Initial assessment of metallurgical interaction of clad/base metal systems

Applied Materials Division

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September 2018

Abstract

Molten Salt Reactors (MSRs), both liquid fuel and solid fuel (e.g., the fluoride salt-cooled high temperature reactors, FHR's) offer several advantages relative to conventional, water-cooled nuclear power systems. However, currently approved ASME structural materials have not been optimized for use in molten salt environments and demonstrating materials performance in molten salts is challenging. Toward the goal of enabling MSR designs, corrosion resistant claddings offer an attractive solution to help mitigate corrosion concerns and enable the use of approved ASME materials. This report assesses metals and alloys that may be effective as corrosion resistant cladding with select structural alloys. The structural alloys of interest are capable of use at high temperatures $\geq 600^{\circ}\text{C}$ for times $\geq 100,000$ hours. Potential cladding alloys were assessed based on their corrosion resistance in both chloride and fluoride based salts, physical properties, mechanical properties, nuclear performance, and resistance to environmental-assisted cracking. Additionally both thermodynamic and kinetic computational modeling were used to assess interactions between the base metal and the cladding. Results to date have identified three candidate alloy systems that help enable MSR designs; nickel, molybdenum, and tungsten based claddings. This report discusses pros and cons of each class of cladding and outlines future work to develop these base metal / clad systems into industrial products suitable for use in commercial nuclear power systems.

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1. Introduction

The Generation IV molten salt reactor concepts, both based on liquid fuel (MSR's, Figure 1-1) or solid fuel (fluoride salt-cooled high temperature reactors, FHR, Figure 1-2), have several desirable attributes and intrinsic safety advantages relative to conventional light water reactors. For example, MSR and FHR designed to operate at relatively low pressure can tolerate high temperatures due to the high boiling point of the molten salts, and many designs display a negative temperature coefficient of reactivity. Furthermore, FHR's typically use high temperature capable fuel (e.g. TRISO fuel particles) and MSR's can be passively shutdown via melting of 'freeze plugs'. A comparison of some key features between light water reactors, MSR's, and FHR's is shown in Table 1-1, which highlights their low operating pressure and higher temperature of operation relative to water cooled reactors as well as the wide range of expected irradiation of core internals from ~1 dpa in some FHR concepts where graphite provides significant shielding to ~200 dpa in liquid fueled designs [1-6].

Despite these advantages, the higher temperature of operation and potentially aggressive environment of molten salt present significant challenges to structural materials that are currently code qualified for high temperature nuclear use. For example, ASME Boiler and Pressure Vessel Code, Section III Division 5 construction materials that are appropriate for molten salt structural applications (i.e. temperatures $\geq 600^{\circ}\text{C}$) are limited. Candidate alloys include 304H, 316H, 800H, Alloy 617 (currently being balloted by ASME code committees) and Alloy 709 (currently being tested by the U.S. Department of Energy to support ASME code qualification) [7]. Notably, most of these alloys were targeted for use in liquid metals and high temperature gas reactor systems and have not been widely assessed for performance in molten salt reactors [8].

Toward the goal of enabling MSR and FHR designs, corrosion resistant claddings offer an attractive solution to mitigate corrosion concerns and enable the use of Code qualified ASME Division 5 materials. This report assesses metals and alloys that may be effective as corrosion resistant cladding with select structural alloys. The structural alloys of interest are those capable of use at high temperatures $\geq 600^{\circ}\text{C}$ for times $\geq 100,000$ hours. Potential cladding alloys were assessed based on their corrosion resistance in both chloride and fluoride based salts, physical properties, mechanical properties, nuclear performance, and resistance to environmentally assisted cracking. Additionally both thermodynamic and kinetic computational modeling were used to assess potential interactions between the base metal and the cladding.

Figure 1-1. Schematic illustration of a liquid fueled molten salt reactor system from Reference [9].

