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ADVANCED GAS COOLED NUCLEAR REACTOR MATERIALS EVALUATION AND DEVELOPMENT PROGRAM

TOPICAL REPORT I:
SELECTION OF CANDIDATE ALLOYS

MASTER

**VOL 3: SELECTION OF SURFACE COATING/
SUBSTRATE SYSTEMS FOR SCREENING CREEP
AND STRUCTURAL STABILITY STUDIES**

**GENERAL ELECTRIC COMPANY
ENERGY SYSTEMS PROGRAMS DEPARTMENT
SCHENECTADY, NEW YORK 12345**

GENERAL ELECTRIC

JUNE 20, 1980

Prepared for
**THE U. S. DEPARTMENT OF ENERGY
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TABLE OF CONTENTS

	<u>Page</u>
1.0 SUMMARY	1-1
2.0 INTRODUCTION	2-1
3.0 VHTR ENVIRONMENT CONSIDERATIONS	3-1
4.0 REQUIREMENTS FOR SURFACE PROTECTIVE SYSTEMS	4-1
5.0 COATING CLASSIFICATION	5-1
5.1 Diffusion Coatings	5-1
5.2 Overlay Coatings	5-2
5.3 Ceramic Coatings	5-2
6.0 COATING PROCESSES	6-1
6.1 Electrophoresis	6-1
6.2 Electroplating	6-1
6.3 Cladding	6-1
6.4 Hot Dipping	6-2
6.5 Thermal Spraying	6-3
6.6 Metallizing	6-3
6.7 Pack Concentration	6-4
6.8 Physical Vapor Deposition	6-5
6.9 Slurry	6-6
6.10 Sputtering	6-6
7.0 DISCUSSION OF PROCESS APPLICABILITY	7-1
8.0 RECOMMENDATIONS	8-1
8.1 Near Term	8-1
8.2 Coating Development and Evaluation Programs	8-2
9.0 REFERENCES	9-1

LIST OF TABLES

<u>Table No.</u>		<u>Page</u>
1	List of Selected DCHT Alloys to be Tested in the Coated and Uncoated Condition	4-7
2	Nominal Compositions of Candidate Alloys for DCHT Screening Program	4-8
3	List of Selected NPH Alloys to be Tested in the Coated and Uncoated Condition	4-9
4	Nominal Compositions of Candidate Alloys for NPH Screening Program	4-10
5	Major Protective Coating Systems	5-5
6	Coating/Coating Processes of Interest for VHTR Application	8-7
7	Coating/Coating Process Recommended for VHTR Testing	8-8
8	Coatings/Coating Processes Recommended for VHTR Testing	8-9
9	Coatings/Coating Processes Recommended for VHTR Testing	8-10
10	Summary of Expanded Coating Evaluation	8-11

TOPICAL REPORT
SELECTION OF CANDIDATE ALLOYS

Volume 3

SELECTION OF SURFACE COATING/SUBSTRATE SYSTEMS FOR
SCREENING CREEP AND STRUCTURAL STABILITY STUDIES

1.0 SUMMARY

Considering the high temperature, low O_2 , high C environment of operation in the Very High Temperature Reactor (VHTR) Systems, the utilization of coatings is envisaged to hold potential for extending component lifetimes through the formation of stable and continuous oxide films with enhanced resistance to C diffusion. A survey of the current state of technology for high temperature coatings has been performed. The usefulness of these coatings on the Mo, Ni and Fe base alloys is discussed. Specifically, no coating substitute was identified for TZM other than the well known W-3 (pack silicide) and Al_2O_3 forming coatings were recommended for the Fe and Ni base structural materials. Recommendations as to coating types and processing have been made based on the predicted VHTR component size, shape, base metal and operational environment. Four tests designed to evaluate the effects of selected combinations of coatings and substrate matrices are recommended for consideration.

2.0 INTRODUCTION

The Very High Temperature Reactor (VHTR) Nuclear Process Heat (NPH) and the Direct Cycle Helium Turbine (DCHT) Systems are being developed to provide an expanded energy capability and to facilitate conservation of or substitution for scarce energy resources. In both cases, the use of high temperature He-cooled reactors will require a knowledge of the long term properties of reactor primary coolant containment materials and of the materials used in constructing related hardware. Because of the very high temperatures required for NPH and DCHT applications, the need is evident for materials testing in the proper He environment in the temperature range from 750^o-1050^oC (1382^o-1922^oF) on those alloys which might serve as materials of construction for heat exchangers, ducting, turbine buckets and vanes and other high temperature structural components.

The objectives of the Advanced Gas Cooled Nuclear Reactor Materials Evaluation and Development Program are to:

1. Evaluate candidate alloys for Very High Temperature Reactor (VHTR) Nuclear Process Heat (NPH) and Direct Cycle Helium Turbine (DCHT) applications, in terms of the effect of the primary coolant exposure and thermal exposure on:
 - Surface stability ("corrosion" resistance) in 10,000 hours.
 - Structural stability in 10,000 hours - changes in microstructure and tensile, impact and fatigue properties.
 - Creep-rupture properties in 15,000 hours.
 - Fatigue properties
 - Low Cycle 10³ to 10⁵ cycle
 - High Cycle 10⁵ to 10⁷ cycle

2. Select and recommend materials for future test facilities and more extensive qualification programs.

The environments in both the NPH and DCHT will consist of He with low levels of impurity gases producing a low O_2 activity and a high C activity. These atmospheres are expected to possess the potential for carburization and internal oxidation of highly alloyed, high strength materials. To date, the realization of self-protecting structural alloy components exposed to the primary coolant gas operating temperatures in the NPH and the working gas in the DCHT has not been demonstrated. Neither has the requirement for a protective coating (or over layer) been established. However, in light of the potential for carburization and material oxidation in each of these environments (NPH and DCHT), the usefulness of coatings and claddings in these systems should be evaluated.

