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INFORMATION BRIEF

Title: Barrier Coatings for Refractory Metals and Superalloys

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Summary: In the closed working fluid loop of the proposed Prometheus space nuclear power plant (SNPP), there is the potential for reaction of core and plant structural materials with gas phase impurities and gas phase transport of interstitial elements between superalloy and refractory metal alloy components during service. Primary concerns are surface oxidation, interstitial embrittlement of refractory metals and decarburization of superalloys. In parallel with kinetic investigations, this letter evaluates the ability of potential coatings to prevent or impede communication between reactor and plant components. Key coating requirements are identified and current technology coating materials are reviewed relative to these requirements. Candidate coatings are identified for future evaluation based on current knowledge of design parameters and anticipated environment.

Coatings were identified for superalloys and refractory metals to provide diffusion barriers to interstitial transport and act as reactive barriers to potential oxidation. Due to their high stability at low oxygen potential, alumina formers are most promising for oxidation protection given the anticipated coolant gas chemistry. A sublayer of iridium is recommended to provide inherent diffusion resistance to interstitials. Based on specific base metal selection, a thin film substrate – coating interdiffusion barrier layer may be necessary to meet mission life.

Background: Conceptual designs for the JIMO space reactor center around a gas cooled Brayton cycle generator[1]. This concept uses a He/Xe working fluid to transfer energy by circulating through the reactor, turbine, regenerator, heat exchanger/cooler, and compressor. As such, material transport through the working fluid and the stability of the materials in contact with the working fluid must be considered from both a thermodynamic and kinetic point of view. Of particular concern are those components which could either act as a source or sink for impurities which may degrade the material properties and, consequently, adversely affect the functioning of the system.

The issues regarding material compatibility center on interstitial embrittlement of the refractory metal and/or decarburization of superalloy materials. Specifically, transport of oxygen, carbon, and nitrogen from the superalloys to the refractory metal can lead to embrittlement of the fuel cladding or other refractory metal structural components resulting in failure of the cladding and release of fission products into the gas stream or unacceptable degradation of structural component characteristics. In addition, substantial loss of carbon from the superalloy can reduce the tensile and creep rupture strengths and make the alloy susceptible to grain boundary fracture.

Literature suggests that impurity concentrations in the He/Xe gas used as a working fluid for high temperature gas reactors (HTGR) can lead to carburization or decarburization of superalloys and refractory metals. Over the mission lifetime, interstitial diffusion rates of carbon into refractory metals and/or out of superalloy materials could lead to significant changes in materials properties. Preliminary mass transport modeling[2] indicated that carbon levels in refractory metals could increase by thousands of ppm, leading to embrittlement. According to the same modeling, oxygen concentrations may decrease in refractory metals. Initial thermodynamic equilibrium modeling of the system shows that at low H_2O concentrations (<2.8E-8 mol frac) chromium-containing superalloys could decarburize forming CO or CO_2.[3] Various studies on high-temperature gas-cooled reactors[4,5,6] have found that impurities intrinsic to or introduced into the He/Xe gas coolant may lead to carburization of refractory metals. Over the mission lifetime, this carburization of refractory metals and decarburization of superalloys could lead to significant changes in materials properties and result in component failure.

To assure compatibility between materials in the plant and the working fluid, one can:

- Select alloys which are not susceptible to gas phase transport,
- Operate the plant with gas chemistry control that enables formation of and assures maintenance of passive scales
- Provide for effective getters to remove deleterious species,
- Condense deleterious impurities in a cold well,
- Provide an effective diffusion barrier on refractory metal alloy and/or superalloy surfaces to gas phase contaminants.

Given the disparity between the typical refractory metal affinities for C, O, and N and those of the superalloys, the first two options may offer very little to no design space in which the working fluid can operate[3]. Such stringent control of the working fluid chemistry over the life of the reactor may be impractical. Alternatively, getters or condensing contaminants in a cold well may be employed to prevent the transport and deposition of contaminants in undesirable locations. While this may benefit the refractory metal sink, this approach offers no benefit to the source and may accelerate damage to the source by, for example, preventing the formation of a passive oxide scale on the superalloy surface.

One more effective means of mitigating the effects of such contaminant transport could be to use environmental barrier coatings to act as diffusion barriers and/ or reaction barriers at the source, sink, or both. In addition to acting as an effective barrier to interstitial transport, the coating must be compatible with the respective substrate and the operating gas system chemistry over the duration of the mission.

This document assesses some potential environmental barrier coatings for candidate refractory metals and alloys in the Prometheus gas cooled Brayton cycle reactor and provides a basis for prioritization and down selection based on available literature data. Similar treatment has been given to coatings to

prevent oxidation and decarburization of superalloys and to mitigate compatibility issues for other potential space plant materials.

Key Factors

The possibility that interstitial embrittlement will limit the performance of refractory metals in a reactor is a function of the materials, environment, design, and duty cycle. At the time NRPCT participation in Project Prometheus was terminated, detailed design parameters had not been established. However, the key factors influencing embrittlement of a refractory metal can be summarized as shown in Table 1. Most significant is the extraordinary duration of the mission. As a result, traditional kinetically limited processes become significant. For example, in the absence of a barrier coating, the diffusion distance for carbon in Ni, Fe, Mo, Ta, Nb and W were calculated to be on the order of centimeters to tens of centimeters over the life of the mission[2].

Table 1: Key Factors Influencing Interstitial Embrittlement of Refractory Metal Alloys

Factor	Description	Space Reactor Conditions
Refractory Alloys	Determines Sensitivity to Interstitials, Oxidation, and Reactions with Coatings	Mo, Ta, and Nb based alloys, See Table 3.
Working Fluid Chemistry	Impurity Concentrations	C, O, N activities, Possibly H. (See Working Fluid Below)
Temperature	Influence diffusion kinetics, stable phases, and solubility limits	850 to 1400K Vessel and Cladding, Lower temperature transients possible.
Surface Area/Mass of Source and Sink	Ratio of sink to source determines rate of burden or loading of interstitial in refractory alloy	Considered in Burden Model[2]
Duration	Long duration raises concerns based on kinetics	15-20 Years

The primary concern for superalloys is the potential for decarburization resulting in loss of grain boundary integrity, reduced toughness, reduced creep strength and the potential for carbon contamination of refractory metals employed elsewhere in the system. The passive oxide scale generated by superalloys in oxidizing environments tends to impede decarburization. However, the working fluid may not provide a sufficiently oxidizing environment to promote scale formation. In this case, alternative barrier coatings may be necessary to mitigate the deleterious effects of decarburization on the superalloys and to restrict communication with the refractory metals via the working fluid. Traditionally, coatings for superalloys have focused on air-breathing environments with substantially shorter service lives than those required for Project Prometheus. The potential lack of a strongly oxidizing atmosphere and the long mission life are the most significant factors influencing coating selection and design. Diffusion of interstitials through the selected coating and harmful effects on the superalloy and refractory metal must be considered over the 15-20 year service life. The effects of carbon/carbon composites and potential coatings will be discussed elsewhere[7]. In addition, silicon carbide (SiC) is also a potential fuel cladding material; however, due to significant differences in compatibility concerns, this material will be treated separately.[8]

Therefore, to function successfully as an environmental barrier, a coating must address these key factors while not introducing secondary degradation mechanisms. Fundamental considerations include:

- Chemical compatibility of the coating with the primary coolant gas
- Barrier efficiency
- Interdiffusion or reaction of coating with base material
- Reaction between coating and material (intermetallics, carbides, etc.)
- Inherent coating phase stability
- Coating adhesion
- Thermal conductivity
- Coefficient of thermal expansion (CTE)
- Coating ductility
- Creep performance
- Fatigue debit due to coating
- Manufacturing concerns including accessibility for the coating process
- Deposition process
- Thickness
- System concerns for down stream components, heat exchanger, generator, etc.
- Radiological impact
- Erosion
- Wear/fretting of coating from flow induced vibrations

Working Fluid

The working fluid is anticipated to be a mixture of helium and xenon. Impurity levels have not been established for the Prometheus reactor; however, the coolant chemistry reported by Graham[9] for the helium cooled High Temperature Reactor (HTR), provides a basis for discussion. The reported levels of impurities are provided in Table 2. From this analysis, it is evident that oxygen is not present as free oxygen, but is rather controlled by the H2/H2O ratio and CO/CH4 ratio. The interactions of these species with the substrate surface provide the mechanism of mass transport for C and O through the working fluid. Nitrogen is present as a free element in the system.