Figure 1-2. Schematic illustration of a fluoride salt-cooled high temperature reactor system from Reference [5].

Table 1-1. Comparison of Potential FHR and MSR Operating Conditions with Conventional LWRs [1-6]

Concept	Fuel	Pressure (MPa)	Coolant Outlet Temp. (°C)	Coolants		Estimated Max. Dose (dpa)	Estimated Lifetime (years)
				Primary	Secondary		
FHR	Solid	0.1	700	FLiBe	e.g. NaNO ₃ -KNO ₃	1	40+
MSR	Liquid	0.1	700	U-Zr-FLiBe	e.g. BeF ₂ , NaF	200	40+
	Liquid	0.1	700	U-Cl	e.g. KCl-MgCl ₂	200	40+
PWR	Solid	16	320	Water	Water	100	60+
BWR	Solid	8	288	Water	Water	10	60+

2. Results and Discussion

Candidate metals and alloys that could be used for corrosion resistance in molten fluoride and chloride salts were first assessed based on their electrochemical potential in the salt of interest. Those metals and alloys with high (i.e. noble) corrosion potentials provide benefit to general corrosion to the structural alloy of interest based on their low thermodynamic driving force to undergo anodic dissolution. Based on their high nobility, candidate alloy systems were identified and selected alloys were further assessed based on their physical properties, mechanical properties, nuclear performance, and resistance to environmentally assisted cracking. Additionally both thermodynamic and kinetic computational modeling were used to assess potential interactions between the base metal and the cladding. The following report summarizes that down selection, compares the properties, and discusses likely benefits and challenges of using the candidate cladding materials.

2.1. Corrosion in Molten Salts

Corrosion of metals in molten salts is an electrochemical process whereby the metal is oxidized and another species is reduced. For example, consider equation 2.1, which illustrates how chromium can corrode while a metallic impurity in the salt (in this case iron) is reduced.

Recently, Shaoqiang Guo and Jinsuo Zhang have reviewed corrosion phenomena in both molten fluoride and chloride salts and have calculated redox potentials for several metals [1]. A comparison of the redox potentials for fluoride and chloride salts, calculated by Guo and Zhang, is shown in Figure 2-1 [10]. In Figure 2-1, the solid lines correspond to the stability of M^{n+} where the metal dissolves and equilibrates with a M^{n+} activity of 10^{-6} , while dashed lines give the redox potential for the oxidants in the salts. At potentials below the solid line, the metal is thermodynamically stable and will not corrode, thus cladding with a high redox potential (i.e. the most noble metals) offer a wide range of thermodynamic stability to corrosion.

As shown for fluoride and chloride salts, the major structural alloy elements (iron, nickel, and chromium), chromium has the lowest redox potential (see red ovals) and is the least resistant to corrosion. Both experiments and calculations show that chromium exhibits higher corrosion rates than iron or nickel [10, 11] and preferential chromium loss from both stainless steels and nickel based alloys has been observed [11-14]. Thus, preventing chromium loss is the primary corrosion concern.

Figure 2-1. Comparison of calculated redox potentials in fluoride (left) and chloride (right) molten salt [10]. The potential of chromium is highlighted in red and metals more noble to chromium are shaded green.

Based on these thermodynamic arguments, cladding with a metal or alloy that is noble to chromium provides a wide range of thermodynamic stability. One caveat to this strategy is that care must be taken to avoid the scenario of a large cathode / small anode which could drive preferential corrosion of the anodic reaction (i.e. chromium loss). Given that concern, then potential cladding elements more noble to chromium are highlighted in green in Figure 2-1, giving the following potential candidates:

Fluoride Salts: Mo, W, Ni, Fe, Nb, Co, and Ta

Chloride Salts: Mo, W, Ni, Ta, and Co

2.2. Cladding selection

Starting with the list of noble elements generated above in Section 2.1 [10] and integrating literature studies on corrosion in molten salts [12, 13, 15-27] some general comments can be made based on the periodic table. Figure 2-2 shows a portion of the transition metals that are potential cladding candidates. As noted in Figure 2-2, chromium is the primary element of concern with the fastest corrosion rates in Fe-Cr and Ni-Cr alloys.