The purpose of this study was to review the current state of technology for high temperature coatings and claddings, determine the applicability of each of these processes for use in NPH and DCHT Systems and to recommend a coating and cladding development and evaluation plan for these systems.

3.0 VHTR ENVIRONMENT CONSIDERATIONS

The use of high temperature, high strength alloys is required in all proposed VHTR systems. This study will, however, confine itself to four major components in the systems listed below:

<u>Component</u>	<u>System</u>	<u>Environment</u>	<u>Temperature, °C</u>
Primary Coolant Ducting	NPH	He	900-1000
Primary System Components: steam reformers, heat exchangers	NPH	He/Process Gas or He/He	450-950
Primary Coolant Ducting	DCHT	He	800-950
DCHT Components: blades, vanes	DCHT	He	260-950

The proposed materials of construction for these components are varied and they will be subjected to two basic atmospheres: impure He and/or process gas. Some components in the NPH systems may be exposed to the attack of process gas on one side and effects of primary coolant on the other. The effects of process gas (high or low BTU gas produced by coal gasification) on materials is being investigated in other programs (1, 2) and will be considered only briefly in this report.

Attempts have been made to define the environment of the primary coolant of various VHTR's. Graham, et. al. (3) estimated the impurity levels in three prototype reactors (Peach Bottom, Dragon and AVR) reporting extremely wide ranges of He loop impurities in the three HTRs. However, the impurity levels found in Peach Bottom and Dragon, listed below are more typical of those expected in future VHTR's.

H ₂	10-200 µatm
H ₂ O	~ 1 µatm
CO	8-10 µatm
CO ₂	0.5-1 µatm
CH ₄	1-23 µatm
N ₂	10-20 µatm

The probable source of these impurities and their effects on oxidation and/or carburization potential of the gas also were discussed. From the calculations of the partial pressure ratios: P_{H_2} / P_{H_2O} and P_{CO} / P_{CO_2} , which control oxidation potential and the ratios: P_{CO}^2 / P_{CO_2} , $P_{CO} P_{H_2} / P_{H_2O}$, $P_{CH_4} / P_{H_2}^2$, and $P_{CO} P_{CH_4} / P_{H_2} P_{H_2O}$ which govern the carburization potential, it was concluded that the oxidation potential is very low while the carburization potential is high for the proposed environment.

The impurity levels chosen for the current surface coating applicability review are based on the levels recommended for the test loop in the GE/DOE program ⁽⁵⁾ and are very close to the levels used in the more recent test program described by Graham ⁽³⁾. However, the composition used in the current coating review listed is highly carburizing in comparison to the range of He impurity levels listed earlier for Peach Bottom and Dragon.

He	50-70	atm
H ₂	400	μatm
H ₂ O	2	μatm
CO	40	μatm
CO ₂	0.2	μatm
CH ₄	20	μatm
N ₂	<20	μatm

Using the data of Richardson and Jeffes ⁽⁴⁾ and Graham, et. al. ⁽³⁾, it is seen that for the chosen impurity levels at 927°C, considering only the oxides of interest, the oxides of Ni, Fe and Co are predicted to be unstable. Conversely, the oxides Al₂O₃, TiO₂, SiO₂ and the oxides of all less noble elements would appear to be stable. The oxides, Cr₂O₃ and NbO₂ are borderline and may be stable or unstable depending on small changes in the O₂ activity.

The carburization potential, on the other hand, is very high and the MC type carbides of groups IVB and VB are predicted to be stable as are the $M_{23}C_6$ type carbides. The potential for carburization, however, does not control carburizing rates. These rates are determined by surface reaction rates, the diffusion of the C through surface oxides and the diffusion of the C into the base metal; none of which are currently well defined. However, the thermodynamic predictions for high carburization have been recently reinforced as testing ⁽³⁾ in a similar environment at the temperatures of 900°- 1000°C., has shown the majority of material degradation to result from carburization with little oxidation, either internally or on the surface, being observed.

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4.0 REQUIREMENTS FOR SURFACE PROTECTIVE SYSTEMS

Very little is known concerning the expected oxidation and/or carburization resistance of the candidate alloys, Tables 1-4, to be tested in the low O_2 , high carburizing atmosphere being used in this program. However, knowledge of these alloy systems and the thermodynamics of oxidation and carburization may permit prediction of alloy or coating performance.

From the earlier discussion, it was concluded that the oxides of Si and all less noble elements would be stable along with the oxides of the transition metals in group IVB and VB (V, Ti, Zr, Ta, Hf). The oxides of Mo and the more noble elements would not be stable. The formation of stable Cr_2O_3 is marginal and conditions may exist that could alternately be reducing or oxidizing to Cr. Therefore, the introduction of Cr in an alloy system must not be considered as positive protection against internal oxidation and/or carburization for long term use in the VHTR environment.

The oxides Al_2O_3 , TiO_2 and SiO_2 appear to offer the greatest potential to form stable, continuous and protective films in this environment. Indeed, documentation of the protective nature of these elements, particularly Al_2O_3 and SiO_2 , in oxidizing environments is overwhelming and need not be referenced here. Investigations have also shown these oxides to be beneficial in reducing the carburization of substrates. (6,7,8,9) Hence, it is tentatively concluded that protective systems in this environment must contain one or more of the oxide formers Al, Ti and Si.