Table 2: Approximate Impurity Levels in HTR Helium Coolant

Coolant Chemistry in Helium Cooled High Temperature Reactor	
Impurity	Partial Pressure (Pa)
H_2	50.0
H_2O	0.1
CO	5.0
CH_4	0.5
N_2	0.5

Alloys

The SNPP was foreseen to employ a variety of materials which must work together. The bulk of the plant was assumed to be constructed from superalloy materials including the turbine, recuperator, much of the piping, and possibly the reactor pressure vessel. Reactor internals including the fuel cladding, block and possibly the reactor pressure vessel were candidates for refractory metal applications. A short list of candidate superalloys and refractory metal alloys is provided in Table 3. These include a number of solution strengthened (Haynes 230, IN617) and precipitation strengthened (PE-16, MarM-247, IN792) superalloys and refractory metal alloys of tantalum (Astar-811C), niobium (FS-85), and molybdenum (Mo-41Re to Mo-47.5Re).

Table 3: Candidate Refractory and Superalloy Compositions

Element	Refractory Alloys					Superalloys				
	FS-85	ASTAR-811C	Mo-41Re	Mo-44.5Re	Mo-47Re	PE16	H230	A617	Alloy 792	Mar-M 247
Nb	62.00%									
W	10.00%	8.00%					14.00%		3.78%	10.00%
Ta	27.00%	90.28%							3.75%	3.00%
Zr	1.00%								0.09%	0.05%
Hf		0.70%							0.52%	1.50%
Mo			59.00%	55.50%	52.50%	4.00%	2.00%	9.00%	1.80%	0.70%
Re		1.00%	41.00%	44.50%	47.50%					
C		0.03%				0.10%	0.10%		0.11%	0.15%
Ni						42.00%	52.69%	49.89%	60.60%	59.30%
Cr						18.00%	22.00%	22.00%	12.50%	8.25%
Fe						33.00%	3.00%	3.00%		0.50%
Si						0.30%	0.40%	1.00%		
Mn						0.20%	0.50%	1.00%		
Ti						1.20%		0.60%	4.10%	1.00%
V										
Al						1.20%	0.30%	1.00%	3.45%	5.50%
B							0.015%	0.006%	0.012%	0.015%
Co							5.00%	12.50%	9.25%	10.00%
Be										
O										
He										

Refractory Metals and Alloys

While the refractory metal alloys have outstanding high temperature properties, oxidation, carburization, and interstitial embrittlement limit can limit their application. Embrittlement limits for refractory metals are shown in table 4. Alloys based on the group V metals, tantalum and niobium, are susceptible to embrittlement by interstitial elements including oxygen, nitrogen, carbon and hydrogen. Alloying with reactive group IVA metals (Ti, Zr, Hf) can reduce interstitials in solution in the base metal by the formation of stable oxide, carbide, and/or nitride inclusions given a suitable heat treatment or high service temperature. Low temperature oxidation, however, on the order of 1000 K, can produce coherent Zr-O clusters within the alloy matrix leading to increased hardness and strength with an associated loss of ductility. Subsequent high temperature heat treatment can recover ductility by the precipitation of zirconium dioxide. Solubility of boron and silicon are very low and are unlikely to cause embrittlement from interstitial mechanisms. However, formation of silicide

intermetallics with refractory metals can form brittle layers and must be considered.

Table 4: Solubility and Embrittlement Limit for Interstitials in Refractory Metals

Interstitial Elements in Refractory Metals				
Refractory Metal	Nb	Ta	Mo	Re
Carbide Phases	NbC, Nb_8C_7, Nb_4C_3, Nb_2C	TaC, Ta_2C	Mo_2C, MoC	No Carbides
Elemental Solubility Limits [12] (ppmw)				
Oxygen	1000	300	1	1
Nitrogen	300	1000	1	<1
Carbon	100	70	<1	<1
Hydrogen	9000	4000	0.1	----
Embrittlement Limit, ppmw[10]	150-500	150-500	<10	----

Molybdenum, tungsten and rhenium have considerably lower interstitial solubility than the group V refractory metals. To prevent embrittlement, molybdenum impurity levels must be maintained below a few ppmw.[11] In contrast to niobium and tantalum, molybdenum has considerably lower affinity for interstitial atoms. As a result, despite the lower embrittlement limit, pickup of interstitials is slower and interstitial embrittlement is not as great a concern for molybdenum alloys as it is for alloys of tantalum and niobium[12]. At higher impurity levels, the refractory metal alloys can be expected to form carbides, oxides, and nitrides given an appropriate environment.

High temperature oxidation severely restricts the application of refractory alloys. Tantalum, niobium, molybdenum, tungsten and rhenium readily oxidize in air. At temperatures as low as 800 °C, oxidation is significant. By 1100 °C, the low oxidation resistance can preclude completely their use in air.[13] For molybdenum, tungsten, and rhenium, this is attributed to the formation of volatile oxides. In contrast, tantalum and niobium form porous or non-protective oxide scales[14] resulting in poor inherent ability to resist oxidation. Therefore, researchers have investigated coatings to enable their application to high temperature structures, primarily for aerospace applications. Noble metals, oxides, intermetallics, aluminides, chromides, silicides, and glasses all have been considered individually or in more complex protection systems. While most of these coatings have been developed to address the rapid oxidation of refractory alloys through the formation of a passive oxide scale, select coatings may serve as general diffusion barriers for interstitial alloys.

Superalloys

Nickel base superalloys have excellent high temperature mechanical properties, particularly creep strength. Superalloys tend to exhibit good oxidation resistance in air-breathing applications due to the formation of passive chromia or alumina scales, depending upon the alloy. The scale also performs the role of a diffusion

barrier, preventing or slowing the ingress of oxygen and the egress of carbon from the alloy. In the absence of a sufficiently oxidizing environment, the oxide scale will not form a protective layer and severe decarburization can occur. Decarburization of superalloys results in significant creep strength reduction and loss of grain boundary strengtheners. Coatings for superalloys have been developed primarily for air-breathing environments and shorter service lives than that of Project Prometheus. These coatings aim at improving oxide scale properties (temperature resistance, bond strength, etc.) and growth rates. Coating systems including aluminides, platinum group metals, intermetallics, chromides and silicides have been investigated.

Literature Review of Coatings:

Overview

Environmental barrier coatings may be categorized as diffusion barriers, reaction barriers, or hybrid coatings. Diffusion barriers prevent ingress by reducing the rate of diffusion. An example of this can be found in hermitic seals, glazes, enamels, etc. In contrast, reaction barriers function by forming stable compounds with the diffusing species, preventing further ingress. An example is incorporation of tantalum in MCrAlY (nickel-cobalt-chromium-aluminum-yttrium) compositions to impede the outward diffusion of carbon from the base metal by the formation of tantalum carbides. In practice, many coatings contain aspects of diffusion barriers and reaction barriers wherein the reaction forms a product that not only ties up the diffusing species but inherently has a slower diffusion rate than the parent material. An example of this is the formation of an alumina scale on the surface of a MCrAlY coating. A natural extension to the coating technology is the formation of hybrid coatings incorporating function specific phases or coating layers.

The literature on environmental barrier coatings is extensive. The vast majority of the coatings, including those for refractory metals, center on improving the oxidation and corrosion resistance of the alloy or addressing interdiffusion and materials compatibility issues between alloys. Despite this body of work, insufficient information exists to identify a single coating as meeting the long term requirements for the JIMO, Prometheus mission. Therefore, what follows is a brief review of the literature identifying specific classes of materials with the *potential* for space applications. For simplicity, coatings will be reviewed by class consisting of metals, intermetallics, and ceramics. Coatings are reviewed by class and "best in class" are identified for future consideration.

Platinum Group Metals and Rhenium

Platinum group metals are potential diffusion barriers[15]. Platinum, rhodium, ruthenium, iridium, osmium and rhenium have been examined as potential diffusion barriers for carbon. Platinum, iridium and osmium have served as oxidation resistant surface coatings. They have been applied as interdiffusion barriers for coatings and composites in high temperature material systems.