The reactive metals (Ti, Zr, Hf, V, Nb, and Ta) are not especially noble and have high solubility for interstitial elements and common salt impurities (e.g. hydrogen (tritium) and carbon in graphite moderated designs). Based on these facts, the reactive metals are likely unsuitable for corrosion resistant cladding. Experimentally, Olson et al. have investigated the corrosion of the Nb-Zr alloy in molten FLiNaK salt at 850°C in graphite crucibles. The Nb-Zr showed extensive corrosion attack and carburization [20]. Furthermore, Laurenty notes that despite tantalum being noble to chromium in fluoride salt, the corrosion product TaF₅ has high solubility in the salt such that solubility driven mass loss can be appreciable [28].

As shown in Figure 2-1, the refractory metals molybdenum and tungsten are very noble in both fluoride and chloride salts. However, these metals and their alloys are body centered cubic with limited solubility in common face centered cubic structural metals. Furthermore, these alloys have modest ductility and low toughness at low homologous temperatures. Alloying additions of rhenium can increase the ductility of both molybdenum and tungsten but the benefits are modest [29] and large additions of rhenium can degrade irradiation resistance as discussed later in this report [30, 31]. Thus while desirable for corrosion, fabricating structures with molybdenum or tungsten cladding and ensuring their long term performance will be challenging.

The Group 8 metals (Fe, Co, and Ni) are ductile, but only nickel provides significant corrosion benefit in both fluoride and chloride salts [10, 19]. Also, both cobalt and nickel can transmute with irradiation and become embrittled. Pure cobalt is hexagonal close packed with somewhat limited solubility for iron and chromium. Lastly, copper is relatively noble [27] and has demonstrated good corrosion resistance in fluoride salt (e.g. sample baskets made of OFHC copper were used in the molten salt reactor experiment (MSRE)). While OFHC copper was generally considered to have good corrosion performance in the MSRE [15, 25, 27], one sample basket (deformed during attempts to retrieve it and exposed to fuel salt for 13,025 hours) showed extensive intergranular cracking [25]. Furthermore, copper introduces a fabrication concerns, i.e. it is well known to cause liquation type cracking in several iron based alloys including austenitic stainless steels [32].

GENERAL METALLURGY

Tradeoffs with several potential metals

Figure 2-2. Summary of tradeoffs with several metals that could be used for corrosion resistant cladding

Based on the initial review above, three candidate alloy systems are recommended for further assessment as described below in Table 2-1: molybdenum, tungsten, and nickel based alloys based on their nobility in both fluoride and chloride salts. Furthermore, tungsten and its alloys can act as an appreciable barrier to tritium release to the environment, which may be another key benefit for some reactor concepts. The limited ductility of molybdenum and tungsten, their body centered cubic crystal structure and irradiation performance are likely challenges for those refractory alloys, while the irradiation performance (notably helium embrittlement) is a key concern for nickel or nickel-based alloys.

Table 2-1. Summary of Potential Metals Considered for Corrosion Resistant Cladding in Molten Salt Reactor Applications.