The incorporation of these elements into a matrix does not necessarily guarantee a protective film. In fact, it has been observed that the more noble oxides of Cr, Ti, Si, Ni, Co are less protective than Al_2O_3 because of faster inward diffusion of O_2 . (10) Oxidation in this environment will be highly selective and internal oxidation may become significant, reducing the mechanical strength of alloys. Kofstad (10) has summarized the mechanism of

selective or internal oxidation stating: "These latter types of alloys (those of Fe, Co and Ni alloyed with less noble metals such as Cr and Al) will either be selectively oxidized or internally oxidized. In a binary alloy, for instance, the selective oxidation involves diffusion of the less noble metal to the surface and the formation of an external, protective scale of the oxide of the less noble metal. At definite sets of temperature and partial pressure of O_2 , selective oxidation will occur above a critical concentration of the less noble metal in the alloy. Smaller concentrations are needed to lower partial pressure of O_2 . At concentrations smaller than the critical level, the alloy will be internally oxidized through formation of particles of the less noble metal oxide in a zone beneath the external oxide scale. The internal oxidation will depend on the rate of growth of the external scale, and on the rates of diffusion of O_2 and the less noble alloying element (s) in the alloy substrate." Most of the alloy systems to be evaluated in this program are not only alloyed with Cr and Al, but also with Ti and Si, so the possibility of internal oxidation definitely exists. For maximum potential protection then, each system should contain the minimum amount of the least noble oxide former present in the alloy that is required to form a continuous external scale. The mechanical and physical properties of this scale will then determine the ultimate protection provided the matrix.

It is calculated that relatively large quantities of these elements would be required to provide external continuous oxide films. For example, the minimum amount of Al required to form a continuous oxide layer on Ni-base superalloys containing Cr is between 4-6 wt. percent. Loss of available Al through Al_2O_3 formation and spallation during cyclic operation of these alloys may be rapid resulting in the formation of less protective oxide scales with subsequent internal oxidation of compositions containing reduced Al contents.⁽¹²⁾

It is easily seen that the large quantities of Al (and possibly Ti and Si) required to form continuous oxides for long term use in cyclic conditions cannot be tolerated by stable (with respect to TCP or liquid phase formation) structural superalloys. Hence, the necessity for the protective coatings which do contain large reserves of the protective oxide forming elements, is understood.

In considering exposure of VHTR processing system ducting to process gases, results of the MPC-IITRI testing⁽¹⁾ show that the potential for sulfidation is high in the environment of coal gasifiers. This testing, plus research performed by Natesan⁽¹⁹⁾ and Perkins⁽²⁾ show that Cr_2O_3 by itself is not protective and sulfur penetrates readily to sulfidize base material. Natesan⁽¹⁹⁾ proposes that spinels of Cr_2O_3 are more protective. Both Perkins⁽²⁾ and the MPC-IITRI work⁽¹⁾ show that Al_2O_3 is protective in the sulfidizing atmosphere of coal gasifiers. These results also demonstrate the effective use of high Al content coatings for maximum protection in cyclic conditions.

To provide complete protection, Chatterji et. al.⁽¹¹⁾ have identified the general requirements a coating should meet. They are as follows:

- 1) It should form a thin, adherent oxide scale, free from defects such as cracks, blisters, etc., and exhibit minimum mass transport coefficients. The oxide scale should not spall off, vaporize, or undergo phase transformations.
- 2) The coating should remain metallurgically bonded to the substrate during both processing and service. Flaws such as cavities and holes should neither be present nor form later at the coating/substrate interface.
- 3) The coating should exhibit diffusional stability with the substrate so that during service, the two do not undergo excessive reaction to lose the composite nature of the system.
- 4) It should not adversely affect the mechanical properties of the substrate.
- 5) The substrate and the coating must have similar heat transfer and thermal expansion characteristics.
- 6) The coating should be resistant to stress rupture, thermal fatigue, and erosion.
- 7) The coating should be ductile at all temperatures, or should undergo brittle-to-ductile transition at a temperature lower than the actual service temperature.
- 8) It should not promote liquid phase formation at or under the coating/substrate interface during high temperature exposure.

- 9) The coating should be thin, uniform, free from flaws and relatively easy to apply and repair if necessary.

It is apparent that no single coating can meet all these requirements; however, to be judged effective a coating must essentially fulfill the first four requirements with the remaining five requirements balanced to obtain the optimum combination of performance and cost.

Each of these requirements should, however, be considered in evaluating every coating system for use in the VHTR-NPH or the DCHT. With reference to requirement (1) in this environment, the oxide film formed on the coating should exhibit minimum mass transport to C in addition to O_2 . Based on the information available, C is formed by gas reactions at the surface of the metal/coating and diffuses inward through the oxide to the metallic matrix. Metal surfaces have been shown to catalyze C deposition. Therefore, oxide layers may also prove beneficial by reducing C formation. The majority of C and O_2 diffusion is predicted to occur along grain boundaries, especially at the lower temperatures. The function of a protective coating is to lower the amount of C and O_2 diffusing into the base metal to a level where precipitation of carbides or oxides is not favored. As pointed out earlier, in those cases where the oxide/metal interface has a sufficiently low O_2 and high Al activity the continuous Al oxide layer will grow inward at this interface. Otherwise, mixed oxides and possibly internal oxidation will occur.