Platinum

Platinum was added to NiAl coated superalloys as a diffusion inhibitor for increased temperature capability. This came in the formation of discrete platinum aluminides and mixed platinum-nickel and platinum-cobalt aluminides

which are stable to higher temperatures than the binary nickel or cobalt aluminide. Platinum as a discrete barrier layer; however, readily absorbs carbon. In studies of carbon in contact with platinum, substantial absorption can occur at temperatures as low as 1150K (875°C)[16]. Reported solubility of carbon varies widely in platinum from <0.02% at 1700 °C to > 0.1 wt% at 1473K (1200°C).[17] Despite the disparity in solubility, there is significant evidence that carbon diffuses rapidly in platinum precluding application as a discrete diffusion barrier.

Rhenium

Rhenium long has been considered for use as a diffusion barrier. Isobe et al.[18] used a thin rhenium layer between molybdenum and graphite to inhibit Mo_2C formation. The effectiveness of the barrier was found to be a function of thickness, temperature, and microstructure. A rhenium barrier coating 5 μm thick resulted in a 20× decrease in the parabolic rate constant for the formation of Mo_2C at 1173K (900°C). The difference was reduced to less than a factor of 2 at 1423K (1150°C). Molybdenum carbide growth rate increased with decreasing rhenium layer grain size suggesting grain boundary diffusion of carbon as the controlling mechanism.

Glass et al.[15] report that carbon diffuses readily through rhenium at high temperatures but is insignificant below ~3000 °F (1923K/1650°C). In light of the report by Isobe et al., one must assume this is with a substantially thick coating or with a small grain boundary volume fraction.

In the evolution of superalloy coatings, Czech et al.[19] incorporated Re into MCrAlY compositions to modify coating diffusion properties. Rhenium and rhenium alloys have been used as interdiffusion barrier layers under aluminide and MCrAlY coatings. Several patents have been issued for rhenium diffusion barriers[20], for alloying to improve bonding of the barrier to the substrate (Re, Ta, Ru, Os alloyed with nickel and/or cobalt[21]), and for alloying to improve barrier oxidation resistance (Re, W, Ru alloyed with Ni, Co, Fe, Al, Cr)[22].

Rhenium metal does not form carbides and has reasonably low carbon solubility. Arnoult and McLellan[23] determined the solid solubility of C in Re, Ru, Rh and Ir. The solubility of carbon in Re is ~1100 ppmw at 1533K (1260°C) and 55 ppmw at 1093K (820°C). Ruthenium and rhodium displayed slightly lower carbon solubility, with iridium having the lowest carbon solubility at 157 and 20 ppmw at 1533K (1260) and 1093K (820°C), respectively. Rhenium is considered ineffective as a carbon barrier above ~1900 K, due to rapid diffusion.

Rovang[24,25] reported the use of CVD rhenium as a diffusion barrier to prevent carbon embrittlement of niobium liner for heat pipes. A 1-5 μm layer of rhenium served as a *partial* diffusion barrier to prevent embrittlement of the niobium heat pipe structure for the SP-100 project.

While rhenium does appear to be a reasonable diffusion barrier, its poor oxidation resistance severely limits applications in air. Rhenium must be protected from oxidizing environments. This has been accomplished by alloying with chromium and aluminum22 as well as by applying oxidation barrier coatings such as iridium, MCrAlY's, and aluminides.

Iridium

Iridium is noted as having an extremely low carbon and oxygen diffusivity[26] making it suitable for protection of high temperature structural materials. Iridium effectively is unreactive with carbon below 2553 K[27] and exhibits limited carbon solubility.[15] Carbon solubility is only ~157 ppmw at 1533K (1260°C) and 20 ppmw at 1093K (820°C)[23]. Iridium exhibits the slowest diffusion of the platinum group metals (PGMs) ($~10^{-18}$ m^2/s)[28] in nickel, followed by ruthenium and platinum. The high hardness of iridium coatings leads to good erosion resistance. Of the platinum group metals, osmium and iridium possess the best oxidation resistance[29]. As such, iridium liners have been applied to the surface of structural rhenium combustion chamber for oxidation protection.[30] While the oxidation resistance of iridium is far superior to that of rhenium, it is limited to short term applications at such high temperatures. Iridium has been considered for coatings on refractory metals due to its high melting temperature (2727K/2454°C), good CTE match with refractory metals[25], and good creep resistance at high temperatures[31]. Iridium forms intermetallic compounds with molybdenum[25] and tantalum[32], which may lead to embrittlement of the surface or compromise coating performance. Iridium coatings tend to fail at high temperatures through an oxide sublimation mechanism[29]. However, this process is quite slow relative to metals such as rhenium or molybdenum. Above 1395K[33], formation of gaseous IrO_3 results in active surface oxidation in air. Typically, alloying additions or oxide overcoats are used to mitigate sublimation losses[29]. Sublimation losses may not be a real concern in the inert gas coolant chosen for the space reactor. Improvement of the oxidation behavior of iridium has been enhanced with a surface layer of iridium aluminide[34]. IrAl forms an aluminum oxide surface layer effectively suppressing excessive surface oxidation. An iridium aluminide alloy or iridium with a surface aluminide seems favorable as an oxidation resistant and diffusion resistant coating.

Osmium

Osmium can be expected to perform as an environmental barrier similar to rhenium and iridium. Its properties are reported to be similar to iridium possessing high hardness. It also has low ductility, similar to iridium. One distinct difference is that the alloy oxidizes to form OsO_4. The oxide not only volatilizes at 413K (140°C) to form a strong oxidizer, but is highly toxic, which may explain its limited use.[35]

Other Metals

Lawther and Sama[36] investigated Hf-Ta alloy coatings. Owing to the stability of hafnium oxide, 80Hf-20Ta alloys were reported to have relatively high oxidation resistance at 3000-4000°F (1922-2477K). Based on this observation, coatings based on Hf-Ta compositions were investigated for tantalum alloy protection. The oxidation behavior of 80Hf-20Ta-0.25Si (R515) slurry coatings were evaluated for protection of Ta-10W refractory alloy. The baseline coating provided protection comparable to bulk Hf-Ta materials with a useful life of about 1 hour at temperatures up to ~3100°F (1977K). Improvement was made by making a duplex coating of HfB_2-10MoSi$_2$ infiltrated with the R515 composition.

This extended the service life to over 100 hours at 2500°F(1644K/1371°C). Since HfO_2 is stable at low oxygen pressures, it is expected that the coatings will be suitable for low oxygen pressures. Oxidation testing between 133 and 1333 Pa (1 and 10 Torr) air pressure further reduced oxidation.

Intermetallics

Intermetallics define a broad class of materials that have been used to provide oxidation protection. Less is known about the behavior of these materials as diffusion barriers for carbon and nitrogen, with or without a surface oxide. Intermetallics including aluminides, chromides, silicides, and beryllides have been investigated for environmental protection. Intermetallic coatings are widely used to protect base alloys from oxidizing environments by the formation of a passive oxide surface scale. Certain "B2" (CsCl structure) intermetallics may also serve as inherent diffusion barriers for interstitial migration.

Aluminides

Aluminide coatings may be formed by the direct application and reaction of aluminum on an alloy surface, or in combination with plating processes of a desired reactant element such as platinum. This technique has been widely applied to superalloys for turbine applications with the primary surface coating being a cobalt aluminide, nickel aluminide, platinum aluminide, or mixtures thereof. The aluminide phase provides a ready source of aluminum to the surface of the alloy to form aluminum oxide in oxidizing environments. Cobalt and nickel aluminide provide oxidation protection up to ~1173K (900°C). Coating life is limited by the loss of aluminum to form the passive scale, loss of aluminum to the base alloy due to interdiffusion and degradation of the thermally grown oxide scale due to tramp element diffusion from the superalloy to the coating / scale interface.

Pt-modified nickel aluminide (NiAl) is widely used for superalloy protection[37]. Two types of Pt-modified NiAl coatings are widely used: a two phase Pt_2Al – (Ni,Pt)Al and a single phase (Ni,Pt)Al[38]. The two phase coating is formed by a high activity vapor alumizing process and is characterized by either a continuous or discontinuous Pt_2Al surface layer with a sub-layer of NiAl. The discontinuous platinum phase is preferred due to the extremely brittle nature of the Pt_2Al and the resulting debit on fatigue properties. Alternatively, the single β-phase (Ni,Pt)Al is typically deposited by a low activity vapor aluminizing process. By comparison, this coating is less brittle leading to more wide spread application. The exact mechanism by which Pt enhances oxidation resistance is unclear; however, it is believed to increase scale adhesion, perhaps by the suppression of interface void formation[39] or by relieving stresses in the scale through enhanced diffusional creep or grain boundary sliding[40] of the thermally grown oxide. The increase in oxidation life as much as three-fold[39] more than offsets the cost incurred due to platinum for most applications.

