Side. Engine Tubes in Red and dome structure in Orange. Source: QNERGY QB80 System Integrator Guide.

High nickel alloys, such as Hastelloy N have been tested in lead thermal convection loops at temperatures of 750 °C. These experiments resulted in complete destruction of the material within four (4) hours of testing.[20] This temperature exceeds those expected during MARVEL operation, however the experiment highlights the limited application of high nickel alloys, such as Hastelloy in molten lead systems. No literature has been found regarding Hastelloy corrosion in lead at temperatures which would bound the MARVEL reactor 400-550°C. It is recommended that Haynes be replaced with 316 series stainless steel.

304L Stainless Steel:

Through conversation with Qnergy, it was learned that 304L stainless steel will require minimal effort to utilize as a replacement material for Haynes used in the existing Stirling Engine design. Corrosive mechanisms for 304L and 316H stainless steel are similar. Elevated temperature service is required for materials that exceed 800°F (~425°C) per ASME BPVC Section III Division 5 for reactor systems and supporting systems. However, per ECAR-6440, the Stirling Engine is a non-safety related component, and is not considered a reactor system or supporting system, due to the Stirling Engines not being required to perform any safety function. Thus, Stirling Engine materials are not restricted to those within ASME BPVC Section III Division 5, rather by the limitations of the material

itself. A report developed by the Nickel Development Institute demonstrates that 304 and 316 stainless steels are able to perform as designed at temperatures up to, but not exceeding 538°C. Austenitic stainless steels are not recommended for use in molten lead at temperatures above 500°C due to reported dissolution occurring within 42 days at continuous operation at 560°C [3]. Dissolution at these elevated temperatures is not effectively controlled by oxygen management. This is attributed to the instability of the chromium and iron oxide film at these elevated temperatures, which results in wetting of the bulk material by the molten lead [5]. Oxygen control has been shown to be an effective corrosion inhibitor in molten lead at temperatures below 500°C [3, 5, 19]. Experiments show that 304L stainless steel exposed to static lead bismuth eutectic did not form a liquid metal corrosion layer after 3,000 hours (84 days) of exposure at 535°C and oxygen content restricted to 3E-6 wt% [19].

At 500°C with oxygen concentrations ranging from 1E-6 to 1E-5 wt%, using ground 304 and 304L experienced a generalized dissolution corrosion rate of less than 400 $\mu\text{m}/\text{yr}$ (0.016in/yr) in slow flowing lead bismuth eutectic, approximately 1 cm/s (0.033 ft/s) [5]. This flow rate can be assumed to be representative since the anticipated flow within the intermediate heat exchanger will be naturally circulating lead.

An issue that has been brought up by Gong et al., is imperfect formation of the protective oxide layer (manufacturing defect and/or improper aging of stainless steel) which will result in localized dissolution (pitting). This phenomenon may not be preventable, as after the pitting has occurred it cannot be stopped using oxygen. This is attributed to the oxygen being captured by the oxide layer that surrounds the pitting which results in continuous dissolution through the matrix at a rate equivalent to the mass transfer between the lead and the steel matrix. Fortunately, this rate is slow, leading to a maximum pitting depth of 0.049 in after two years at comparable conditions to MARVEL for 316L stainless steel, and similar steels (such as 304L) [5].

7.4.2.4 ***Corrosion of 316H Under Molten Na and K***

NaK (22.2% sodium, 77.8% potassium, by weight, liquid from -12.6°C to 785 °C, density of 866 kg/m³ at 21°C and 855 kg/m³ at 100°C) is an alloy of sodium (Na) and potassium (K) used as a coolant in nuclear reactors. It is particularly useful because it remains liquid at room temperature and is commercially available in various grades. NaK is highly reactive with air or water, and therefore must be handled with special precautions. Quantities as small as one gram can be a fire or explosion risk. Despite these disadvantages, NaK is often used because it does not require continual heating to remain in a liquid state. NaK is used in many other heat transfer applications for similar reasons.

Apart from its wide liquid temperature range, NaK has a very low vapor pressure, important in the absolute vacuum of space.

Studies have shown that corrosion by liquid metal can be a physical process, a chemical process, or both. When regular steel is exposed to liquid metal, some of its constituents can dissolve into the liquid and may react with the impurities in the liquid. Also, the liquid can penetrate the steel along the grain boundaries or other defects, which changes the microstructure, composition, and surface morphology and thus the properties of the material to some depth (typically tens of microns in depth) into the material. Such changes can become significant with time and may eventually lead to material failure. Compared with liquid sodium, which has been used as a coolant in many terrestrial fast breeder reactors, studies on corrosion by liquid NaK are not plentiful, and most of them for its use as a nuclear reactor coolant were carried out prior to 1970.

Chemical corrosion results from reactions between the materials of construction and the impurities in the liquid metal. Given that some level of impurities generally exists, chemical corrosion is very common. It produces simple or complex corrosion products on the solid material surface or in the liquid that may stimulate or suppress interaction. The products may be soluble, loosely or tightly adherent, and affect the net corrosion rate. Like penetration corrosion, chemical corrosion can lead to interstitial impurities' redistribution or partition of the impurities between the liquid and solid materials. It can also result in chemical compound formation, surface layer deposition, and particle formation in the liquid. Thus, chemical corrosion poses a risk to general chemical stability within environments and may result in unpredictable behavior of materials during operation.

For steel materials, there will be a leaching solution corrosion that results from the selective dissolution of the alloy constituents (Ni, Mn, Cr, C). The leaching solution corrosion has been described as a combination of dissolution and chemical reaction mechanisms. It removes alloy constituents at various rates, which results in a composition change of the surface layer. If the layer continues to develop and the removal of the alloy constituents exceeds a specific minimum threshold level, the layer will become a new phase layer[21]. For example, a ferrite layer has been observed on Type 316 stainless steel ~SS316H after being exposed to liquid sodium[22].

Stress corrosion is another important concern in liquid-metal corrosion. The combination of the dissolution and mechanical stress can cause cracking of the materials, which has been observed at bends in a liquid sodium-potassium (NaK) loop. Failure of components has been observed at the Waste Calcining Facility (WCF) at the INL. This system used

heated NaK to provide heat via a bayonet heater to the fluidized bed of the WCF. Failures were observed in fittings, such as elbows and T's. These fittings were exposed to external stresses resulting in their failure. The failures primarily consisted of cracking within or near welds of the fittings. Failure was also noted in cold regions of the piping loop, due to carburization of the steel in the cold region. Mass transfer effects were assumed to be caused by both the temperature and oxygen content within the NaK. By minimizing the oxygen and carbon content within the NaK, carburization due to mass transfer, and carbon impurities can be minimized. Since the main failure mechanism associated with fittings is attributed to external stresses, the design of any NaK containing system should be such that thermal and mechanical stresses are minimized [23].

Solution corrosion results in weight loss, surface recession, and phase changes and the potential for the development of cracks, crack propagation and contamination of the liquid. All these phenomena are potentially serious problems for materials in liquid-metal systems. This may present as decarburization resulting from the loss of carbon from low-alloy steel by liquid sodium. This causes significant property changes of the steel at the operation temperature for short times, which may lead to mechanical failure of the components containing the liquid-metal coolant. Decarburization has been shown to occur in non-isothermal systems, resulting in decarburization of the hot section, and carburization of the cold section. Carburization can result in mechanical transformations of the material resulting in decreased ductility and hardened strength [4]. By maintaining oxygen content below 50ppm and carbon below 30ppm within the NaK, carburization and decarburization is expected to be minimal, and not result in deleterious mechanical or chemical effects on 316H stainless steel [4].