Element or Alloy Base	Comments	Conclusion
Mo	Noble in both F and Cl salts, BCC, limited ductility	Assess
W	Noble in both F and Cl salts, BCC, limited ductility. Also is a tritium permeation barrier	Assess
Ni	Noble in both F and Cl salts, FCC, ductile, transmutes to He with irradiation	Assess
Nb	Noble in F salts, BCC but ductile, reactive metal with high H and C solubility	X
Co	Marginal nobility in Cl salts may have benefit in F salts, transmutes with irradiation	X
Ta	Noble in F salts but TaF ₅ has high solubility, BCC but ductile, reactive metal with high H and C solubility	X
Cu	Corrosion resistant in F salt and noble in Cl salt but can cause weldability issues with austenitic stainless steels. When exposed to fuel salt, MSRE showed extensive IG cracking of OFHC Cu sample capsule [15, 25, 33]	X
Fe	Least noble in F salt, anodic to Cr/CrCl ₃	X
V	No benefit in terms of nobility, reactive metals with high H and C solubility. May have some potential in 'high entropy' alloys – needs further assessment	X

Given these three alloy systems, five candidate alloys are recommended for further assessment: (1) Mo-TZM, (2) commercially pure tungsten, (3) a dilute W-(3-5)Re alloy for added ductility and potentially improved nuclear performance, (4) Ni-201, and (5) Hastelloy N or a similar Ni-low chromium alloy. These recommendations are summarize below in Table 2-2

Table 2-2. Recommended Alloys to Assess as Corrosion Resistant Cladding for Molten Salt Reactor Applications.

Element or Alloy Base	Comments	Recommended Alloy
Mo	Mo-TZM is commercially available. For ductility benefit, large additions of Re are required (~50%) which likely results in nuclear penalty via $\text{Re}(n,\gamma) \rightarrow \text{Os}$	Mo-TZM
W	Commercially pure tungsten is commercially available. Recent research indicates that dilute W-(1-5)Re alloys [31]	W (CP)
		W-(3-5)Re
Ni	Ni-201 is commercially available and low carbon minimizes embrittlement with thermal aging. Low chromium (Hastelloy N) developed for MSRE with good experience [34]. Variants may have alloying to mitigate tellurium embrittlement [24].	Ni-201
		Hastelloy N or variant

2.3. Physical Properties

Table 2-3 compares and contrasts selected physical properties of the candidate cladding alloys and example structural alloys that either are approved (316H and 800H) or are undergoing approval (Alloy 617) for high temperature use by the ASME. Notably, the physical properties of molybdenum and tungsten based alloys are significantly different than the structural alloys that they could be used with. Specifically, they melt at much higher temperatures (complicating fusion welding), are of a different crystal structure (BCC vs. FCC) and have a much smaller coefficient of thermal expansion (which could result in significant thermally induced stress). Additionally, tungsten alloys have a larger thermal neutron cross section relative to nickel (4.5 Barns) or iron (2.6 Barns). Cladding with Ni-201 or a variant of Hastelloy N ensures similar physical properties to the FCC nickel or iron based structural alloys.

Table 2-3. Comparison of Physical Properties of Candidate Cladding Alloys and Structural Alloys [29, 34-38].

Alloy	Melting Range (°C)	Crystal Structure	Thermal Conductivity at 25°C (W/m-K)	CTE at 25°C (10 ⁻⁶ /K)	Thermal Neutron Cross Section (Barns)
Candidate Cladding					
Mo-TZM	2623	BCC	142	4.8	2.6
W (CP)	3422	BCC	160	4.5	18.4
W-(3-5)Re	3300-3350	BCC	70	4.5	21.8
Ni-201	1435-1446	FCC	79.3	13.2	4.5
Hast N	1300-1400	FCC	13.1	13.0	---
Example Structural Alloys					
316H	1375-1400	FCC	15.0	16.0	---
800H	1357-1385	FCC	10.6	14.2	---
Alloy 617	1332-1380	FCC	13.4	11.6	---

2.4. Mechanical Properties

The elastic modulus, ductile to brittle transition temperature (DBTT) and tensile properties of candidate cladding and structural alloys are given below in Table 2-4. As shown, the BCC refractory alloys are stiffer than the structural alloys with room temperature Young's moduli of 325 GPa (Mo-TZM), 411 GPa (W-CP), 400 GPa (W-(3-5)Re) versus (196-211 GPa) for the structural alloys. Additionally, it is important to note the ductile to brittle transition temperature for the Mo and W based cladding (determined via tensile testing, not impact testing for >20% reduction in area). As shown in the table, the DBTT for Mo-TZM is near room temperature but occurs ~300°C for the tungsten alloys. Additionally, the ultimate tensile strengths of Mo and W are high and the tensile ductility low relative to the structural alloys.