High concentrations of C will either precipitate as carbides at this interface or diffuse into the metal in search of other heterogeneous nucleation sites. In alloys without additives of Hf, Nb and Ta, C will diffuse readily along base metal grain boundaries precipitating as $(Cr, Mo)_{23}C_6$ or MC carbides such as TiC or VC. In alloys containing significant amounts of Mo and W, the precipitation of $(Mo, W)_6C$ may be preferred over $M_{23}C_6$ at high temperature ($927^\circ C$). C penetration especially along grain boundaries may be extensive, resulting in reduced mechanical properties. It is theorized that alloys containing Hf, Nb, and Ta, on the order of 3 weight percent total, would be more resistant to damaging carburization as precipitation of $(Mo, Cr)_{23}C_6$ and $(Ti, V)C$ at grain boundaries would be reduced by the

preferred precipitation of (Hf, Ta, Nb) C more uniformly throughout the matrix. It is not proposed that the introduction of Hf, Ta or Nb in an alloy will reduce the total C concentration, but rather it will disperse the precipitation of carbides thus reducing their detrimental effects on mechanical properties. This technique has been successfully used by aerospace workers to uniformly distribute carbide precipitations in powder metallurgy superalloys.

Low ductility can be significant problem, especially in coating with high Al contents. The relationship between Al content and the brittle to ductile transformation temperature (Requirement 7) has been established for Al coatings⁽¹²⁾ and is lower than the operating temperature of the NPH nad DCHT components. However, thermal fatigue can still strain the coating beyond its fracture limit causing cracks which may extend into the base metal.

The high vapor pressure of aluminides could also cause vaporization of Al from the surface of coatings in low oxygen environments.⁽¹⁷⁾ The O_2 activity in the NPH and DCHT must be high enough to permit the formation of self-healing Al_2O_3 films to prevent loss of Al in this manner.

The lack of metallurgical bonding, Requirement 2, has historically been a potential problem for coatings applied by mechanical deposition at low temperatures. Heat treatment for diffusional purposes after deposition is generally performed in these cases and is usually quite satisfactory.

Inward diffusional stability of coatings should be of second order importance at $900^\circ C$ ⁽¹⁴⁾, however, at high temperature in systems with non-scaling oxide films or in systems exhibiting high solubility for this coating, this mode of degradation can become significant.

In regard to Requirement 4, mechanical properties in extreme environments are often improved by the incorporation of an environment resisting coating. The effects of candidate coatings on alloys must be determined for these environments after both short and long term exposure. These data must be compared to uncoated materials of the same exposure.

Another important requirement (9), or restriction in this case, is the ability to easily apply and repair the coating. The physical process of coating the inside of small diameter process heat or coolant tubes or ducts itself eliminates several of the coating processes from serious consideration. Here the difficulties of application must be balanced against the cost and performance to determine viable solutions.

TABLE 1

LIST OF SELECTED DCHT ALLOYS
TO BE TESTED IN THE COATED AND UNCOATED CONDITION

Alloy Type	Alloy	Application	Surface Treatment ^(b) For Testing	
			Screening Creep	Unstressed Exposure
Molybdenum-Base (Wrought)	TZM	Blade, Vane	UC	UC & C
Nickel-Base ODS Alloy	YD-Ni	Vane	(No Tests)	UC
	MA-754	Vane	UC	UC
	YD-NiCrAl	Vane	(No Tests)	UC
Nickel-Base Superalloy (All Cast Except Wrought U-720)	MM-0011 (MM-247) ^(a)	Blade, Vane	UC	UC
	Rene' 125*	Blade, Vane	-	-
	Rene' 80	Blade, Vane	UC	UC & PO
	Rene' 100	Blade, Vane	UC	UC
	U-720	Blade, Vane	UC	UC
	M-21	Blade, Vane	(No Tests)	UC & PO
	IN-792*	Blade, Vane	-	-
	B-1900*	Blade, Vane	-	-
	Alloy 713LC	Blade, Vane	UC	UC, C, C+PO
	IN-738	Blade, Vane	UC	UC
	NX-188	Blade, Vane	UC	UC
	MM-004*	Blade, Vane	-	-
Wrought Nickel- Base Austenitic	Hastelloy X	Duct	Included as NPH alloys.	
	Inconel 617	Duct		

*Alternate Selection

(a) To be evaluated in both conventionally cast and directionally solidified forms.