The stability of platinum aluminide and platinum modified aluminides is strongly dependent on the coating process, substrate material, and service conditions. Degradation mechanisms include; loss of aluminum due to oxidation, loss of aluminum due to interdiffusion with the substrate, and loss of thermally grown oxide scale adhesion. The first is required to form the thermally grown aluminum

oxide that, once formed, provides the primary protection against rapid continued oxidation. As the aluminide coating incorporates constituents from the base metal into the coating structure, the coating oxidation performance is strongly substrate dependent. Furthermore, high activity coatings result in greater incorporation of secondary base metal alloying elements into the coating structure than low activity aluminides, further influencing performance. Small additions (<0.5wt%) of elements such as hafnium[41] and yttrium can enhance scale adhesion whereas "tramp" elements such as titanium, sulfur and phosphorus can degrade oxide scale adhesion. In addition, interdiffusion of platinum into the substrate can lead to brittle topologically close packed (TCP) phase formation compromising the integrity of the interface.[42,43]

Despite the limitations, platinum aluminide demonstrates higher temperature stability than plain nickel aluminide, extending both coating life and operating temperature capability. Platinum aluminides have been used at temperatures to 1448K (1175°C); however, life is typically only a few thousand hours. The microstructure of the coating continues to evolve as aluminum is depleted, mostly from the inward diffusion of aluminum and platinum into the substrate. In service, commercially available RT22, formed by a high activity process evolves from an initial $PtAl_2 + \beta$-NiAl to a single phase β-NiAl which then evolves to a γ-Ni/γ'-Ni$_3$Al and ultimately to γ-Ni solid solution. While diffusion is evident at 1273K (1000°C), these coatings are generally stable and provide serviceability for 10,000 hrs or more. Gobel suggests that in some systems, formation of immobile precipitates of Cr, Mo, and W act as barriers to further interdiffusion.[43] These precipitates dissolve at temperatures above 1474K (1200°C).

As an alternative to conventional platinum aluminides based on β-(Ni,Pt)Al, Gleeson[44] proposed high-platinum, low –aluminum materials that reside in the γ-Ni/γ'-Ni$_3$Al phase field [Ni-29.5Pt-22.1Al (at.%)] for high temperature oxidation resistance. Coatings of this material have the potential of lower aluminum loss to the substrate due to a reduced concentration gradient. Despite lower aluminum content, these coatings retain good oxidation resistance similar to β-(Ni,Pt)Al after 2000 hours cyclic oxidation at 1373K (1100°C) (1 hour cycles) and 1000 hours at 1474K (1200°C) (100 hour cycles).[41]

Platinum aluminides have shown good performance from 1273K (1000°C) to ~1473K (1200°C) for operation in the thousands of hours in oxidizing, primarily gas turbine, environments. Depletion of the coating due to oxidation and interdiffusion is evident at these temperatures and increases with time. No information is available regarding oxidation performance in reduced oxygen environments which would allow extrapolation to the Prometheus coolant loop. However, since most of the coating depletion is due to interdiffusion with the substrate, and depletion rates are substrate dependent,[43] accurate determination can only be made considering the coating by evaluation of substrate/coating system. Given the long mission life for the Prometheus reactor (15-20 years), application of platinum aluminide coatings are likely to be appropriate for components operating below 1123-1173K (850-900°C).

Iridium and ruthenium aluminides are considered as possible environmental barrier coatings for space applications due to their high temperature phase stability and stable aluminum oxide formation. While pure iridium aluminide is brittle, alloying with nickel and cobalt improve the coating ductility and oxidation

resistance[45]. Microstructure and grain size of iridium coatings are highly process dependent. This produces marked differences in oxidation performance for (Ir,Ni)Al coatings formed by iridium deposition followed by outward diffusion of Al and Ni during heat treatment. In contrast, vapor phase aluminizing over iridium coated substrates produces high quality coatings with little influence of the iridium deposition process on cyclic oxidation performance at 1273 and 1423K.

Serviceability of many iridium base alloys in oxidizing environments is limited by the volatility of iridium trioxide (IrO_3). IrO_3 forms at temperatures greater than 1395K. Alloying iridium with aluminum substantially reduces the oxidation óver pure aluminum. In the binary system, this requires aluminum content in excess of 55 mol% in order to form a continuous alumina scale.[46] Lower aluminum contents improve oxidation resistance over pure iridium, but lead to continuous weight loss after a short (minutes) incubation period.[45] Adding 10% cobalt or nickel to form a substitutional aluminide, (Ir,Ni)Al or (Ir,Co)Al, improves scale adhesion and dramatically reduces weight loss by two orders of magnitude over the uncoated iridium at 1673K. The benefits derived from Ni or Co additions are believed to result from the extended stability range for the B2-IrAl phase. [33] It has been suggested that iridium aluminide coatings are suited for Mo alloys due to similar coefficients of thermal expansion. However, further testing is needed in order to determine if various iridium aluminides form a stable oxide in the proposed coolant environment.

Ruthenium aluminide has the highest temperature stability of the platinum group aluminides. Tryon studied the behavior of ruthenium in contact with a nickel based superalloy and found that while solubility for nickel was low, ruthenium reacted with tantalum and aluminum in the superalloy to form Ru_2AlTa.[47] Distribution of intermetallic phases relative to the interface suggested interdiffusion distances on the order of 10-20 μm after 168 hours at 1373K (1100°C). This observation suggests that RuAl would react with Ta, precluding its direct application on Ta-base alloys without an intermediate layer. Ruthenium aluminide also forms a very stable B2 intermetallic[48]. The B2 phase exhibits slow interdiffusion rates with Mo, on the order of 10^{-19} mm^2/sec at 1373K (1050°C).[49] It is very non-reactive with most elements (excluding Ta and Al).

The room temperature mechanical properties (fracture toughness and ductility) for RuAl are considered good for an intermetallic compound.[50] Two phase alloys of Ru-RuAl are stronger and show an order of magnitude higher yielded strains than the single phase RuAl due to formation of a eutectic phase along the grain boundaries.[51] This is the pertinent information known on RuAl and very little information if any is currently available on RuAl as a coating. Testing would need to be conducted in order to determine if RuAl is a viable coating option for the proposed environment and mission duration.

Silicides

Historically, protective coatings for refractory metal alloys have focused extensively on silicides. The oxidation resistance of silicides is attributed to the formation of an amorphous silica (SiO_2) layer when the surface ($MoSi_2$, Mo-Si-B, etc.) is oxidized by the environment. Silicides perform well in high temperature, oxidizing environments and have been used as protective coatings for refractory

metals, particularly niobium, tantalum, and molybdenum. Silicide coatings may be produced through cementation processes with either the base metal or with another metal, such as molybdenum, deposited prior to cementation.

Two reaction mechanisms have been identified for the oxidation of $MoSi_2$.[52] Below 1073K (800°C), the primary reaction produces MoO_3 and SiO_2, with MoO_3 having the potential to disintegrate in an oxidizing atmosphere. The oxide is non-protective, and pesting occurs. Above 1073K (800°C), the primary reaction products from surface oxidation are stable Mo_5Si_3 and SiO_2.

In addition to surface oxidation, direct application of $MoSi_2$ on refractory metals results in interdiffusion and reaction with the substrate.[53,54] Mo_5Si_3 forms as an interlayer between the $MoSi_2$ and the base metal. Glass[53] observed that when a $MoSi_2$ coating was applied by a CVD process onto Mo and subsequently exposed to high temperature oxidation, significant growth of Mo_5Si_3 occurred at the interface. Comparing parabolic growth rates for the $(Metal)_5Si_3$ substrate layer and surface oxidation SiO_2 layers reveals coating loss to the substrate is 2.5-3 orders of magnitude faster than that due to surface oxidation and the formation of SiO_2. Therefore, defect-free coating life will be limited by silicon depletion into the substrate.[55] Significant life extension may be possible by the application an interdiffusion barrier.