Table 2-4. Comparison of Mechanical Properties of Candidate Cladding Alloys and Structural Alloys [29, 34-38].

Alloy	Young's Modulus at 25°C (GPa)	DBTT, >20% RA (°C)	UTS (MPa) at 25°C	% Elongation at 25°C
Candidate Cladding				
Mo-TZM	325	~25	750	~10%
W (CP)	411	~300	~1200	<1%
W-(3-5)Re	400	<300	~1100	~1%
Ni-201	207	NA	345	>40%
Hast N	219	NA	800	40%
Example Structural Alloys				
316H	200	NA	515	40%
800H	196	NA	531	50%
Alloy 617	211	NA	734	60%

2.5. Performance under Irradiation

The performance under irradiation for candidate cladding alloys is a complex topic that likely depends on the specific reactor design and the component that they are used with. While a comprehensive treatment of these effects are beyond the scope of this report, Table 2-5 details selected topics that will be of interest, including void swelling, irradiation creep, and some transmutation reactions that will be of interest.

Table 2-5. Comparison of Selected Irradiation Behavior for Candidate Cladding Alloys.

Alloy	Void Swelling	Irradiation Creep	Transmutation	Comments
Mo-TZM	< 5% @ 10 dpa	Needs Investigation	$^{98}\text{Mo}(n,\gamma) \rightarrow \dots\ ^{99}\text{Tc}$ $^{100,101}\text{Mo}(n,\gamma) \rightarrow \dots\ ^{101}\text{Ru}$	Note appreciable abundance of several isotopes
W (CP)	<5% @ 10 dpa*		$^{184,186}\text{W}(n,\gamma) \rightarrow \text{Re} \ (\rightarrow \text{Os})$	(3-5)Re may suppress void swelling
W-(3-5)Re				
Ni-201	< 1 % @ 10 dpa 0.12%/dpa at 600°C		$^{58}\text{Ni}+n \rightarrow ^{59}\text{Ni}+\gamma$ $^{59}\text{Ni}+n \rightarrow ^{56}\text{Fe}+^4\text{He}$ $^{59}\text{Ni}+n \rightarrow ^{56}\text{Co}+H$	Embrittlement by fission product Te may be a concern
Hast N				Modified alloys are resistant to Te embrittlement

2.6. Metallurgical Compatibility

The metallurgical compatibility of the candidate cladding alloys and base metals is also a concern for nuclear applications. These interactions can be assessed via materials modelling as outlined in Figure 2-3. As shown, for a given base metal each of the five candidate cladding alloys can be assessed for their metallurgical compatibility via (1) Scheil solidification modelling, (2) phase stability, (3) interdiffusion kinetics and (4) solid state precipitation kinetics. The Scheil solidification modelling gives insight into the ability to fusion weld the clad onto the base metal and provides quantitative information on the solidification temperature range as well as the second phases that form during solidification. Phase stability can be explored via both experimental and computational phase diagrams. The thermodynamic phase stability is then further considered via diffusion and precipitation kinetics, which give insights into the temperature regimes and rate at which second phases form.

Figure 2-3. Illustration of the methodology used to assess the metallurgical compatibility of selected ASME base metals and candidate cladding alloys for corrosion resistance in molten salts.