Chromium carbides precipitate in stainless steels at temperatures between 430°C and 815°C. This results in an increase of intergranular corrosion in aqueous solutions, but has not been observed in low oxygen sodium systems[4]. Zimmerman further notes that though sensitization and sigma formation have been observed in sodium systems, it has not resulted in failure[4].

Common austenitic grades of stainless steel including 304, 316, and 347 are reported to have near unlimited life in sodium and NaK systems at temperatures up to 1000°F (537.78°C), so long as oxygen content is limited to 10-25 ppm and carbon and halogen content within the fluid is kept as low as possible (<30ppm)[12]. Small amounts of hydrogen gas are expected to diffuse through the fuel cladding due to the thermal cycling of the fuel. This amount of hydrogen is not anticipated to be significant, however, it does play a role in the corrosion phenomenon that has been observed in sodium systems.

Hydrogen introduction to NaK is anticipated to have very little impact on corrosion of stainless steels in the NaK system as reported in INL/RPT-22-68555 Rev.0. Hydrogen content within the NaK, if it exceeds anticipated amounts reported in INL/RPT-22-68555 Rev.0, may result in increased pitting corrosion on the surfaces of the stainless steels [9]. The corrosion rate of stainless steels is largely dependent on oxygen concentration and temperature in NaK systems. As either of these variables increases, corrosion rates likewise increase [9]. As the average operating temperatures of the MARVEL system are estimated to be less than 1000°F (537.78°C), with a maximum NaK temperature of 1,015°F(546.11°C), it is anticipated that all stainless steels exposed to NaK shall experience little to no adverse effects due to their exposure during MARVEL's two-year operating window. Limitations on oxygen and carbon content restrict the observed corrosion rates at temperatures up to 1100°F (593.33°C) results in a corrosion rate between 0.00025 to 0.001 inches per year (0.006-0.025 mm per year). The efforts to minimize impurities within the NaK system by cleanliness and inert atmosphere further serve to mitigate factors which may attribute to adverse chemical attack by NaK.

7.4.2.5 *Secondary Material Interaction with Na and K*

Beryllium:

Beryllium metal acts as an internal neutron reflector [24], as such it performs a critical function in activity control within the MARVEL system. Beryllium has been reported to be resistant to molten sodium up to 1000°F (537.78°C), with no evidence of stress or intergranular corrosion. This temperature can be extended to 1200°F if oxygen levels within the sodium are minimized. At temperatures at or above 1200°F it has been reported that the beryllium will migrate to other materials in a composite system. Beryllium does form insoluble oxides (BeO) in oxygen containing sodium more preferentially than sodium, however these oxides do not form a stable surface layer and thus offer no corrosion resistance. For stability of NaK and minimization of sludge formation oxygen content must be minimized[21].

Zirconium Hydride:

Uranium Zirconium hydride is internal to the fuel pin and will only be exposed in the event of a fuel cladding failure[25, 26]. Zirconium forms an adherent and insoluble oxide, resulting in corrosion of the zirconium metal being dependent on the diffusion of oxygen through this oxide coating [21]. Zirconium as it oxidizes can become severely embrittled due to intrinsic absorptions of oxygen into the Zirconium matrix. Thus, due to the unlikely

occurrence of fuel cladding failure, and subsequent exposure to low oxygen NaK, the corrosion that will be experienced by the uranium zirconium hydride will be minimal and protected by the formation of an adherent zirconium oxide layer, maintaining the bulk material properties.

Molybdenum:

Molybdenum is a component of the MARVEL fuel system and is internal to the fuel cladding. It will only be exposed to NaK in the event of a fuel cladding failure. Molybdenum is considered to be inert to sodium, which is corroborated by experiments reported by Foust et al [2] where molybdenum exposed to NaK at 1400°F (760°C) for 3000 hours presented no evidence of corrosion. It is possible for molybdenum and sodium to react and form sodium-molybdate. This compound was observed on molybdenum rubbing surfaces, whereby a film of sodium-molybdate was formed on the rubbing surfaces resulting in reduced friction. Sodium-molybdate formation is dependent on the presence of oxygen within the sodium environment for its formation. The low oxygen content of the NaK minimizes the formation of sodium-molybdate. No adverse effects are expected during any accident scenarios where NaK may be exposed to molybdenum.

BNi-5 Braze:

BNi-5 is a nickel-based brazing alloy suitable for applications working at high temperatures[27]. The high level of alloyed chromium in BNi-5 results in a good hot gas and acid corrosion resistance. The high melting range of BNi-5 makes it suitable for applications working at very high temperatures, for instance, EGR coolers for trucks and automotive metal catalytic converters. Thus, BNi-5 is recommended as the best brazing material for use in NaK systems. Nickel-based brazing alloy has been tested by DOE Laboratories and has been confirmed to perform as designed in nuclear reactors, and NaK environments[28-30].

Nickel Alloys:

Predominantly nickel alloys (Ni>50 wt%) have been studied for use in sodium systems. Large numbers of these tests are conducted in excess of 1200°F (648.89°C), since austenitic stainless steels are limited by their mechanical strength above these temperatures. At temperatures below 1300°F (704°C), nickel-based alloys suffer little corrosion. Common grades such as Inconel 600 and Nimonic 80A experience 6.1 to 4.9 thousandths of an inch per year (0.155-0.124 mm per year) of material loss respectively at a temperature of 1202°F (650°C) [2]. This indicates that for high nickel alloys exposed

to NaK at MARVEL temperatures less than 1000°F (537.78°C) there should be negligible corrosion, and no impact on operation during MARVEL's two-year lifetime.

Graphite

Graphite is contained within the fuel rod and will only be exposed to NaK in the event of a cladding failure, thus there is little risk of NaK and graphite interacting. Though the risk of graphite exposure to NaK is minimal, it is important to understand the phenomena that graphite will experience in the event of this exposure. This will ensure that proper procedures are in place to account for phenomena occurring after a cladding failure. Graphite has been observed to experience swelling or dilation, cracking or spalling and corrosion and mass transfer at temperatures above 1200°F (648.89°C) [2]. Experiments reported by Foust et al [2] indicate that at elevated temperatures, sodium readily soaks into the graphite pores resulting in up to 100% of the pores being filled with liquid sodium at 1022°F (550°C). In another experiment, also reported by Foust et al, at a temperature of 1355°F (735°C) 90% of the graphite was impregnated. It was further noted that on the addition of a small amount of potassium, these effects are exacerbated. There is conflict in literature regarding how graphite behaves in sodium. An earlier report generated by North American Aviation under the auspices of the Atomic Energy Research Department indicates that corrosive attack of the graphite occurs in the presence of the carburization of the containment material. However, they do corroborate phenomena observed by Foust et al, that graphite was wetted by sodium at temperatures above 150°C, and sodium is absorbed within the pores. Further tests with graphite partially submerged in sodium demonstrate sodium uptake within the graphite is due to capillary action. The unsubmerged graphite was saturated such that all the voids were occupied by sodium. They do note minor dimensional changes indicative of swelling due to sodium exposure, with a 0.74% increase in diameter and 0.37% increase in length, after a one (1) week exposure in 500°C sodium [31]. Contrary to Foust et al, studies by North American Aviation indicate that dilation, and subsequent adsorption of sodium is not entirely due to physical entrapment within the graphite pores. Rather, there appears to some extent that sodium is held within the graphite via chemical bonds, due to changes of the Hall coefficient of the graphite. This indicates that graphite exposure to sodium will likely cause irreparable damage to the graphite possibly negatively impacting the ability of graphite to perform as a moderator. Since the information available is primarily concerning graphite interactions with sodium, with some indication that potassium additions to sodium exacerbate the observed phenomena, it is difficult to predict the behavior of graphite in NaK. Due to this limited information, it may prove beneficial to

development of procedures for an experiment to be conducted to determine how graphite behaves in NaK.