Most of the development on refractory metal silicide coatings has been for the protection of molybdenum. This experience has been transferred to the protection of tantalum and niobium alloys. However, significant differences in the oxidation behavior exist such that direct translation is not possible. Unlike $MoSi_2$ or WSi_2, which form a nearly pure SiO_2 surface scale at high temperatures, tantalum and niobium oxides do not evolve as gases and are, therefore, incorporated into the scale structure. During the initial stages of tantalum or niobium silicide oxidation, both refractory metal oxide and silica form simultaneously producing a physical mixture. This mixed oxide layer, $(Refractory Metal)_2O_5$-SiO_2, has a higher oxygen diffusivity and more rapid scale growth than the pure SiO_2 formed on $MoSi_2$ or WSi_2. Therefore, although niobium and tantalum silicides provide a measure of oxidation protection to the refractory metal alloys, high growth stresses in the mixed-oxide layer lead to cracking and spallation.[56]

Silicides rely on the formation of a continuous silica scale. Low temperature and/or insufficient oxygen partial pressure can lead to disruption in the silica scale resulting in rapid loss of material. If the loss is due to low temperature and instability in the refractory metal oxide state, the process is referred to as pesting. If the supply of oxygen is insufficient to create and maintain stable SiO_2, SiO, which is volatile, may be preferentially formed resulting in active oxidation.[53]

There is some evidence that boron, tungsten, or germanium additions may reduce the problem of low temperature pesting by increasing the fluidity of the resulting amorphous silica scale. Nomura and colleagues[57] used a plasma spray technique to deposit a boron doped Mo_5Si_3 (consisting of Mo5Si3, Mo_3Si, and Mo_5SiB_2) coating onto a Mo-ZrC composite. After an initial period of rapid oxidation and weight loss at 1673K, the oxidation rate decreased with subsequent weight gain due to surface passivation via a continuous borosilicate scale. The boron decreases the viscosity of the amorphous scale leading to

shorter passivation times and less overall material loss due to oxidation. In similar fashion, addition of germanium suppresses low temperature oxidation by lowering the viscosity of amorphous SiO_2. This lower temperature glass enhances oxidation resistance at low temperatures, helps prevent pesting, eliminates spallation, and may increase coating life by an order of magnitude.[53]

Filippi[58] evaluated the oxidation resistance of T-222 coated with a slurry W-Mo-V-Ti silicide. During heat treatment and subsequent service, the formation of TiO_2 rich silica scale substantially reduced oxidation of the alloy. Negligible change in alloy oxygen, nitrogen and carbon content was noted as a result of high temperature exposure. Oxidation was observed within coating cracks (fissures) and from pores traversing the coating. Furthermore, substrate recession resulted from reaction between the T-222 and the coating at temperatures between 811 and 1589K.

While there has been an extensive discussion of the oxidation resistance of silicides, there is little information available concerning carbon and nitrogen diffusion resistance. Refractory metals are strong carbide formers (Ta and Nb) and are expected to form carbides in contact with any source of carbon. In addition, silicides such as $MoSi_2$ can react with carbon to form the so-called Nowotny phase CMo_5Si_3, further impeding the motion of carbon in the system.[59]

Despite the merits of silicides for protection of refractory metals in high temperature oxidizing environments, the use of silicide coatings may not be practical for the direct Brayton space reactor design. High-temperature, lightly-oxidizing environments can prevent the formation of a passive silica scale, which limits the protection provided by the silicide coating. Preoxidation is not a practical solution given the tendency toward SiO formation at low oxygen pressures, leading to loss of passivity. An additional concern for the Prometheus mission is crystallization of amorphous silica to cristobalite.[60] As a result of the volume changes associated with this phase change, the surface scale can crack and lose its protective character.

Two ceramics (silicon nitride and silicon carbide) form passive silica scales analogous to the oxidation of silicide coatings. As a result, these coatings suffer from similar limitations to silicide coatings. When coated on superalloys, silicon carbide and silicon nitride react rapidly to form cobalt[61] and nickel silicides. Therefore, while these materials may form diffusion barriers, reactions and surface volatility preclude their use as an environmental barrier coating for the space reactor.

Ceramics

Nitrides, Carbides and Borides

While nitride coatings are most widely known for their excellent hardness and wear characteristics, they have also found wide-scale use as a diffusion barrier at temperatures from 673K (400°C) to >1273K (1000°C). Nitride materials have found applications in many fields, from electronics to gas turbine engines. Nitrides have been used as single phase coatings or combined with carbides. They have been deposited as thin films, 0.1 to 10 microns thick, in crystalline form or as amorphous layers. Many nitrides are stable to temperatures in

excess of 2273K (2000°C); however, service temperature is restricted in air to less than ~773K to 1173K (500 to 900°C) due to oxidation. Despite this limitation, nitrides may still play a vital role in the development of a protective coating system for high temperature gas reactors.

Nitrides are used extensively in the electronics industry as diffusion barriers, insulating layers, or dielectrics. As electronic devices shrink, interdiffusion plays an increasingly critical role in the performance of components. Nitrides have been employed to prevent reaction and interdiffusion between conductors and semiconductor or dielectric substrates during metallization from 673 to 973K (350 to 650°C). The most commonly studied nitride is titanium nitride (TiN)[62]; however, numerous other nitrides have been investigated including zirconium nitride (ZrN)[62,63], tantalum nitride (TaN)[64,65], tungsten nitride (WN) [66,67], and molybdenum nitride (MoN$_x$)[68].

Nitrides have also been considered as diffusion barriers for gas turbine applications. Coad[69] examined the application of TiN as a diffusion barrier between a MCrAlY coating and a superalloy gas turbine component. If adequately protected from oxidation, TiN layers deposited by sputter ion plating were stable up to 1273K (1000°C). The coating reduced the interdiffusion zone thickness by a factor of three to five, but in no case was it completely effective in preventing interdiffusion. Telama[70] similarly found TiN to be effective at inhibiting diffusion between FeCrAlY and Incoloy800 and between CoNiCrAlYTa and MA6000 up to 1273K (1000°C); however, the barrier was ineffective at 1373K (1100°C) and above. Lu[71] tested 2-5 µm thick TiN coatings as a barrier between CoNiCrAlYTa and IN738LC between 1123 and 1323K (850 and 1050°C). No sign of interdiffusion was evident after 3000 hours of exposure at 1123K (850°C). At 1223K (950°C), the barrier was less effective; however, diffusion was sufficiently reduced as to prevent massive TaC formation.

More recently, Gorman[72] extended this concept to include diffusion barriers consisting of oxides, nitrides, and their mixtures to prevent interdiffusion between a superalloy and a protective coating containing a platinum group metal (Pt, Pd, Rh, Ru, Ir). While nitrides and oxynitrides are included in this patent, oxide diffusion barriers (alumina or zirconia) are listed as "preferred". This may be due to the potential oxidation of the nitride film should it be exposed to air.

Kvernes et al.[73,74], found further reduction in interdiffusion rates for mixtures of TiN+TiC. These were examined along with the base TiN and Ta barriers deposited between FeCrAlY – IN617 and FeCrAlY-SIS2343 couples. The mixed TiN+TiC barrier provided considerable improvements over the single phase nitride barrier. After 70 hours exposure at 1173K (900°C), no interdiffusion zone was detected. In contrast, a diffusion zone of 70 µm formed in the absence of the barrier. Substantial improvements were also shown for the single phase tantalum barrier which was annealed for 5 days at 1273K (1000°C). The Ta barrier reacted with the substrate to form a combined interdiffusion zone and Ta$_2$Ni reaction layer only 20 µm thick despite the higher temperature. No reaction was detected between the FeCrAlY and Ta barrier.

Wang et al.[75] used amorphous layers of Al-O-N and Cr-O-N to act as a diffusion barrier between superalloy components and NiCoCrAlY overlay coatings. Efficiency of the barriers was investigated at 1173 and 1323K (900 and 1050°C).

While inhibiting loss of Al to the substrate, Al-O-N degraded the overall performance of the MCrAlY. In contrast, Cr-O-N proved to be an effective diffusion barrier. In this system it was not the oxy-nitride that prevented reaction, but rather reaction between the barrier and the MCrAlY which formed a well bonded, continuous aluminum oxide scale at the interface impeding significant interdiffusion. As such, these coatings should be viewed as a means to form a diffusion barrier in service, rather than an inherent diffusion barrier.