The phase stability of the representative base materials (iron or nickel based) and cladding alloys (nickel, molybdenum, or tungsten based) is shown in Figure 2-4. In Figure 2-4, the approximate operating temperature range of FHR's and MSR's (~550°C-750°C) is highlighted in red. These phase diagrams illustrate what phase is stable in the pure base metal (i.e. at an X-axis value of 1) and the effect of increasing amount of cladding alloy (moving from the right hand axis toward the left). Consider the Fe-Ni diagram, this illustrates that BCC iron is stable at MSR operating temperatures in pure iron but with increasing nickel, the FCC phase forms with a few weight % of nickel and the FCC phase is completely stabilized at 750°C with ~5 wt.% nickel. The wide range of solubility of nickel for both iron and nickel based alloys is highlighted by the green arrows.

Conversely, molybdenum and tungsten have very limited solubility in iron in this temperature range with BCC and Laves phases forming (red arrows, top row). The solubility of molybdenum and tungsten is better in nickel-based alloys with significant stability of the FCC phase before delta (Ni-Mo) or BCC (Ni-W) phases form. The calculations illustrate that Mo and W may be more compatible with nickel based alloys than stainless steels due to their greater solubility in nickel relative to iron. Of course, these are simplified calculations that required further investigation with compositions closer to the structural and cladding alloys.

Figure 2-4. Comparison of binary phase diagrams for base metals (Fe and Ni) and candidate cladding (Ni, Mo, W) alloys. The red areas highlight FHR and MSR operating temperatures.

The next assessment of the phase stability utilizes more complex compositions. Figure 2-5 compares the solubility of nickel and molybdenum in a ternary alloy that represents 316 stainless steel (i.e. Fe-17wt.%Cr-2.3wt.%Mo-xx wt.%Ni). In Figure 2-5, the left hand axis represents the pure alloy with increasing amounts of nickel (left hand plot), molybdenum (right hand plot) and the red shaded regions highlight likely operating temperatures. As shown for 316 diluted with nickel, the alloy is face centered cubic with the sigma phase also being stable and as expected nickel widens the FCC phase field. In contrast, the right hand phase diagram illustrates the

complex effect of alloying with BCC molybdenum. As Mo dilution increases, the FCC phase field shrinks and the deleterious mu-phase is stabilized.

ALLOY / CLAD PHASE DIAGRAMS

Ni has best compatibility, limited solubility of Mo

316 + Ni

~ 316 → increasing nickel

316 + Mo

~ 316 → increasing molybdenum

Figure 2-5. Illustration of the effects of dilution with nickel (left) and molybdenum (right) on the phase stability of a Fe-Ni-Cr alloy near the 316 stainless steel composition.

Results from a different software package (JMatPro v.10) are summarized in Figure 2-6. The left hand plots are Scheil solidification simulations illustrating the difference in behavior between 316H and 316H diluted with 20% molybdenum. As shown, molybdenum acts to widen the solidification temperature range (given by the vertical black lines) and stabilizes Laves and carbide phases during solidification. Note that large solidification temperature ranges are often associated with increased risk of solidification-type cracking during fusion welding and Laves phases can degrade mechanical properties by scavenging alloying elements and acting as void nucleation sites.

Figure 2-6 shows more complex Scheil solidification (left) and phase stability (right) lots. These calculations account for nearly the complete base metal composition, building on the predictions of Figure 2-5 that only included iron, nickel, and chromium for 316H. Note the differences in phase stability that occur with 20% dilution with molybdenum. For example, with Mo dilution,

there is much greater stability of ferrite (pink squares), and the embrittling sigma phase (orange diamonds) Laves phase (green circles) chi phase (gray circles) and p-phase (gray asterisks).

Figure 2-6. Illustration of the effects of molybdenum dilution on the solidification behavior of 316H (left) and on the phase stability (right).

The effect of molybdenum dilution on the time-temperature-transformation kinetics (estimated with JMatPro Software, v.10) of selected phases (sigma, chi, and Laves) is shown in Figure 2-7. The TTT kinetics of 316H are given on the left while the diluted alloy (addition of 20 wt.% Mo in total) is on the right. As shown, increased molybdenum shifts the precipitation kinetics to shorter times. Additionally, the nose of the sigma curve is moved to higher temperatures. These simulations can help guide processing to fabricate cladding as well as experiments to assess the effects of these second phases on the integrity of the corrosion resistant cladding.