Table 5: Type 304 Stainless Steel Chemical Composition,[32]

Standard	AISI (UNS)	C, ≤	Si, ≤	Mn, ≤	P, ≤	S, ≤	Cr	Ni
ASTM A276/A276M	304 (S30400)	0.08	1.00	2.00	0.045	0.030	18.0- 20.0	8.0- 11.0

7.5 Requirements

7.5.1 Governing Requirements

Governing requirements are copied from TFR-2576. Information contained within TFR-2576, shall take precedence over any conflicts that may exist between it and this ECAR.

Requirement 3.6.3.1: Chemical Compatibility

The primary coolant shall not chemically react with materials in the fuel cladding, the intermediate heat exchanger, and the reactor vessel at normal operating and postulated accident conditions.

Rationale: The primary coolant cannot degrade the materials it comes in contact with which would challenge the primary coolant boundary. [FOR-868 Sections 3.5.2.1 and 3.5.2.4]

Requirement 3.6.3.2 Cover Gas Purity

The IGS shall limit the impurity levels in the argon cover gas to those specified below:

- Water: 6 ppm
- Oxygen: 5 ppm
- Hydrogen: 2 ppm
- Nitrogen: 15 ppm

- Carbon: 5 ppm
- Krypton: 0.3 ppm
- Xenon: 0.02 ppm
- Neon: 6 ppm

Rationale: Argon cover gas supplied to the reactor systems must be of sufficient purity to avoid corrosion and reaction with NaK. [FOR-868 Section 3.51.7] (M.10.3.14)

7.5.2 Requirements Generated in This Report:

Oxygen content in Lead

Oxygen serves as a corrosion inhibitor, by maintaining oxygen levels within 1E-6wt% to 1E-4wt%, sufficient oxygen is available for maintenance of the protective oxygen layer on the stainless-steel surface, while not enough oxygen to generate large quantities of lead oxide that may accumulate and impact flow characteristics within the intermediate heat exchanger.

Oxygen Content in NaK

Oxygen serves as a corrosion inhibitor, and by maintaining oxygen levels within 10-25 ppm, ensure that selected stainless steels will not be corroded due to exposure to molten NaK.

Carbon Content in NaK

Carbon excessive impurities in NaK have the potential to carburize exposed stainless steels, resulting in decreased ductility and increased hardness. This effect can be minimized by maintaining a carbon content within the NaK to less than or equal to 30ppm.

Halogen Content in NaK

Halogens are a known corrosive agent in stainless steels. By maintaining a total concentration of halogens to less than or equal to 30ppm, the corrosive impact of halogens can be avoided.

7.5.3 Pre-Operation, Post-Operation and Maintenance

Per ANS 15.8 -3.5, pre-operational checklists shall be developed and used to verify that systems are ready to operate. Following this precedent, the following operational testing and monitoring methods for first time start up, and pre-operational startup and post operation are described.

7.5.3.1 *Initial Start Up*

Before initial startup of MARVEL, cleanliness of the vessels must be assured to prevent any contamination of the metal coolants which could impact their ability to function as a heat transfer media, along with mitigating any undesirable reactions which could result in excessive corrosion of containment materials. Cleanliness of all components within the primary and secondary coolant subsystem is accomplished according to INL standard STD-7022 Level B. This standard is designed for reactor fuel assemblies, wetted coolant surfaces and reactor coolant system components. Ensuring all components meet these requirements, which includes being visually free of grease, cutting oils, iron oxides, physical contaminants, and limits the size and count of particles, will ensure that there is no debris due to the manufacturing process. Further this will reduce the amount of cleaning required prior to the introduction of liquid metal coolant. This cleaning process also ensures that there will be effective mass transfer to allow for inert atmosphere to be introduced within the coolant subsystems, with no contaminants preventing oxygen transfer from the stainless steels into the atmosphere for removal.

Prior to introduction of coolant fluids, an inert atmosphere must be achieved, atmosphere will be measured and tested to ensure that it meets requirements as specified in Table 1 for argon. Inert atmosphere is achieved by introducing a vacuum on the primary coolant subsystem, and then flushing first with argon, to remove air from lower plenum, and then helium to flush residual air out of elevated trapped surfaces. In addition, a small partial fraction of hydrogen is flushed <3% H₂, to allow for extraction of oxygen from stainless steel surfaces. This inert atmosphere must be maintained during the filling of both coolants and is accomplished by use of penetrations into both the primary coolant subsystem and secondary coolant subsystem. After initial coolant fill, the level of the coolant must be confirmed via visual inspection. Cover gas composition and pressure shall also be measured to confirm that no changes in cover gas composition have occurred during installation of liquid coolant, which would indicate formation of undesired compounds, such as oxides.

If lead is used, the temperature in the secondary coolant sub-system shall be maintained at or above the melting point of lead while the Stirling engines are submerged in the lead to ensure that there is no damage to the structural integrity of the Stirling engine tubes.

Lead shall be melted to above its melting point prior to filling such that it remains molten once it enters the intermediate heat exchanger. The temperature of the intermediate heat exchanger coolant shall be monitored to ensure that the temperature remains above the melting point of the lead.

7.5.3.2 ***Pre-Operation (Normal Startup)***

For pre-operation testing, it is assumed that lead, NaK and fuel have been loaded. There are multiple actions that need to be tested before the reactor can be started up, with the purpose of ensuring that gas, fluids, and containment materials are in suitable condition for reactor operation.

For proper reactor operation, pressures of inert gases utilized in the primary coolant subsystem, secondary coolant subsystem, and guard vessel must be within prescribed range. Since reactor systems are not hermetically sealed, and reactor environment temperature and gas content will fluctuate throughout the year, it is expected that the inert gas pressure will change and need to be adjusted accordingly to fall within reactor operating parameters. Further, temperatures of the system should be confirmed to be within operating ranges, particularly the secondary coolant subsystem, which must be at or above the melting point of lead (if used) to ensure proper heat conversion to electrical energy via the Stirling engines.

Pressures should be tested within the cover gas systems, particularly before and after filters in the cover gas systems. This will allow for excessive pressure drops indicative of clogging due to aerosolization of molten metal, or metal oxides to be detected. In addition, all systems shall be tested for leaks, namely, gas and coolant fluids. This will provide confidence that all systems are functioning as intended, the primary coolant boundary is maintained, and the reactor is in a safe operating condition.

The temperature and pressure of every system shall be tested to ensure that the reactor is ready for startup. Temperature should be high enough to ensure that the secondary coolant is molten to prevent damage to the Stirling engine. Further, proper flow rate of cover gas shall be confirmed to ensure the proper sweeping of generated radionuclides and vapors.

7.5.3.3 ***Post Operation***

Post-operation inspection will occur following reactor shutdown. For many of the tests there will be a delay to allow radiation levels to reduce to levels where personnel can safely enter the TREAT facility.

Sampling of the cover gas space after operation is essential for the maintenance of coolant properties, stability of primary coolant boundary, and monitoring of fuel stability. Cover gas should be tested to ensure that it is of proper composition and pressure. Further testing for radionuclides should be conducted to monitor activation of cover gas (Argon 41) and generation of volatile radioactive constituents such as polonium-210 in secondary coolant subsystem.

Temperatures should be monitored during all reactor operations, and during post operation, temperature should be confirmed to align with conditional states, hot standby, reactor shutdown, etc. Temperature fluctuations can be indicative of fluid flow, reactivity, or chemistry control failure. Temperature also plays a role in pressure management, as it can be assumed that the gases utilized follow the ideal gas law, and since volume is constant, pressure will increase proportionally to temperature. Thus, if temperature cannot be controlled, this may result in pressure exceeding design basis.