Ahlroth et al.[76] investigated TiN, TiC, and their mixtures to serve as reaction barriers between W fibers and a Ni matrix in metal matrix composites. His results show that sputtered TiC, TiN and TiC+TiN interlayers, 0.5 to 2 μm thick, effectively hindered interaction between the fibers and matrix. Annealing heat treatments at 1200K (927°C) for 114 hours produced a diffusion zones <1μm thick. This can be compared to 23-30μm diffusion zones in the absence of the barrier layer. In contrast, similar barriers applied by CVD produced little or no benefit in reducing interdiffusion. No explanation was given for the difference in performance as a result of coating process.

Nitrides appear to serve as effective barriers for metal and carbon diffusion below ~1123K (850°C). Thin films have also shown considerable benefit in slowing metal and carbon migration at temperatures up to ~1273K (1000°C).[70] Oxidation of the nitride is still a concern and may limit application as a surface coating. Titanium nitride is restricted to <873K (600°C) for service in air. Additions of chromium and aluminum to the nitride can increase service temperature. Aluminum additions to titanium nitride (AlTiN) extend this temperature to ~1073K (800°C).[77] Chromium nitride can operate at ~973K (700°C) by forming a passive chromium oxide scale. Tantalum nitride is reported to oxidize between 823 and 993K (550 and 720°C). CrTaN is serviceable above ~1073K (800°C); however, active oxidation is reported below 1073K (800°C).[78] Therefore, while some nitrides do serve as effective diffusion barriers, oxidation severely limits their application in air environments.

The space reactor working fluid is expected to have virtually no free oxygen. The oxygen potential is limited by the CO/CO_2 ratio and the H_2/H_2O ratio. In such environments, the oxidation behavior can be substantially different than in air. Bouzouita[79] observed a fundamentally different oxidation behavior of TaN when exposed to CO/CO_2 environments. Rather than forming tantalum oxide and evolving nitrogen, in these environments, oxidation occurs by the inward diffusion of CO_2 to form a bilayer TaON sub-surface layer and a tantalum oxide surface layer. Further oxidation is limited by the diffusion and reaction with the TaON layer.

Walters[80] examined the use of thin films as diffusion barriers between platinum and molybdenum. Diffusion barriers of TiN, TiC, TiB_2, TiB_2/TiC, TiB_2/TiC and TaC were deposited between a molybdenum (TZM) substrate and a platinum coating and evaluated at temperatures between 1473 and 1673K (1200 and 1400°C). For these systems, TiB_2 and TiC reacted with the base metal even at the lowest temperature. TiN showed promise for application at 1473K (1200°C), but readily degraded at higher temperatures. Of the barriers evaluated, TaC offered the most promise. While reaction did occur between the Mo substate and the TaC as well as TaC and the Pt overlayer, it was determined that this reaction occurred during the coating process. Furthermore, the subsequent heat

treatment produced no change in the microstructure of the coating with up to 10 hours exposure.

Borides, particularly titanium diboride, have been used to prevent reactions between the fibers and matrix in composite materials. By acting as a diffusion barrier, titanium diboride has been used to protect SiC fibers in intermetallic matrices, Ti particles in glass matrices, and boron fibers in aluminum matrices. Silicon carbide fibers (SCS-6) react with Ti_2AlNb to form titanium carbides and titanium aluminum carbides[81]. TiB_2 deposited on the fiber surface prior to hot isostatic pressing at 1203K (930°C) prevents reaction by stopping carbon and titanium diffusion. Long term heat treatment results in TiB_2 transforming to TiB by slow reaction with the matrix. No titanium carbide or titanium silicide is present prior to loss of the TiB_2 coating illustrating the effectiveness of the coating at preventing carbon and titanium diffusion. TiB is not an effective barrier layer. Vincent[82] demonstrated the use of a 1µm thick TiB_2 layer as a diffusion barrier in the production of aluminum melt infiltrated boron fiber-reinforced composites. Reaction-formed TiB_2 functioned efficiently as a diffusion barrier during processing to 973-1143K (700-870°C).

Glass-ceramics reinforced with ductile Ti particles degrade through formation of brittle Ti_5Si_3[83] which limits the composite strength and toughness. Bilayer TiB_2/C and titanium boride nitride (Ti(B,N)) coatings were investigated as diffusion barriers. Interfacial reaction was reduced and mechanical properties were improved with the introduction of the barrier layers.

The potential for nitrides, carbides and borides to perform as effective environmental barriers is dependent on operating temperature. At low temperatures, or for short times, they have been effective for engineering applications. At higher temperature, the behavior is dependent on the environment and oxygen potential. Nitrides have been effective as interdiffusion barriers. As such, these coating may still find application as a sub-layer to prevent inward migration or reaction of other environmental barrier coatings with the base metal.

Hybrid Concepts

A review of potential coatings for refractory metals has been presented. Many coatings have attractive features; however, no single coating stands out as appropriate over all conceivable operating conditions. Given the uncertaintly in the working fluid environment, it is conceivable that a hybrid or functionally layered coatings, will be necessary to meet the mission requirements. As an example, iridium is attractive for its slow interstitial diffusion. Surface aluminizing may be required to prevent surface oxidation and a carbide may be necessary to prevent excessive interdiffusion. Reactive elements such as Ti, Zr, and Hf may be added to remove C,N and O that penetrate to the refractory metal.[84] While a simpler path is desired, one should not ignore the possibility of using a hybrid where necessary. The true need will be based on the final chemistry of the working fluid and results of transport and interdiffusion studies.

Manufacturing of Barrier Coatings

<u>Cementation of Aluminides and Silicides</u>

Base metal and alternative diffusion aluminide coatings can be produced using a variety of techniques. These include cementation processes, which produce the aluminide coating in one, long step; and other processes that deposit aluminum on the substrate and then require a separate step to diffuse aluminum into the substrate, producing the final coating. Cementation processes can be divided into pack and slurry processes. Pack processes consist of a powdered source of aluminum and an inert packing material that provides structural support and prevents sintering of the aluminum powder. A halide gas is then introduced either through incorporation of a halide compound or through gas streaming. The halide gas reacts with the aluminum source, producing a gaseous aluminum halide compound. The aluminum halide compound decomposes on the surface of the substrate, depositing aluminum. The aluminum then diffuses into the substrate, producing the final coating. The diffusion step is a slow process and requires long times at high temperatures. Slurry processes were developed to aluminize larger parts or complex geometries. In slurry processes, the source material is applied with or without a halide compound by dipping, spraying, or brushing. The slurry is dried, leaving behind a coating of pack material. The part is then heated to drive the reaction and diffuse aluminum into the part, creating the aluminide coating. Cementation processes are carried out in controlled atmospheres (vacuum or inert gas) to prevent material oxidation. Similar cementation processes can also be performed to produce silicide coatings.

<u>Other Aluminide and Silicide Processes</u>

Although less common, aluminide coatings can also be deposited using alternative techniques to cementation. Aluminum metal can be deposited using hot dip, chemical vapor deposition, fused salt processes, and physical vapor deposition. The substrate is then heat treated to allow aluminum to diffuse and generate the aluminide coating. Hot dip processes consist of dipping the part into a molten bath of aluminum to coat the part. The molten aluminum is covered with a flux to prevent metal oxidation. This process generally produces poor quality coatings due to poor process control and is limited to simple geometries. Chemical vapor deposition (CVD) is similar to pack cementation with the exception that the halide carrier is generated externally. CVD is capable of coating recessed areas and complex shapes with good quality aluminide coatings. The elevated temperatures associated with CVD provide for diffusion of aluminum into the substrate; however, further heat treatments may be required to produce the final coating. CVD processes are commonly used to generate modified silicide coatings, such as $MoSi_2$. Aluminum and silicon can be deposited from fused salt baths using both electrolytic and electroless techniques. Further processing is similar to hot dipping. Physical vapor deposition (PVD) can be used to deposit both aluminide and silicide coatings using evaporative techniques. PVD is a line of sight process.

<u>Platinum Group Metals and Rhenium</u>

Platinum group metals (PGMs) can be deposited for space applications using CVD, PVD, and electrodeposition. Organometallic CVD is a developed technology for depositing iridium, rhenium, and other PGMs (Ultramet). CVD

processes offer the high throwing power necessary to coat complex components in the space plant and core with a uniform coating. Coating uniformity is a critical issue for PGM barrier coatings in that coating defects may result in failure. PVD is capable of depositing PGM coatings; however, line of sight restrictions may make its use problematic. Electrodeposition from fused salts or aqueous solutions can also be used to deposit PGM coatings. Electrodeposition of coatings on complex geometries will be difficult and may result in non-uniform coatings.