(b) UC - Uncoated

C - Coated

PO - Preoxidized

C + PO - Coated Plus Preoxidized

TABLE 2
NOMINAL COMPOSITIONS OF CANDIDATE ALLOYS
FOR DCHT SCREENING PROGRAM⁽⁵⁾

Nominal Composition (Wt. %)											
Alloy	C	Ni	Cr	Al	Ti	Co	Ta	Mo	W	Nb	Other
<u>Mo-Base</u>											
Unalloyed Mo (Rx)	0.02	-	-	-	-	-	-	Bal.	-	-	
TZM	0.015	-	-	-	0.45	-	-	Bal.	-	-	0.09 Zr
<u>ODS Alloys</u>											
YD-Ni	-	Bal.	-	-	-	-	-	-	-	-	2.0 Y ₂ O ₃
MA-754	0.07	Bal.	20.5	0.3	0.5	-	-	-	-	-	0.6 Y ₂ O ₃
HD-8077	-	Bal.	16	4.0	-	-	-	-	-	-	0.8 Y ₂ O ₃
MA-757	-	Bal.	16	4.0	-	-	-	-	-	-	0.6 Y ₂ O ₃
YD-NiCrAl	-	Bal.	16	4.0	-	-	-	-	-	-	1.0 Y ₂ O ₃
MA-755	0.07	Bal.	15	4.5	3.0	-	-	3.0	5.5	-	2.5 Ta, 1.0 Y ₂ O ₃
MA-956E	-	-	21	5.0	-	-	-	-	-	-	0.6 Y ₂ O ₃ , Bal. Fe
<u>Ni-Base Superalloys</u>											
<u>Very High Strength</u>											
Rene' 125	0.11	Bal.	8.9	4.75	2.5	10.0	3.8	2.0	7.0	-	1.5 Hf
TRW-VIA	0.13	Bal.	6.0	5.4	1.0	7.5	9.0	2.0	5.8	0.5	0.5 Re, 0.5 Hf
MM-200	0.15	Bal.	9.0	5.0	2.0	10.0	-	-	12.5	1.8	
MM-246	0.15	Bal.	9.0	5.5	1.5	10.0	1.5	2.5	10.0	-	
MM-002	0.15	Bal.	9.0	5.5	1.5	10.0	2.5	-	10.0	-	1.5 Hf
MM-247 (MM-0011)	0.16	Bal.	8.3	5.5	1.0	10.0	3.0	0.7	10.0	-	1.5 Hf
<u>High Strength</u>											
B-1900	0.1	Bal.	8.0	6.0	1.0	10.0	4.3	6.0	0.1	0.1	
Rene' 100	0.18	Bal.	9.5	5.5	4.2	15.0	-	3.0	-	-	
Rene' 80	0.17	Bal.	14.0	3.0	5.0	9.5	-	4.0	4.0	-	
IN-792	0.21	Bal.	12.7	3.2	4.2	9.0	3.9	2.0	3.9	-	
M-21	0.13	Bal.	5.7	6.0	-	-	-	2.0	11.0	1.5	
<u>Intermed. Strength</u>											
IN-738	0.17	Bal.	16.0	3.4	3.4	8.5	1.7	1.75	2.6	0.9	
Alloy 713LC	0.05	Bal.	12.0	5.9	0.6	-	-	4.5	-	2.0	
Rene' 77	0.07	Bal.	15.0	4.25	3.5	14.2	-	4.2	-	-	
MM-004	0.05	Bal.	12.0	5.9	0.6	-	-	4.5	-	2.0	1.3 Hf
NX-188	0.04	Bal.	-	8.0	-	0.1	-	18.0	-	-	
Udimet-720 (a)	0.04	Bal.	18.0	2.5	5.0	15.0	-	3.0	1.3	-	0.03 Zr
<u>Low Strength</u>											
MM-421	0.15	Bal.	15.5	4.25	1.75	10.0	-	1.75	3.5	1.75	
Udimet 500	0.08	Bal.	19.0	3.0	3.0	18.0	-	4.0	-	-	
SEL-15	0.07	Bal.	11.0	5.4	2.5	14.5	-	6.5	1.5	0.5	
IN-731	0.18	Bal.	9.5	5.5	4.7	10.0	-	2.5	-	-	

(a) Wrought alloy; all other Ni-base superalloys are cast.

TABLE 3

LIST OF SELECTED NPH ALLOYS
TO BE TESTED IN THE COATED AND UNCOATED CONDITION

Alloy Type	Alloy	Application (a)	Surface Treatment (b). For Testing	
			Screening Creep	Unstressed Exposure
Wrought Iron-Base Austenitic	Alloy 800H	D, L, V, I, R	UC & C	UC & C
	Incoloy 802	D, L, V, I, R	UC	UC
	Incoloy 807	D, R, I	UC	UC
	Incoloy DS	D, L, I	UC	UC
	HD-556	D, L, R, V, I	UC	UC
	DIN 1.4981*	D, L, R	-	-
	Sanicro 32X*	D, L, V, I, R	-	-
Cast Iron-Base Austenitic	Manaurite 36XS	D, R	UC	UC
	Manaurite 900	D, R	(No Tests)	UC
	HK-40	D, R	UC	UC
	IN-519	D, R	UC	UC
	Manaurite 36X*	D, R	-	-
	Hastelloy X	D, L, V, R, I	UC	UC
Wrought Nickel-Base Austenitic	Inconel 617	D, L, I, R	UC & C	UC & C
	Inconel 618E	D, L, I, R	(No Tests)	UC
	Inconel 625*	D, L, V, I, R	-	-
	Nimonic 86*(c)	D, L, V, I, R	-	-
	Mo-Re 2	D, R	UC	UC
Cast Nickel-Base Austenitic	Super 22H*	D, R	-	-
	Supertherm*	D, R	-	-
	MA-956E	L, I	UC	UC

*Alternate Selection

(a) Legend: D - Ducting R - Reformer Tube
 L - Liners I - Intermediate Heat Exchanger
 V - Valves

(b) UC - Uncoated
 C - Coated

(c) Equivalent of IN-586.