Post operation should include periodic inspection of internal surfaces in contact with molten metals. This should include visual and ultrasound inspection to determine the status of the primary coolant boundary. This is conducted to determine the effectiveness of coolant chemistry control, and corrosion mitigation efforts. This inspection also serves as an early detection method for weakening of the primary coolant boundary, such as excessive material loss, selective leaching and pitting corrosion, which may lead to compromising the function of the primary coolant boundary. This will allow restorative action to take place to prevent further degradation of the primary coolant boundary.

7.5.3.4 Maintenance

Periodic maintenance of coolant systems must be conducted to ensure the safe operation of the MARVEL reactor system. Fluid levels should be tested periodically to confirm that there is sufficient coolant for reactor operations. This will also serve as confirmation that leak detection equipment is working properly. This maintenance may also include filtration of coolant fluids to ensure no oxides have formed, and re-purification to restore chemistry within the coolants. In addition, sampling of coolant fluids and testing for corrosion products such as Ni, Fe, and Cr should be conducted.

Due to some lead and NaK vapor formation, it is likely that some vapors will be entrained in cover gas filter systems, necessitating the filters replacement periodically during MARVEL's lifetime. This replacement allows for cover gas to be properly cleaned prior to entering the cover gas spaces and protects HVAC equipment from contamination.

Maintenance of valves and connections is required to prevent leaks, which may result in cooling fluid contamination, or facility contamination. Seals may become brittle as they will be exposed to neutron flux, and high temperatures, and shall be inspected and replaced if defects are found.

Sensors should also be maintained via calibration and replaced as necessary. Periodic calibration shall be conducted following manufacturer specifications. And in the case a sensor fails to be calibrated, it shall be replaced with a functionally identical sensor.

7.6 End of Life

A separate decommissioning and decontamination (D&D) plan was developed and will dictate the implementation of decommissioning and decontamination of fluids, and systems described in this report. For additional information on the D&D plan refer to document WFO-BEA-001.

7.7 Conclusions

Alloy 316/316H/316L have good oxidation resistance in intermittent service up to 1600°F (871°C) and in continuous service to 1700°F (927°C). Continuous use of Alloy 316 in the 850°F (454.4°C) to 1550°F (843.3°C) temperature range is not recommended due to possibility of carbide precipitation but performs well in temperatures fluctuating above and below this range. Alloy 316H (UNS S31609) is a high carbon modification of Alloy 316 developed for use in elevated temperature service. The alloy has higher strength at elevated temperatures and is used for structural and pressure vessel applications at temperatures above 932°F (500°C). However, the higher carbon content of 316H also delivers higher tensile and yield strength than 316/316L and its austenitic structure provides excellent toughness down to cryogenic temperatures. Operating temp for MARVEL is 532°C, and operational conditions are such that that stainless steel will not have significant corrosion during its operation lifetime. The corrosion resistance of Alloy 316H is comparable to Alloy 316/316L and is superior to Alloy 304/304L in moderately corrosive environments. It is often used in process streams containing chlorides or halides. The alloy resists atmospheric corrosion, as well as moderately oxidizing and reducing environments. It also resists corrosion in polluted marine conditions.

Alloy 316H is non-magnetic in annealed condition. It cannot be hardened by heat treatment; however, the material will harden due to cold working. It can be easily welded and processed by standard shop fabrication practices.

Each metal in a molten stage is active. At the targeted operation temperature, sub-500°C, so long as oxygen content is properly controlled within the lead melt (1E-6wt% to 1E-

4wt%) corrosion of structural materials, 316HSS and 304SS is minimized to a conservative rate of 0.025 inches per year (0.635 mm per year) using LBE corrosion data [5]. Though corrosion rates can be minimized with oxygen control, surveillance and periodic maintenance will be required. Surveillance should be conducted to ensure that oxygen content within the lead is within the required range, and testing should be conducted to monitor rate of corrosion to ensure it falls within design parameters. Maintenance at a minimum will require lead oxide slag removal and cleaning of surfaces, particularly of the Stirling engine tubes to ensure adequate performance is achieved. Though lead is no longer being used as the secondary coolant for MARVEL, the requirements and recommendations generated are still valid for systems under similar operating conditions.

Fuel Cladding, 304SS submerged in NaK will not be subject to significant corrosion or erosion. Literature indicates that 300 series stainless steels have near unlimited lifetime in NaK, so long as temperature is below 1000°F (537.78°C) and oxygen is restricted to 10-25ppm. Minor risk to the stability of the 304SS cladding exists due to thermal cycling of the fuel element. This cycling will result in the diffusion of hydrogen gas. The quantity is not anticipated to be significant, however, its presence may result in a localized decrease in oxygen around the fuel elements potentially causing localized corrosion, namely pitting. It is recommended that periodic sampling of the NaK be performed to ensure that oxygen content is within appropriate ranges, and corrosion products are not detected.

Haynes, which composes the Stirling engine tube and dome will be exposed to the molten lead environment. Due to the high nickel content of Haynes, these components will likely experience rapid corrosion. Thus, these Haynes components shall be replaced with 304 series stainless steel to ensure that the Stirling engines will be able to survive the molten metal environment for the six-month operating life of the Stirling engine.

Beryllium metal, which acts as the internal neutron reflectors has been shown to be resistant to corrosion in molten sodium environments. Beryllium has been shown to form insoluble beryllium oxides that do not form a stable surface layer, thus no corrosion protection. This indicates the need for oxygen control within the NaK system to minimize oxide formation which could impact the function of moving components.

Fuel pins contain two materials of note that may be exposed to NaK in the event of a fuel cladding failure. When exposed to oxygen, zirconium hydride will form an adherent insoluble oxide which results in its corrosion depending on oxygen diffusion through the metal. Due to the low oxygen content of the NaK in the event of fuel cladding failure, corrosion of zirconium hydride is expected to be minimal. Graphite within the fuel pin offers poor corrosion resistance to sodium. This results in sodium being adsorbed by the

graphite. This effect is exacerbated by the addition of potassium and neutron flux. Thus, the swelling caused by NaK exposure is expected to be significant. However, due to the limited effect of corrosion on the 304SS fuel rod cladding, it is unlikely that either of these materials will be exposed to NaK during MARVEL's operational life.

Lead and NaK may interact during operation if there is a failure in the primary coolant boundary. Previous successful usage of NaK as a coupling fluid in pressure transmitters for service in molten lead bismuth systems has shown there are no adverse reactions between lead and NaK. Lead's greater density than NaK will result in displacement of NaK and coalescence of lead at the lowest point of the primary coolant vessel. This coalescence may inhibit flow characteristics and inhibit heat transfer around the core where the lead may collect.

8.0 REFERENCES

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9.0 APPENDIX

Appendix A: MARVEL Reactor Welding Comments 09/15/22

Appendix B: MARVEL Reactor - Weldability Comments 09/18/2023

Appendix A

MARVEL Reactor Welding Comments 09/15/22

Tate Patterson
15 Sept. 2022

Material: 316H
ASME Sec. IX, P-No. 8, Group No. 1

Table 1. Chemical composition of 316H plate according to ASTM A-240 (plate/sheet).

	Fe	Cr	Ni	Mo	Si	Mn	C	N	Cu	S	P
Nom.	Bal.	17.0	12.0	2.5	0.75	2.00	0.07	-	-	0.030	0.045
Min.	Bal.	16.0	10.0	2.00	-	-	0.04	-	-	-	-
Max.	Bal.	18.0	14.0	3.00	0.75	2.00	0.10	-	-	0.030	0.045

Table 2. Chemical composition of ER 16-8-2 from AWS A5.9 for GTAW.