Oxides and Other Ceramics

Oxides, carbides, nitrides, etc can be deposited using CVD with appropriate precursors. PVD processes, including EB-PVD and reactive ion sputtering are capable of producing ceramic coatings. Other potential processes for depositing ceramic coatings include fritting to produce glassy coatings and thermal spray. It is important to note that the performance of coatings is heavily dependent upon processing.

Process Comparisons

Given the complex geometries and shapes present within the space power plant design, non-line of sight processes seem best suited for producing environmental barrier coatings, (EBCs) regardless of the final down select of coating(s). CVD processes likely would be a practical solution for depositing barrier coatings that must be continuous throughout the plant. Small defects in barrier coatings can result in loss of substrate protection. CVD or slurry cementation seems appropriate for the deposition of aluminide or silicide diffusion coatings, given component geometry and size.

Experimental Approach:

Today there is no coating material proven to possess the unique combination of diffusion barrier, chemical compatibility, oxidation resistance, and mechanical and physical properties required to serve as an EBC over the life of the Prometheus reactor. Thermodynamic considerations may limit some applications while kinetic considerations will play a role in all possible systems. Limited data prevents a definitive EBC selection based solely on the literature. There are a number of materials that possess one or several attractive properties making each of them worthy of consideration. It may then be possible to select the proper material or combination of materials necessary to meet the required functionality and service life.

Identification of a suitable EBC, or the fundamental need for an EBC, can only be determined through appropriate testing. The process, shown in Figure 1, involves the diffusion of interstitials from the source to the working fluid, gas phase transport through the working fluid, and reaction at the refractory metal or diffusion into the refractory metal. Variation of the transport process may include dissolution of second phase particles (carbides) at the source or precipitate formation at the sink. The process may be altered by the incorporation of EBCs at the source, sink, or both.

In addition to the interstitial transport phenomena, interdiffusion and reaction between the EBC and the base metal can have a marked influence on the functionality of the coating and base metal properties. Reaction layers, including

intermetallics and solid solutions, can lead to changes in melting point, ductility, adhesion, fatigue performance, etc. within the structural alloys. Conversely, they can also be beneficial; limited interdiffusion increases bond integrity, interface oxidation reduces diffusion, etc.

The transport processes may be modeled, but testing is required to establish the material dependent parameters for the various mechanisms. Individual process models exist for dissolution, diffusion, precipitation, gas phase absorption, oxidation and convective transfer. However, the complete process is very complex and relies heavily on test data to determine the numerous material parameters involved. A testing strategy is therefore required to evaluate candidate barriers and enable the down select of the most promising coatings. Testing is further required to enable the extrapolation and life prediction from the laboratory tests to ensure performance over the mission duration.
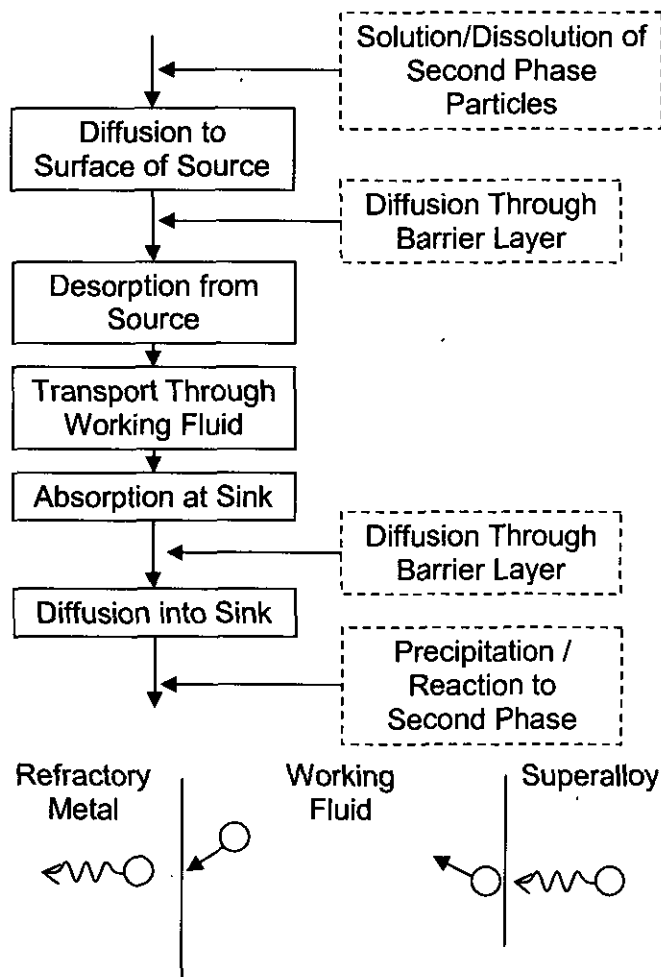

Figure 1: Flowsheet for Coating Materials Testing

Laboratory diffusion testing consists of short term tests (to provide rapid screening) and longer term tests (for developing life prediction). Short term test parameters, while relevant, are grossly accelerated and many secondary parameters are neglected for simplicity. The relatively low cost and short duration enables rapid elimination of EBCs with excessive interfacial or corrosion reactions, poor coating adhesion, or gross mechanical incompatibility. They provide a basis to quickly focus further evaluation on the most favorable systems. In contrast, long term tests are typically more complex, are preformed over a range of time, temperature, and other key parameters, and provide a basis for life prediction. Irradiation is known to influence diffusion and phase stability of materials. However due to high cost, limited control and limited space, it is impractical to run frequent long term tests under irradiation. The test approach is, therefore, to examine the irradiation effects only on a very limited basis for final model verification. Deviations from the out-of-pile testing can be accommodated through the use of adjustment factors to deliver a final interstitial transport model. A summary of some standard diffusion tests and possible mission specific test are provided in Table 5.

Table 5: Summary of diffusion tests in support of EBC evaluation and transport modeling. Interface acronyms: SA=superalloy, C=coating, RM=refractory metal alloy, G=gas. Key Variables: T=temperature, I=interface, P=system pressure

Table 5

Diffusion Tests in Support of Barrier Coating Selection for Refractory Metals and Superalloys

Short Term Tests

Purpose	Interface	Test	Key Variables	Output	Note
Screening Tests	SA-C / RM-C	Diffusion Couples	T, t	Interface Stability, Rxn's and Interdiffusion	Basic test for coating / substrate compatibility
	SA-G / RM-G / C-G	Single Pass Retort	T,t,Gas Chem, P, Flow	Transport Process and Solid-gas interactions	Basic test for gas transport from known/fixed gas chemistry
	SA-G / RM-G / C-G (SA-C / RM-C)	Capsule	T,t,Gas Chem, P	Transport Process and Solid-gas interactions	Inexpensive test for long term exposure and gas transport.

Long Term Tests

Purpose	Interface	Test	Key Variables	Output	Note
Life Prediction	SA-G / RM-G / C-G (SA-C / RM-C)	Capsule	T,t,Gas Chem, P	Transport Process and Solid-gas interactions	Inexpensive test for long term stability, Gas reactant depletion
	SA-G / RM-G / C-G (SA-C / RM-C)	Single Pass-Double Retort	T,t,Gas Chem, P	Transport Process Kinetics / Fixed Chemistry	Forced convection, fixed or steady state chemistry
	SA-G / RM-G / C-G (SA-C / RM-C)	Loop Test	T,t,Gas Chem, P	Transport Process Kinetics / Depleting Chemistry	Natural convection loop. Hot and cold wells. Closed system equilibrium and kinetics. Limited capacity.

Irradiation Tests

Purpose	Interface	Test	Key Variables	Output	Note
Irradiation Adjustment to Life Prediction	SA-G / RM-G / C-G (SA-C / RM-C)	Capsule	T,t,Gas Chem, P, Fluence	Irradiation adjustment to life prediction model	By comparison to long term test data and prediction, adjust factor for irradiation may be generated for model
	SA-G / RM-G / C-G (SA-C / RM-C)	Diffusion Couples	T,t,P, Fluence	Irradiation adjustment to life prediction model	By comparison to long term test data and prediction, adjust factor for irradiation may be generated for model

Coatings may be used to retard the transport of interstitials and other contaminants. To meet the full functional requirements, the coating must also maintain the mechanical integrity of the base metal and provide adequate adherence throughout the mission. Tests for the mechanical property debit due to the coating include thermo-mechanical fatigue, high cycle fatigue, creep and creep rupture, based on observed interaction and mission critical parameters.