TABLE 4

NOMINAL COMPOSITIONS OF CANDIDATE ALLOYS FOR
NPH SCREENING PROGRAM⁽⁵⁾

Nominal Composition (Wt. %)														
Alloy	C	Ni	Cr	Fe	Si	Mn	Co	Mo	W	Nb	Al	Ti	Cu	Other
<u>Wrought Fe-Base Austenitics</u>														
Alloy 800	0.04	32.5	21	Bal.	0.5	0.75	-	-	-	-	0.4	0.4	0.4	
Alloy 800H	0.08	32.5	21	Bal.	0.5	0.75	-	-	-	-	0.4	0.4	0.4	
Incoloy 802	0.35	32.5	21	Bal.	0.38	0.75	-	-	-	-	0.6	0.75	-	
Incoloy DS	0.05	37	18	Bal.	2.3	1.1	-	-	-	-	-	0.2*	0.5*	
Sanicro 32X	0.07	31	21	Bal.	-	-	-	-	3	-	0.35	0.35	-	
HD-556	0.10	20	22	Bal.	0.6	1.5	20	3	2.5	0.1	0.3	-	-	0.9 Ta
Incoloy 807	0.08	40	20	Bal.	1.0*	1.0*	8	-	5	1.0	0.4	0.4	0.5*	
DIN 1.4981	0.05	16	16	Bal.	0.5	1.5*	-	2	-	0.5	0.1*	0.1*	-	
<u>Cast Fe-Base Austenitics</u>														
IN-519	0.30	24	24	Bal.	1.0*	1.0*	-	-	-	1.5	-	-	-	
HK-40	0.40	20	26	Bal.	1.8*	1.5*	-	0.5*	-	-	-	-	-	
Manaurite 36X	0.40	34	25	Bal.	1.5	1.5	-	-	-	1.5	-	-	-	
Manaurite 900	0.15	32	21	Bal.	1.0	1.5	-	0.3	-	1.5	-	-	-	
Manaurite 36XS	0.40	34	26	Bal.	2.0*	2.0*	-	-	2	1.5	-	-	-	
Mo-Re 1	0.45	37	26	Bal.	1.5	1.5	-	-	1.4	-	-	-	-	
HP-50	0.50	35	26	Bal.	2.0	-	-	-	-	-	-	-	-	
<u>Wrought Ni-Base Austenitics</u>														
Hastelloy X	0.10	Bal.	22	18.5	0.5	0.5	1.5	9	0.6	-	-	-	-	
Hastelloy X-280	0.10	Bal.	22	18.5	0.5	0.5	-	9	0.6	-	-	-	-	
Hastelloy S	0.02	Bal.	15.5	1	0.4	0.5	-	14.5	-	-	0.2	-	-	0.02 La
Nimonic 75	0.12	Bal.	19.5	2.5	0.5	0.5	-	-	-	-	0.15	0.4	0.25	
Nimonic 80A	0.05	Bal.	19.5	1.5	0.5	0.5	1.0	-	-	-	1.4	2.3	0.1	
Nimonic 90	0.06	Bal.	19.5	1.5	0.75	0.5	18.0	-	-	-	1.5	2.5	-	
Nimonic 86	0.05	Bal.	25	-	0.5	0.5	-	10	-	-	-	-	-	0.03 Ce
Inconel 600	0.08	Bal.	15.5	8	0.25	0.5	-	-	-	-	-	-	0.25	
Inconel 601	0.05	Bal.	23	14	0.25	0.5	-	-	-	-	1.4	-	0.5	
Inconel 617	0.07	Bal.	22	-	1.0*	1.0*	12.5	9	-	-	1.0	0.6*	0.5*	
Inconel 625	0.05	Bal.	22	3	0.25	0.25	-	9	-	4.0	0.2	0.2	-	
Inconel 618E	0.05	Bal.	23	15	-	-	0.1*	-	6	-	-	-	-	
<u>Cast Ni-Base Austenitics</u>														
IN-638	0.5	35	26	Bal.	0.3	0.3	15	-	5	1.0	-	-	-	
IN-643	0.5	Bal.	25	3	0.3	-	12	0.5	9	2.0	-	-	-	0.25 Zr
Supertherm	0.5	35	26	17	1.6	-	15	-	5	-	-	-	-	
Mo-Re 2	0.4	50	33	-	0.3*	0.3*	-	-	16	-	1.0	-	-	
22H	0.5	48	28	Bal.	1.0	1.3	-	-	5	-	-	-	-	
Super 22H	0.5	48	28	Bal.	1.0	1.3	3.2	-	5	-	-	-	-	
<u>ODS Alloys</u>														
HD-8077	-	Bal.	16	-	-	-	-	-	-	-	4.0	-	-	1.5 Y ₂ O ₃
MA-754	0.07	Bal.	20	-	-	-	-	-	-	-	0.3	0.5	-	0.6 Y ₂ O ₃
MA-755	0.07	Bal.	15	-	-	-	-	3	5.5	-	4.5	3.0	-	1.0 Y ₂ O ₃ , 2.5 Ta
MA-956E	-	-	20	Bal.	-	-	-	-	-	-	5.0	0.4	-	0.5 Y ₂ O ₃

* Max.

5.0 COATING CLASSIFICATION

Several excellent reviews of coating processes are currently available and were used extensively in preparing this report. The recent papers by Chatterji, et. al. (11,13), Grisaffe⁽¹⁴⁾ and Goward⁽¹⁵⁾ were most helpful and are recommended to the reader who desires more detail.

Coatings systems for high temperature alloys can be classified into three general groups: diffusion coatings, overlay coatings and ceramic coatings. Within each of these general groups, many different methods of application are available. Table 5 summarizes the major techniques which are used to apply these coatings plus the major advantages and disadvantages associated with each process. Of the three general coating groups, diffusion and overlay are of major importance being used extensively throughout industry. Ceramic coatings are of lesser importance and are not used to the same extent as are the metallic coatings.

5.1 Diffusion Coatings

Diffusion coatings are formed via deposition of metallic constituents on the surface of parts followed by diffusion of these coatings into the part either during subsequent deposition, if performed at high temperature, or after deposition is completed using a high temperature heat treatment. In either event, the final product is a metallurgically bonded alloyed surface for the component. Al, Cr or Si are the most commonly deposited elements with aluminizing being the most widely used of the three. In this case, the diffusion of Al into the matrix material forms metal aluminides which upon exposure, form continuous, protective Al_2O_3 layers. These scales have the potential to quickly reform in the event of oxide spallation. Chromizing and siliconizing produce Cr and Si rich layers resulting in protective layers of chromia and silicides respectively. The major advantages of diffusion coatings is the ease with which complex components can be coated and the low cost of application.