	Fe	Cr	Ni	Mo	Si	C	N	Cu	S	P
Nom.	Bal.	15.5	8.0	1.5	0.48	0.10	-	0.75	0.03	0.03
Min.	Bal.	14.5	7.5	1.0	0.30	-	-	-	-	-
Max.	Bal.	16.5	9.5	2.0	0.65	-	-	0.75	0.03	0.03

ASME BPVC Sec. III Div. 5

Table HBB-I-14.1(a)
Permissible Base Materials for Structures Other Than Bolting

Base Material	Spec. No.	Product Form	Types, Grades, or Classes
Types 304 SS and 316 SS [Note (1)], [Note (2)], [Note (3)]	SA-182	Fittings & Forgings	F 304, F 304H, F 316, F 316H
	SA-213	Smls. Tube	TP 304, TP 304H, TP 316, TP 316H
	SA-240	Plate	304, 316, 304H, 316H
	SA-249	Welded Tube	TP 304, TP 304H, TP 316, TP 316H
	SA-312	Welded & Smls. Pipe	TP 304, TP 304H, TP 316, TP 316H
	SA-358	Welded Pipe	304, 316, 304H, 316H
	SA-376	Smls. Pipe	TP 304, TP 304H, TP 316, TP 316H
	SA-403	Fittings	WP 304, WP 304H, WP 316, WP 316H, WP 304W, WP 304HW, WP 316W, WP 316HW
	SA-479	Bar	304, 304H, 316, 316H
	SA-965	Forgings	F 304, F 304H, F 316, F 316H
	SA-430	Forged & Bored Pipe	FP 304, FP 304H, FP 316, FP 316H

- (1) These materials shall have a minimum specified room temperature yield strength of 30,000 psi (207 MPa) and a minimum specified carbon content of 0.04%.
- (2) For use at temperatures above 1,000°F (540°C), these materials may be used only if the material is heat treated by heating to a minimum temperature of 1,900°F (1,040°C) and quenching in water or rapidly cooling by other means.
- (3) Nonmandatory Appendix HBB-U provides nonmandatory guidelines on additional specification restrictions to improve performance in certain service applications.

Weldability Analysis

To prevent solidification cracking in austenitic stainless steels, it is crucial to form ferrite during solidification that is usually retained in the weld metal. Although ideal for welding, ferrite is deleterious for high temperature strength and can lead to precipitation of embrittling phases. The equations of the chromium-to-nickel equivalencies according to the WRC-1992 diagram are shown on the axes in Figure 1. The calculations for the 316H and ER 16-8-2 filler metal is shown in the following equations:

$$\begin{aligned} 316H: Cr_{eq} &= 17.0 + 2.5 = 19.5 \\ 316H: Ni_{eq} &= 12.0 + 35 * 0.07 = 14.5 \end{aligned}$$

$$\begin{aligned} ER1682: Cr_{eq} &= 15.5 + 1.5 = 17.0 \\ ER1682: Ni_{eq} &= 8.0 + 35 * 0.10 + 0.25 * 0.75 = 11.7 \end{aligned}$$

Ideally, these values should be calculated using the material test records (MTRs) or other measured values for the material being welded. This is important because elements such as nitrogen will be present, which is a potent austenite stabilizer.

Figure 1 shows where 316H and ER 16-8-2 filler metal will fall relative to an arc welding process, such as gas tungsten arc welding (GTAW). GTAW will be a relatively high dilution process and shift the ferrite number (FN) towards the base material composition. Given the nominal compositions, a FN of ≈ 1 is highly likely to result in solidification cracking. Solidification cracking will be further manifested with high restraint geometries or thick-section welds requiring multi-pass welding. From a welding perspective, 316L would always be the material of choice to avoid solidification cracking through a decreased nickel equivalence and minimizing carbide formation in the heat affected zone (HAZ).

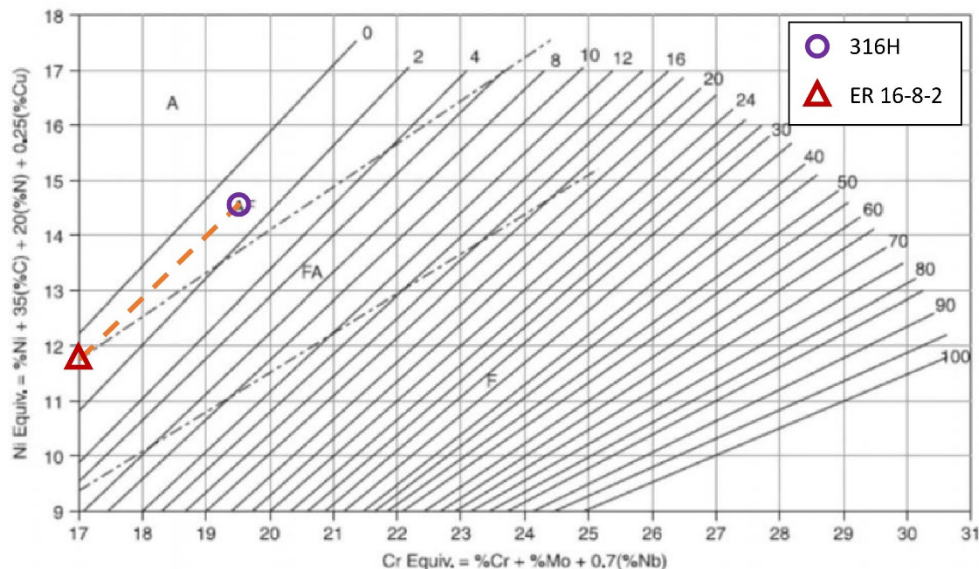


Figure 1. WRC 1992 diagram with 316H and ER 16-8-2 compositions connected via a tie line. [1]

Chemical Compatibility of Marvel Components

The constitution diagram only elaborates on the fusion zone susceptibility to solidification cracking and does not indicate the reactions occurring in the HAZ. If solidification cracking is avoidable and the welds can qualify according to ASME BVPC Sec. IX specifications, the greatest concern is sensitization in the HAZ. Sensitization is a result of the heat from welding creating chromium carbides near the fusion boundary. These carbides will reduce the corrosion properties of the 316H. If corrosion is not a concern due to the NaK eutectic and assuming the welds will not be exposed to the environment, corrosion is less of a concern.

However, the additional issue with carbide precipitation is reheat cracking or relaxation cracking at elevated temperatures. This is particularly a problem in components that cannot be given a post weld heat treatment (PWHT). This has been studied and documented in literature, specifically for 316H [2]. Heat treatment to correct HAZ carbide precipitation will have to be performed close to 1000°C to achieve dissolution of the $M_{23}C_6$ carbides. The M designates metal and may include chromium, molybdenum, etc. Two different time-temperature-transformation (TTT) diagrams are shown in Figure 2. The issue with performing a PWHT is that the entire weld component will need to undergo this heat treatment. If only the weld region is heat treated, a new heat affected zone will be created by the heat treatment, which will have the same carbide precipitation issues.