Figure 2-7. Comparison of the time-temperature-transformation kinetics for the sigma, chi, and laves phases in 316H stainless steel (left) with the same alloy diluted with 20 wt.% molybdenum (right)

2.7. Other Kinetic Considerations

In addition to precipitation kinetics, other solid state mass transport phenomena need to be considered. These include chromium diffusion through the cladding and the interdiffusion rate between the cladding and the base metal. If chromium diffusion through the cladding is sufficiently fast, then degradation (e.g. grain boundary chromium loss) could still be a concern. Diffusion data for nickel, molybdenum, and tungsten are compared between 500°C and 700°C in Figure 2-8. As shown, Cr diffusion is fastest in nickel and slowest in tungsten. The diffusion rates can be used to estimate a penetration distance of chromium into nickel, molybdenum, and tungsten via an ' $x=\sqrt{Dt}$ ' analysis for a representative temperature (700°C) and time (40 years). As shown in the right hand plot of Figure 2-8, the penetration distance into nickel is only ~10 microns, < 1 micron for molybdenum and << 1 micron for tungsten. This analysis shows that chromium loss through the cladding is unlikely to be a concern.

Figure 2-8. Diffusion data for nickel, molybdenum, and tungsten in chromium (left) and estimated diffusion distance after 40 years at 700°C (right).

In addition to chromium diffusion through the cladding, the interdiffusion rate between the base metal and the cladding is of interest (i.e. diffusion in a composite slab) [39]. This calculation helps understand both the extent of the zone that may undergo metallurgical interactions in-service (e.g. second phase precipitation) and the time scale of concern. As a first assessment of this, the interdiffusion profiles between and FCC iron (γ -Fe) base material and candidate cladding metals are shown in Figure 2-9. In Figure 2-9, the diffusion profiles are estimated for a time of 60 years and a temperature of 750°C. Consistent with their diffusivity, the potential reaction zone for nickel is on the order of ± 100 microns from the original interface, while the slower diffusing tungsten results in a potential reaction zone of ± 10 microns [36].

Figure 2-9. Estimated interdiffusion provides for nickel and tungsten in FCC iron after 60 years at 750°C.

Another kinetic consideration for some reactor designs is the permeation rate of tritium through the structural alloys. Tritium is radioactive and release to the environment must be limited. Hydrogen permeation data for several metals and selected other materials are summarized in Figure 2-10 from the work of Causey, Karnesky and San Marchi [40]. As shown in Figure 2-10, hydrogen permeation through austenitic stainless steels, nickel, and molybdenum is relatively high (see black arrow). However, tungsten (and presumably dilute tungsten alloys – blue arrow) offer orders of magnitude lower permeability. Thus, in addition to being a very noble metal in fluoride and chloride salts, corrosion resistant tungsten coating have the added benefit of action as a hydrogen (tritium) permeation barrier.

Figure 2-10. Summary of tradeoffs with several metals that could be used for corrosion resistant cladding

2.8. Fabrication of Cladding

The relative ease of fabricating the candidate cladding alloys via several different industrial processes is summarized in Table 2-6. In Table 2-6, the ranking is based on engineering judgement of effectively applying the cladding to FCC iron or nickel based alloys either approved or undergoing approval for ASME Boiler and Pressure Vessel Code Section III Division 5 construction materials (i.e. 304H, 316H, 800H, Alloy 617 and Alloy 709). The rankings are given on a relative scale of five increments from likely unsuitable (black circle) to industrially proven methods (white circles).