5.2 Overlay Coating

The bonding, cladding or deposition of a highly oxidation or corrosion resistant alloy to structural materials not as resistant to attack is a widely used method of providing protection to the structural member. Adherence of the coating may initially be mechanical, as is the case in thermal sprayed coatings, but final bonding is generally metallurgical with a small amount of diffusion being accomplished by high temperature treatment during or after application of the coating. Typically, the alloys used as overlay coatings range from clad stainless steels to electron beam deposited MCrALY's (where M is Fe, Ni or Co). Major advantages of these types of coatings are (1) potential for improved coating ductility, (2) coating compositional flexibility and (3) the ability to apply thick coatings.

5.3 Ceramic Coatings

Ceramic coatings are generally applied by one of three methods: slurry, thermal spraying or sputtering. Application by thermal spraying and slurries benefit from high deposition rates. The largest single drawback to using ceramic coatings for protection is that they do not possess the ability to reform oxide layers; thus spallation of the ceramic will generally result in direct exposure of the base metal.

TABLE 5

MAJOR PROTECTIVE COATING SYSTEMS

Process	Applicable Coating Group	Advantages	Disadvantages
Electrophoresis	Diffusion Overlay	Compositional Flexibility Control of Coating Thickness	Limited to Small Components Little Experience Requirement for HIP
Electroplating	Diffusion Overlay	Simple, Inexpensive Process	Deposition of Alloys Not Possible Non-Uniform Deposits
HIP-Cladding	Diffusion Overlay	Thick Coatings Possible Some Composition Flexibility	Lack of Coating/Substrate Compatibility Low Ductility of Alloyed Foil Requirement for HIP
Hot Dipping	Diffusion Overlay	Compositional Flexibility	Matrix Exposed to Very High Temp. Non-Uniform Deposits
Thermal Spraying	Ceramic Diffusion Overlay	High Deposition Rates Compositional Flexibility	Non-Uniform Deposits Porous Structures Possible Line of Sight Deposition
Metallizing	Diffusion	Any Material Can Be Coated	Deposit Must be Higher in Electromotive Series than Base
Pack Cementation	Diffusion	Complex Shapes Easily Coated	Limited by Size of Available Pack
Physical Vapor Deposition	Diffusion Overlay	High Deposition Rates Compositional Flexibility	Coating Defects Line of Sight Deposition Elaborate Vaporization Equipment
Slurry	Ceramic Diffusion Overlay	Compositional Flexibility	Porous Structures Possible Line of Sight Deposition
Sputtering	Ceramic Diffusion Overlay	Compositional Flexibility	Elaborate Equipment Required Coating of Complex Shapes Difficult Low Deposition Rates

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6.0 COATING PROCESSES

Taken alphabetically, the methods of application of high temperature coatings are described as follows:

6.1 Electrophoresis

Widely used in the automobile, appliance and office equipment industries⁽¹⁸⁾, electrophoresis has yet to gain industrial use in the high temperature coating field. The process is based on the movement of suspended particles through a fluid media resulting from an electromotive force applied to the suspension. Components to be coated and the walls of the coating tank generally serve as opposite charged electrodes. The particles in suspension are electrically attracted to the component and uniformly deposited. The as-deposited coating is generally porous requiring densification by hot isostatic pressing (HIP) prior to diffusion heat treatment.⁽¹¹⁾ There is very little reported experience as to the applicability of the process to high temperature applications and it does not appear to warrant additional attention for use on VHTR components.

6.2 Electroplating

The plating of material by electrolysis of metals in aqueous media is a well known and widely used process especially for Ni, Cr and Al plating. The majority of uses are low temperature; however, high temperature applications have also been employed for some time. The deposition of layers of different elements, which are then diffused together, provides the ability for alloy deposition. As deposited, bonding is purely mechanical and diffusion at high temperature is required to insure adequate metallurgical alloying and adhesion to the substrate⁽²⁰⁾.

6.3 Cladding

Cladding of structural components with a second alloy to provide

resistance is generally performed in lieu of substituting the second alloy for the structural component for one of the two following reasons: (1) the quantity of material requiring protection is large and a thin cladding is cheaper than total replacement or (2) the alloy possessing the corrosion resistance does not possess the mechanical properties required in the design. An example of the former is the cladding of carbon steel with a high Cr stainless steel for corrosion resistance. The systems of greater interest, representing the latter case, is the cladding of turbine blades with sulfidation resistant alloys. Several such cladding alloys have been developed. Two Fe base alloys (GE-2541 and GE-1541) containing 25 or 15 Cr, 4 Al and 1 Y have shown excellent resistance to attack in sulfidizing and oxidizing atmospheres. Inconel 671 (Ni-50Cr) also has shown potential in selected environments. Attempts to substantially strengthen these alloys have thus far failed ⁽²²⁾, however, this concept is still being pursued. ⁽²⁾ This technique involves bonding a thin foil of coating material on the substrate. Preforming of the cladding is usually required with final fit and diffusion bonding to complex parts performed by hot isostatic pressing.