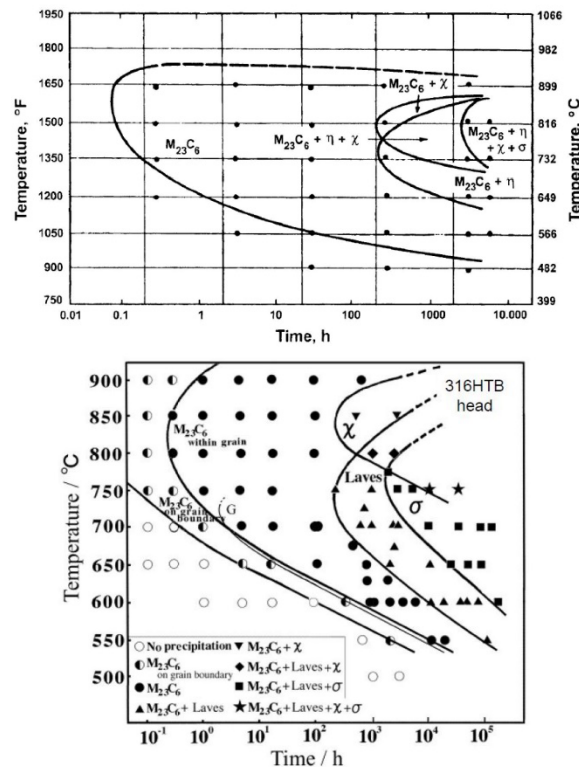


Figure 2. Time-temperature-transformation diagram for 316 stainless steel (top) [3] and 316H stainless steel (bottom) [4].

The other weldability concern is related to the thermal fatigue. Data is not readily available on thermal fatigue for 316H weldments. A literature search is still underway to find information regarding thermal cycling of 316H. The temperatures are within the carbide precipitation regime and heating and cooling will induce stresses that may exacerbate precipitation kinetics. The precipitation and stresses may result in localization of stresses along the grain boundaries, which may manifest into a reheat cracking phenomenon and result in intergranular cracking and premature failure.

Final Welding Comments

It is important that the welds are designed to be in areas that will see minimal stress and are not in highly constrained areas to reduce residual stresses during fabrication. The short lifetime (≈ 2 years) is a benefit to this reactor but attempting to increase the lifetime will only exacerbate the precipitation issues discussed. Personally, I would be reluctant to put any thermally cycled 316H weld into service without the data to support its behavior.

Machining Issues

I wrote in my notes that temperatures may be as high as 540-620°C. Is this correct?

If so, ASME BPVC Sec. III Div. 5 requires 316H to be heated to 1040°C and quenched. If the components are quenched, I expect there to be a large amount of internal stress that will result in deformation during machining. The more material removed, the greater the distortion that may occur.

How much distortion will occur, I have no idea and cannot say. I am not sure if this will be predictable, especially if components are sourced from numerous suppliers.

References

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Appendix B

MARVEL Reactor - Weldability Comments 09/18/2023

Tate Patterson
Welding Engineer
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18 Sept. 2023

1. Introduction

The MARVEL microreactor design was chosen to utilize Type 316 stainless steel within the high temperature regime of the reactor. This includes the primary heat exchanger that will transport a liquid metal eutectic mixture. The decision to use 316H stainless steel (SS) is based on its Section III, Division 5 qualification for high temperature reactors. Type 316H stainless steel has enhanced high temperature strength, creep performance, and corrosion resistance compared to the other possible alloy selections. However, 316H SS has a higher carbon content than 316 or 316L, where the H and L indicate high and low carbon, respectively. This higher carbon concentration exacerbates weldability issues, which include solidification cracking and a phenomenon known as sensitization that reduces the corrosion resistance of 316H SS. Examples of reduced corrosion adjacent to welds on austenitic SS alloys exposed solely to atmospheric conditions are shown in Figure 1. This reduction in corrosion resistance is a result of the heat input during welding creating chromium carbonitrides ($\text{Cr}(\text{C},\text{N})$). When Cr becomes bonded with the carbon or nitrogen in the steel, it can no longer form a passive chromium oxide (Cr_2O_3) layer on the surface. Therefore, the corrosion resistance of the material is reduced. Specifically, these carbides form along the grain boundaries, and result in a local depletion that is susceptible to attack. This has been an issue that has plagued the use of higher carbon (>0.04 wt%) austenitic SS for decades. However, the high carbon in austenitic stainless steels is optimal for maintaining high temperature creep strength. This is only when the material maintains a uniform distribution of carbides that impede dislocation motion.



Figure 1. Examples of sensitization occurring in the heat affected zone in stainless steel components. Dark regions adjacent to the welds are areas of accelerated corrosion due to carbide precipitation during welding.

1/8

Chemical Compatibility of Marvel Components

The construction codes for nuclear reactors will include the American Society of Mechanical Engineers (ASME) Boiler and Pressure Vessel Code (BPVC) Section III Rules for Construction of Nuclear Facility Components. For high temperature reactors, where mechanical and thermal stresses are induced due to cyclic operation and high temperature creep, ASME BPVC Section III, Division 5: "High Temperature Reactors" [1] dictates the design rules. However, Section III, Division 5 does not cover other material factors, such as corrosion, erosion, and radiation induced effects. Sec. III, Div. 5 is only applicable to core support structures and pressure-retaining components. Additionally, Sec III, Div. 5 is split into two major sections, which include Subpart A and Subpart B. Subpart A contains the rules for low temperature service, and Subpart B contains the rules for high temperature service. For welding qualification, procedures must be developed and pass criteria according to ASME BPVC Section IX: "Qualification Standard for Welding, Brazing, and Fusing Procedures; Welders; Brazers; and Welding, Brazing, and Fusing Operators" [2]. Section IX also does not define welding criteria, material compatibility, etc. It only mandates the requirements to qualify weld parameters, welders, and welding operators, but all mandates within Section IX can be superseded by the construction codes (i.e., Sec. III, Div. 5).

Therefore, the specific codes for construction of the internal components within the MARVEL microreactor will not mandate or define the specific requirements regarding corrosion and/or thermally induced fatigue conditions that may be imposed through reactor operation. Proper engineering judgement must be made to ensure sound operation of the MARVEL reactor, and this document attempts to elucidate on the issues that result from welded 316H SS joints. The main issue that will be considered is sensitization and corrosion performance regarding welds, but other potential issues such as solidification cracking, reheat cracking, and thermal fatigue are mentioned. Also, this document does not address liquid metal embrittlement (LME) of austenitic SSs via liquid metals.

2. Type 316 Stainless Steel

The materials permitted for use in low temperature applications with their associated maximum operating temperatures are shown in Figure 2. All operating temperatures above the values shown in Figure 2 are within high temperature service Sec. III, Div. 5, Subpart B [1]. Within Subpart B, metallic alloys can fall under Class A Metallic Pressure Boundary Components, Class B Metallic Pressure Boundary Components, or Class SM Metallic Core Support Structures. "Elevated temperature service" is defined as any component(s) or core support structure(s) experiencing temperatures above those listed in Figure 2, whether it is via normal operation or emergency/fault conditions.

Table HAA-1130-1 Values of T_{max} for Various Classes of Permitted Materials	
Materials	T_{max} , °F (°C)
Carbon steel	700 (370)
Low alloy steel	700 (370)
Martensitic stainless steel	700 (370)
Austenitic stainless steel	800 (425)
Nickel-chromium-iron	800 (425)
Nickel-copper	800 (425)

Figure 2. Table extracted from Sec. III, Div. 5 for low temperature service considerations.

Chemical Compatibility of Marvel Components

Type 316 SS is an austenitic stainless steel permitted for use in welded structures. Division 5 [1] does not distinguish a difference between carbon contents in 316 SS, but it mandates that the carbon concentration must be greater than 0.04 wt% as shown in Figure 3. Thus, a 316L or 316H stainless steel is not defined within Sec. III, Div. 5 [1]. However, 316L has maximum carbon concentration defined within ASME BPVC Section II: "Ferrous Material Specifications (Beginning to SA-450)" [3] of 0.030 wt%. Therefore, the 316 SS can only be a 316 SS or a 316H SS. The only difference being the maximum allowable carbon concentration. Type 316 SS has a maximum carbon concentration of 0.08 wt%, and Type 316H is allowed a carbon concentration ranging between 0.04 and 0.10 wt%. Type 316 (UNS 31600) can either fall within a 316L (UNS 31603) or a 316H SS (UNS 31609) designation. The chemical compositions for 316 SS and 316H SS are shown in Table 1.