Surface-dependent properties can be tied intimately to crack initiation events within the coating. It is well established that coatings, particularly those that react with the surface of the substrate, can alter the mechanical performance of

the component. High cycle fatigue and thermo-mechanical fatigue are known to be sensitive to coatings. Coatings can either produce a healing effect on surface flaws, or more often, produce critical flaws that lead to failure. Development of coating cracks is a particular concern for brittle coatings. Aside from potential local loss of environmental protection, coating cracks may serve as a critical flaw for service embrittled structural elements.

Loss of coating can have a devastating effect on the component. As most coating properties degrade with service, performance evaluations need to consider not only new material properties, but also properties after considerable aging. An understanding of coating loss and degradation mechanisms is required to ensure component life. Interdiffusion, interfacial phase formation, mechanical discontinuities, oxidation, alloy depletion, and thermal stresses can all contribute to coating spallation. Coating processing, including surface preparation and deposition process, is important in defining coating adhesion. Depending on design and operational parameters (gas velocity, entrained particulate matter, contact geometry, etc.), erosion and wear may also be critical parameters.

The potential need.for EBCs has been identified due to interstitial transport between components in the Prometheus reactor. While the need for a diffusion barrier is the primary driver for adding a coating, mechanical integrity of coating and base metal are equally important. A comprehensive coating evaluation must include testing for diffusion and mass transport, reactions, mechanical integrity of the coating and substrate, and durability in the reactor environment.

Discussion: Thermodynamic considerations identified interstitial transport as a potential mechanism whereby embrittlement and subsequent failure of the refractory metal reactor components could occur. In most of the thermodynamic analyses considered, carbon, and oxygen migrate from superalloy components to refractory metals with the working fluid as the transport medium. While thermodynamics indicate that such a process should occur, at present there is no information to indicate that transport of interstitials through the working fluid occurs at a rate sufficient to jeopardize the mission. In parallel to the current effort, transport kinetics testing was being considered prior to termination of NRPCT participation in the Prometheus program.[85] In absence of such test results, it is impossible to definitely state that an environmental barrier coating is needed for the refractory and/or superalloy to perform their function. For the sake of closure; however, the remainder of the discussion assumes that coatings are required.

Existing environmental barrier coatings for superalloys and refractory metals rely primarily on thermally grown oxide films to provide protection, with iridium providing the only exception. These coatings have been designed for use in highly oxidizing environments where self-healing can occur through the formation of additional alumina, chromia or silica. Given the uncertainty in the coolant chemistry, it is unknown if oxide scale formers can provide adequate protection for superalloys or refractory metals over the life of the mission. The inherent diffusion protection provided by the unoxidized aluminide or silicide coatings is unknown. Iridium has inherent barrier properties; however, it lacks the ability to self-heal in oxidizing environments.

All current data for potential coatings was taken in oxidizing environments (aluminides, silicides) and/or very high temperatures (silicides, iridium). These technologies are mature for air-breathing environments, but have not been used extensively in closed system He/Xe environments. Existing service life expectancy from these coatings is substantially shorter than the envisioned mission life. Given all of these factors, the risk of using existing data for the current mission is substantial.

Uncertainty in the space reactor working fluid and chemistry changes that occur in a closed system presents a significant challenge. For example, under a fixed coolant chemistry defined by Graham in Table 2, silica formers would actively oxidize evolving SiO(g), chromium in the superalloys would not oxidize to form chromia and only the alumina formers would produce protective oxide scales. Furthermore, coatings of iridium and rhenium would not evolve as oxides even at the highest design temperatures.

Given the substantial difference between the experience base and the proposed working fluid environment, a ground-up environmental barrier coating development is likely to be required. The nature of the coating will be intimately linked to the space reactor working fluid and the possible range of chemistries encountered as gas constituents are removed due to reaction or permeability through the piping itself. Given the current uncertainty in the working fluid chemistry, hybrid coating architectures appear most favorable. For EBC applications in the presence of oxygen, an aluminide surface is most desirable. In the absence of oxidizing conditions, aluminides may offer little resistance to interstitial diffusion. As such, a sublayer of iridium appears most promising. Finally, depending on the nature of the substrate, a diffusion barrier such as tantalum carbide may be required.

The necessary coating is intimately tied to the space reactor working fluid. This was clearly illustrated in the course of numerous NRPCT discussions and meetings related to materials and in greater detail by Frederick[8] in which stable operating envelopes for various oxides were considered. Working fluid starting chemistry and changes to the chemistry during the mission must be considered in the selection of an appropriate coating system. If testing confirms that impurity transport kinetics are unacceptable, then coatings may hold the answer.

Recommendations: Given the stability of alumina scales, alumina-forming coatings are recommended for further investigation for the environmental protection of superalloys. It is recommended that the aluminide coating be based upon a platinum group metal (e.g., iridium) to take advantage of improved stability and the potential for platinum group metals to behave as inherent diffusion barriers should the coolant chemistry not support alumina scale formation.

Recommended coatings for investigation for refractory metals include aluminides, and platinum group metals. In oxidizing environments, evaluation of platinum, iridium and ruthenium aluminide with and without an iridium sublayer is recommended. For applications at lower oxygen potential, pure iridium may be considered. Screening tests are recommended to determine if barriers are required to prevent interdiffusion between the substrate and the base metal.

Each coating type has potential pitfalls. Alumina scales are expected to be stable in the working fluid; however, aluminides have not been routinely used on refractory metals and would require substantial development. Iridium-based layers may provide an attractive alternative to scale formers, depending upon coolant chemistry. Iridium does not provide active oxidation protection; however, the incorporation of an aluminide surface layer over iridium may provide the best of both worlds in that an effective barrier layer would be combined with the potential for active protection by the scale forming layer. Concerns over the ductility of the aluminide exist.

It is important to note that these recommendations are for further investigation only. It is not the purpose of this report to provide a down-selected coating. Further testing of these coatings and other potential candidates would have been necessary for down-selection. It is possible that current technologies will not provide adequate performance for either material in the gas coolant over the life of the mission. Ground-up development of coating technology may be required.

Significance to the NR Program: Investigation of environmental barrier coatings for the protection of space reactor internals is based on the possibility that gas phase transport of interstitials may degrade the mechanical behavior of refractory metals, superalloys or other potential materials. Had Prometheus gone forward, it is entirely likely that environmental barrier coatings could have been required to meet mission life requirements. Insufficient information is available to definitively identify one coating as appropriate for the application and significant development is required. Any development program should, however, be predicated on the results of a kinetics evaluation for the uncoated system.
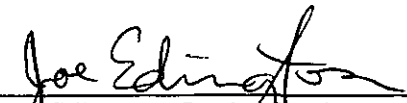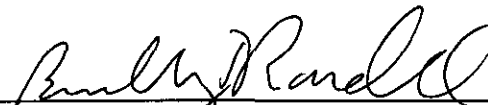
Future Action: At present, there is no future action due to the termination of NRPCT participation in the Prometheus space power plant program. However, had the program continued, future actions would hinge on first demonstrating that interstitial transport through the vapor phase is significant through either a closed loop, natural convection loop or double retort tests. If such transport is significant, further development would look to 1) define the chemistry of the working fluid since so much depends on whether or not an oxide will form, 2) down select the refractory metals and superalloys of interest, 3) down select or develop the coatings based on the working fluid and base metal and 4) provide proof testing for concepts and final recommendations.
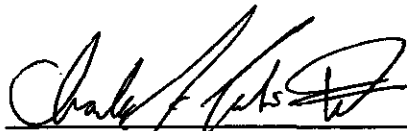
Acknowledgments: The authors would like to acknowledge the thoughtful reviews and insightful discussions of Dr. Wayne Ohlinger and Dr. Matthew Frederick.
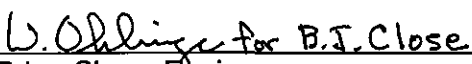
Prepared by:

Stephen M. Sabol, Principal Engineer
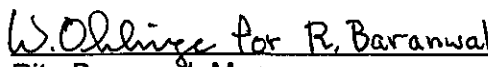Space Reactor Materials Engineering
MT-Advanced Materials Technology

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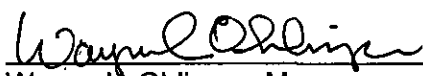MT-Advanced Materials Technology

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