In general, the refractory alloys are unsuitable for fusion welding due to their high melting points and low solubility in the FCC base materials. Lower temperature processes that minimize mixing (e.g. thermal spraying or brazing) are more feasible. Similarly, solid state joining processes such as explosion bonding (or friction stir application) are feasible but likely require significant development. Lower temperature processes such as sputtering or plating further minimize intermixing of the base material and cladding but typically do not produce metallic bonding between the base metal and cladding. Furthermore, the effects of thermal cycling and in-service degradation (e.g. precipitation of brittle intermetallic phases) need to be assessed.

In contrast, the Ni-201 or Hastelloy N variant claddings are very compatible with ASME base materials and fusion welding as well as several other industrially processes are likely viable options for cladding. Note that recent work by Feng et al. [41] has shown the feasibility of gas-tungsten-arc-welding nickel 201 onto 316 stainless steel. For fusion weld cladding, one consideration is process optimization to minimize the dilution of the cladding with the base material (chromium). Low dilution welding processes likely offer significant cost advantages since fewer layers of cladding will need to be applied.

Table 2-6. Comparison of the Ability to Fabricate Candidate Corrosion Resistant Claddings via Several Industrial Processes

<div> ○: Industrially Proven ◐: Limited Development ◑: Significant Development ◒: Large Scale Development ●: Likely Unsuitable </div>				
	CP-W / W-(3-5Re)	Mo TZM	Ni-201	Hast N Variant
Fusion Arc Welding	●	●	◐	◐
Advanced Fusion Welding	◑	◑	◐	◐
Thermal Spray	◐	◐	◐	◐
Brazing	◐	◐	◐	◐
Explosion Bonding	◐	◐	○	◐
Co-extrusion or co-rolling	◑	◑	◐	◐
Diffusion Bonding	◑	◑	◐	◑
Vapor Deposition	◐	◐	◐	●
Sputtering	○	○	○	◑
Plating	◐	◐	○	●

3. Summary

The present assessment has identified three alloy systems (Ni, Mo, and W) that provide corrosion resistance in both chloride and fluoride salts of interest to advanced reactor systems. For those systems, five alloys are recommended for further investigation: Nickel-201, a modified Hastelloy N (modified to resist Te embrittlement), Mo-TZM, commercially pure tungsten and a W-(3-5 Rhenium alloy).

As discussed in the report, each of these alloy systems have advantages and disadvantages that need to be further assessed in order to develop solutions that enable application of current ASME construction materials in MSR and FHR designs.

- The nickel-based alloys Ni-201 and a modified Hastelloy N provide corrosion resistance, desirable mechanical properties, and metallurgical compatibility with ASME base materials. However, transmutation of nickel to helium is a concern and resistance to tellurium embrittlement may need to be demonstrated. These alloys are likely readily fabricable via several conventional processes.
- Both molybdenum and tungsten alloys offers very good corrosion resistance in fluoride and chloride salts. However, their high melting points, BCC structure, limited ductility, and limited solubility in FCC structural alloys present significant challenges. For their successful application, fabrication processes that minimize mixing of the base material and cladding (e.g. solid state joining processes) should be developed.
- Tungsten and dilute tungsten alloys also act as a tritium permeation barrier relative to austenitic structural alloys. The combination of corrosion resistance and a tritium barrier may offer unique benefit to some reactor designs.

Acknowledgments

The research was sponsored by the U.S. Department of Energy, under Contract No. DE-AC02-06CH11357 with Argonne National Laboratory, managed and operated by UChicago Argonne LLC. Programmatic direction was provided by the Office of Nuclear Energy.

The authors gratefully acknowledge the support provided by Alice Caponiti, Director, Office of Advanced Reactor Technologies (ART), Sue Lesica, Federal Manager, ART Advanced Materials Program, Lou Qualls of Oak Ridge National Laboratory, National Technical Director, ART Molten Salt Reactors Campaign.

The time spent by Xuan Zhang of Argonne National Laboratory in reviewing this report is greatly appreciated.

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