Table HBB-I-14.1(a) Permissible Base Materials for Structures Other Than Bolting			
Base Material	Spec. No.	Product Form	Types, Grades, or Classes
Types 304 SS and 316 SS [Note (1)], [Note (2)], [Note (3)]	SA-182	Fittings & Forgings	F 304, F 304H, F 316, F 316H
	SA-213	Smls. Tube	TP 304, TP 304H, TP 316, TP 316H
	SA-240	Plate	304, 316, 304H, 316H
	SA-249	Welded Tube	TP 304, TP 304H, TP 316, TP 316H
	SA-312	Welded & Smls. Pipe	TP 304, TP 304H, TP 316, TP 316H
	SA-358	Welded Pipe	304, 316, 304H, 316H
	SA-376	Smls. Pipe	TP 304, TP 304H, TP 316, TP 316H
	SA-403	Fittings	WP 304, WP 304H, WP 316, WP 316H, WP 304W, WP 304HW, WP 316W, WP 316HW
	SA-479	Bar	304, 304H, 316, 316H
	SA-965	Forgings	F 304, F 304H, F 316, F 316H
	SA-430	Forged & Bored Pipe	FP 304, FP 304H, FP 316, FP 316H
	(1) These materials shall have a minimum specified room temperature yield strength of 30,000 psi (207 MPa) and a minimum specified carbon content of 0.04%.		
	(2) For use at temperatures above 1,000°F (540°C), these materials may be used only if the material is heat treated by heating to a minimum temperature of 1,900°F (1,040°C) and quenching in water or rapidly cooling by other means.		
	(3) Nonmandatory Appendix HBB-U provides nonmandatory guidelines on additional specification restrictions to improve performance in certain service applications.		

Figure 3. Excerpt from Division 5 showing weldable alloys and additional requirements for 316 SS [1].

Table 1. Chemical composition of 316H plate according to Sec. II Part A [3]. Values represent maximums unless ranges are specified.

	Fe	C	Cr	Ni	Mo	Si	Mn	S	P
316	Bal.	0.08	16.0-18.0	11.0-14.0	2.00-3.00	0.75	2.00	0.030	0.045
316H	Bal.	0.04-0.10	16.0-18.0	11.0-14.0	2.00-3.00	0.75	2.00	0.030	0.045

Sec. II Part A also mandates a grain size of ASTM 7 or coarser and a minimum annealing temperature of 1040°C. This is reiterated in Sec. III, Div. 5 with the heat treatment requiring cooling by quenching in water or rapidly cooling by other means.

3. Type 316 SS Weldability

The following will outline the issues that must be considered when welding 316 stainless steels. This will include solidification cracking, thermal fatigue performance, sensitization, and reheat cracking. All of these issues are exacerbated with increasing carbon concentrations.

3.1. Solidification Cracking Susceptibility

Based on the current understanding, it is believed that filler metal ER16-8-2 was selected for welding. The following evaluation of cracking susceptibility and possible ferrite content in the weld metal will be evaluated based on this analysis. The chemical composition for ER16-8-2 is shown in Table 2. From a solidification cracking susceptibility perspective, it is desirable to have primary ferrite solidification in the weld metal. This is known to reduce cracking susceptibility compared to a primary austenite solidification mode. Residual stress and joint design will also worsen the susceptibility to solidification cracking. [4]–[7]

Table 2. Chemical composition of ER 16-8-2 from AWS A5.9 for GTAW [8].

	Fe	Cr	Ni	Mo	Si	C	N	Cu	S	P
Nom.	Bal.	15.5	8.0	1.5	0.48	0.10	-	0.75	0.03	0.03
Min.	Bal.	14.5	7.5	1.0	0.30	-	-	-	-	-
Max.	Bal.	16.5	9.5	2.0	0.65	-	-	0.75	0.03	0.03

Although ideal for mitigating weld solidification cracking, ferrite is deleterious for high temperature strength and can lead to precipitation of embrittling phases. The equations of the chromium-to-nickel equivalencies according to the WRC-1992 diagram are shown on the axes in Figure 4. The calculations for the 316H and ER16-8-2 filler metal is shown in the following equations:

$$\begin{aligned} 316H: Cr_{eq} &= 17.0 + 2.5 = 19.5 \\ 316H: Ni_{eq} &= 12.0 + 35 * 0.07 = 14.5 \end{aligned}$$

$$\begin{aligned} ER1682: Cr_{eq} &= 15.5 + 1.5 = 17.0 \\ ER1682: Ni_{eq} &= 8.0 + 35 * 0.10 + 0.25 * 0.75 = 11.7 \end{aligned}$$

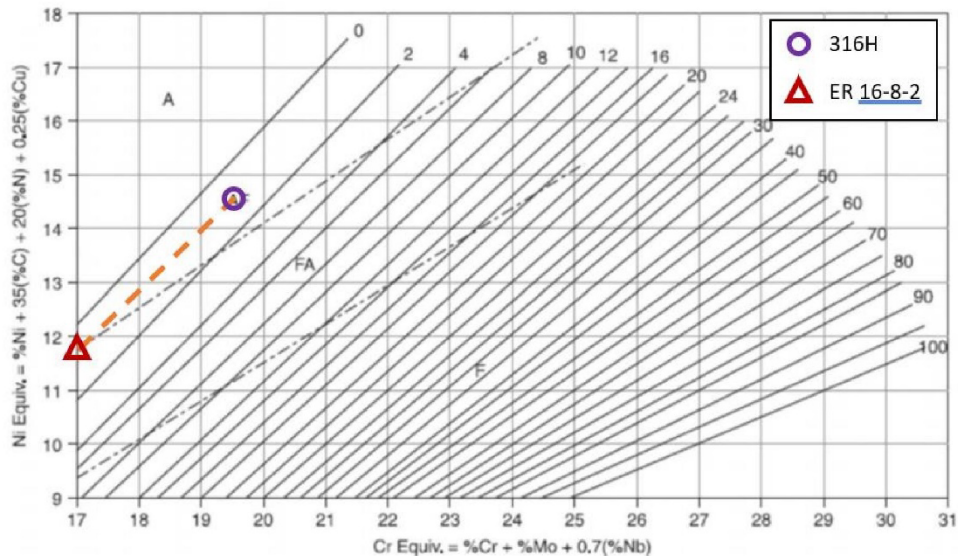


Figure 4. WRC 1992 diagram with 316H and ER 16-8-2 compositions connected via a tie line. [9]

The constitution diagram only approximates the fusion zone susceptibility to solidification cracking based on the ferrite number (FN) or ferrite percentage, as shown Figure 4. Generally, any austenitic alloy with a FN less than 5 is susceptible to solidification cracking. However, solidification cracking should be avoidable using gas tungsten arc welding (GTAW) with proper welding parameters, joint designs, and low stress. Therefore, 316 SS welds should be qualifiable according to ASME BVPC Sec. IX specifications. Additionally, the required nondestructive evaluation (NDE) should identify solidification cracks in the final component fabrication prior to service operation.

3.2. Thermal Fatigue

Another weldability concern is related to thermal fatigue. Data is not readily available on thermal fatigue for 316H weldments. The operation temperatures are within the carbide precipitation regime and heating and cooling will induce stresses that may exacerbate carbide precipitation kinetics. The combination of precipitation and stresses may result in localization of stress along the grain boundaries, which may manifest into premature failure. This will be exacerbated if sensitization cannot be eliminated in the weld heat affected zone (HAZ). The following list contains some of the historical failures of weldments in nuclear applications that were believed to be due to thermal fatigue [10].

- 1) French Phenix liquid-metal fast breeder reactor (LMFBR)
 - fatigue or creep-fatigue cracking due to repeated thermal transient loading
- 2) British Dounreay Fast Reactor (DFR)
 - fatigue cracking in a primary circuit pipe weld
- 3) Clinch River Breeder Reactor Plant
 - weld cracking in components subjected to repeated thermal transient loading

3.3. Sensitization

Sensitization is a phenomenon in austenitic SS that results when thermal conditions develop areas that allow for the formation of chromium carbides. Specifically, these chromium carbides form along the grain boundaries, and locally deplete the regions adjacent to the grain boundaries of Cr by bonding the Cr atoms to carbon/nitrogen within the material. Once in the form of a Cr(C,N), oxygen can no longer bond with the chromium to develop a passivating oxide layer that gives stainless steel its corrosion resistance. During the welding process, the high heat input caused by welding will result in sensitization in the HAZ. Examples of this are shown in Figure 1. The majority of the carbides that form are likely Cr_{23}C_6 carbides, generically referred to as M_{23}C_6 , where "M" stands for metal and can be other elements such as molybdenum. Heat treatments to correct HAZ carbide precipitation should be performed above 1000°C to achieve dissolution of the M_{23}C_6 carbides. According to Sec. III, Div. 5 [1], the minimum heat treatment temperature must be 1040°C. A time-temperature-transformation (TTT) diagram that shows the stability range of M_{23}C_6 and other detrimental phases is shown in Figure 2. The red, dashed line overlaid on the TTT diagram represents the approximate cooling time needed to prevent reprecipitation of carbides after forming a solid solution above 1000°C.

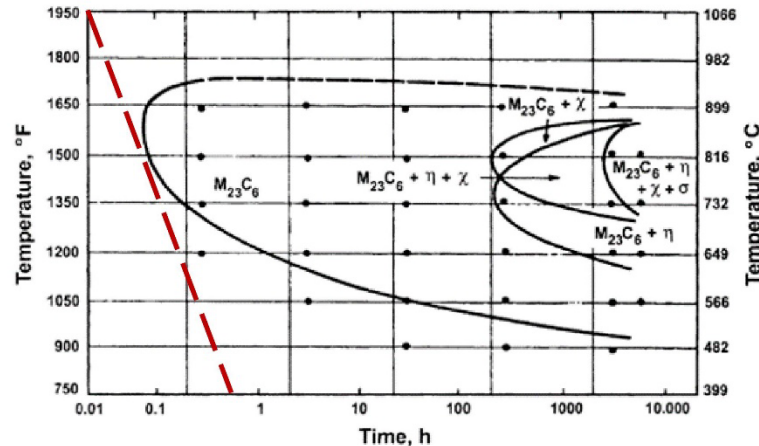


Figure 5. Time-temperature-transformation diagram for 316 stainless steel [11]. The dashed line approximates a maximum cooling time to mitigate reprecipitation of carbides.

3.4. Reheat Cracking

An additional issue with carbide precipitation is reheat cracking or relaxation cracking at elevated temperatures. This is particularly a problem with components that cannot be given PWHT. This has been studied and documented in literature, specifically for 316H [5]. Applying a PWHT is one of the main solutions to eliminate reheat cracking.

4. Post Weld Heat Treatment

Sec. III, Div. 5 [1] mandates that all pressure vessels and pressure vessel parts shall be given a post weld heat treatment as defined in Division 1, NB-4620 and shown in Figure 5. However, Sec. III, Div. 1 – Subsection NB Class 1 Components” [12] does not require nor prohibit a post weld heat treatment for P-Number 8 materials, and 316 SS is categorized as a P-Number 8, Group 1 material in Section IX [2]. Therefore, according to Sec. III Div. 5 [1], 316 SS does not require a PWHT, but it is strongly advised that a PWHT be performed on any weld that is within a critical area of the reactor.

HBB-3357 Thermal Treatment

All pressure vessels and pressure vessel parts shall be given the appropriate postweld heat treatment prescribed in Division 1, NB-4620.

Figure 6. Excerpt from Sec. III, Div. 5 stating PWHT requirements for pressure vessels. [1]

5. Final Welding and PWHT Comments

It is always best to perform a PWHT on welded 316H stainless steel to mitigate sensitization, reheat cracking, or thermal fatigue issues regarding the weldment. Under the same stresses as the base

material, failure will likely be associated with the welded joint if the conditions of the material are not restored to the original properties. The only way the HAZ can be restored to the base metal properties is to perform a solutionizing PWHT followed by quenching. All inspection procedures should be performed according to the applicable ASME, American Welding Society, and American Society for Nondestructive Testing codes and standards. It is advised to heat treat to at least 1060°C to exceed the minimum temperature, hold for a time long enough for all components to reach and soak above at temperature above 1040°C, and quench via water from 1060°C within six minutes of removing the weldments from the furnace.

Note that LME was not considered in this document. It is a crucial aspect of the internal heat exchanger, and any weld subjected to liquid metal will likely be the highest location of attack in relation to the base material. A thorough understanding of the liquid eutectics and their interaction with 316 SS is crucial prior to operation.

6. References

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Appendix A

Table HBB-I-14.10B-2 Stress Rupture Factors for Type 316 Stainless Steel Welded With SFA-5.22 EXXXT-G (16-8-2 Chemistry); SFA-5.4 E 16-8-2; and SFA-5.9 ER 16-8-2										
U.S. Customary Units										
Temp., °F	10 hr	30 hr	100 hr	300 hr	1,000 hr	3,000 hr	10,000 hr	30,000 hr	100,000 hr	300,000 hr
850	1.00	0.96	0.91	0.91	0.91	0.90	0.89	0.88	0.87	0.86
900	1.00	0.94	0.88	0.82	0.81	0.80	0.77	0.76	0.74	0.72
950	1.00	0.93	0.86	0.86	0.85	0.83	0.83	0.81	0.79	0.78
1,000	1.00	0.93	0.90	0.90	0.90	0.89	0.87	0.87	0.85	0.85
1,050	0.92	0.92	0.92	0.92	0.92	0.92	0.92	0.93	0.90	0.86
1,100	0.91	0.91	0.93	0.94	0.94	0.96	0.96	0.96	0.97	0.96
1,150	0.91	0.91	0.93	0.95	0.95	0.96	0.98	0.99	0.99	1.00
1,200	0.89	0.89	0.90	0.92	0.93	0.97	0.99	1.00	1.00	1.00
SI Units										
Temp., °C	10 h	30 h	100 h	300 h	1 000 h	3 000 h	10 000 h	30 000 h	100 000 h	300 000 h
450	1.00	0.97	0.92	0.92	0.92	0.91	0.91	0.90	0.89	0.88
475	1.00	0.95	0.89	0.84	0.84	0.83	0.80	0.79	0.77	0.76
500	1.00	0.93	0.87	0.85	0.84	0.82	0.81	0.79	0.77	0.76
525	1.00	0.93	0.88	0.88	0.88	0.86	0.85	0.84	0.83	0.82
550	0.97	0.93	0.91	0.91	0.91	0.90	0.89	0.90	0.87	0.85
575	0.92	0.92	0.92	0.93	0.93	0.93	0.93	0.94	0.92	0.89
600	0.91	0.91	0.93	0.94	0.94	0.96	0.96	0.97	0.97	0.97
625	0.91	0.91	0.93	0.95	0.95	0.96	0.98	0.99	0.99	1.00
650	0.89	0.89	0.90	0.92	0.93	0.97	0.99	1.00	1.00	1.00

Figure 7. Section III, Division 5 table showing the stress reduction factors (SRFs) for 316 SS welded with ER16-8-2 filler metal.