Additional work at NASA ^(23,24) found that FeCrAlY cladding systems diffused rapidly into superalloy substrates thus losing the ability to form protective layers of Al_2O_3 after long term use. General Electric also has evaluated this concept extensively and has a contract with DOE ⁽²⁶⁾ to develop and evaluate cladding systems for use in combined cycle power plants. This process is inherently limited by the ductility of the cladding, with Al contents usually maintained below 6%. Aluminizing of the part prior to or after cladding has been found to improve long term corrosion resistance. ^(26,27)

6.4 Hot Dipping

Coatings may be applied by the relatively unsophisticated method of dipping into a bath of molten metal. Low temperature coatings of Zn and Sn for steels have been used successfully for many years. ⁽²⁰⁾

It is seen that the coating alloy must have a melting point substantially lower than the alloy to be coated. Of the elements suitable for protection at high temperatures, only Al has a sufficiently low melting point.⁽²⁰⁾

Generally, withdrawal rates are very difficult to match to temperature to obtain uniform coating thicknesses.⁽¹⁸⁾ This process is not recommended for VHTR components.

6.5 Thermal Spraying

Ceramic, cermet and metallic coatings may be applied to substrates by propelling small particles of the object materials, which have at least one constituent being heated to the point of plasticity or liquidity, onto substrates. Essentially any material that melts prior to evaporation can be deposited by this technique. The velocity of propelled particles can be varied from subsonic to over Mach 3. Four general processes are used. They are: (1) Metalizing - the melting and propelling of a wire fed through a combustion flame, (2) flame spraying - the heating and propelling of powders via combustion gases, (3) plasma spraying - heating and acceleration of powders provided by the dissociation and ionization of gases, and (4) D-Gun, a Union Carbide process which heats and propels powders using the instantaneous pressure release of a small internal combustion process.

Aerospace has put these processes to good use in the areas of abrasion resistance, thermal barriers, repair (rebuild) of components, gas path abradable seals and corrosion resistant coatings.

Bonding of coatings is purely mechanical. Maximum bond strength is obtained by high temperature diffusion after deposition. Uniform deposition is difficult on complex shapes and the process is strictly line of sight. Control of coating quality has traditionally been difficult in this process.

6.6 Metallizing

Metallizing is a high temperature electrolyte process carried out at

temperatures sufficiently high to diffuse the coating during deposition. Molten fluoroide baths serve as the electrolytes and contains fluxes to maintain oxide free surfaces for deposition. ⁽²⁸⁾ Metallizing has not been used on a large scale as a coating technique for high temperature components ⁽¹¹⁾ and will not be considered further in this review.

6.7 Pack Cementation

Of the coating processes developed for high temperature applications, pack cementation is industrially the most important because of its wide use, ease of application and low cost. This process is primarily used to produce Al rich coating for turbine operations. It has however, been used to deposit a number of elements such as Cr, Ti, Si, Ta, B, Sn, Mo, Cd, Be and Nb on a wide variety of substrates. In this process, the metal to be deposited (in powder form), an inert filler material such as Al_2O_3 , an activator such as a halide salt and the component to be coated are placed in a retort, covered and heated in a controlled atmosphere furnace. The process of coating is by chemical vapor deposition as the heated activator volatilizes forming a volatile compound with the metal to be deposited. Since the activity of the metal to be deposited is higher in the volatile compound than in the component to be coated, the compound decomposes on the surface of the component. Here the metal is deposited and the halide released to react with additional powder metal. ⁽²⁹⁾ The deposited metal diffuses into the component reducing the surface activity thus permitting additional precipitation at the surface.

There are various modifications of the pack cementation process, such as halogen streaming, ⁽²¹⁾ vacuum pack ⁽³⁰⁾ and the slurry pack process ⁽³⁰⁾, all resulting in basically the same final product.

The process of aluminization by pack cementation has been thoroughly studied and deserves additional consideration in this report in light of its potential for use on VHTR components.

Based on early work by Goward and Boone,⁽³¹⁾ it was theorized that there are two general classes of aluminide pack cementation coatings; high activity and low activity. High activity coatings are applied at low temperatures (1400°-1800°F) with a large source of Al. The high activity of Al results in the formation of Ni_2Al_3 on nickel alloys. Ni_2Al_3 has a high defect concentration thus permitting rapid inward diffusion of Al. The Ni_2Al_3 phase is undesirable because of its low melting point and brittle nature and high temperature diffusion heat treatments are used to convert it to NiAl , the desired phase.⁽¹⁴⁾

In the low activity process, the temperature is raised and the activity of Al in the pack is lowered. NiAl is formed directly in the pack deposition/diffusion cycle, with Ni the primary diffusing species, diffusing outward in this instance.

In more recent work, Rairden et al.^(32,33) claim that the two processes (high and low activity) are essentially the same. Their work shows that a rapid deposition of Al occurs in the early stages of processing (i.e., during heat up to temperature) with the deposited Al molten.

6.8 Physical Vapor Deposition

Realizing the compositional restriction of diffusion coatings and claddings, work was initiated in the 1960's to develop a deposition process which would effectively coat turbine components with alloys highly resistant to oxidation and sulfidization. Physical vapor deposition, which consists of vaporizing a continuously fed ingot in a vacuum with an electron beam,⁽³⁹⁾ was identified as having the greatest potential to apply a series of experimental alloy coatings based on the FeCrAlY system developed by Wukusick and Collins.⁽⁴⁰⁾ Although more protective than conventional aluminide coatings, the diffusional stability of the Fe-Al phases was determined to be poor in comparison to NiAl or CoAl . Therefore, more recent developments have resulted in the NiCrAlY ,⁽⁴¹⁾ and CoCrAlY ⁽⁴³⁾ coating alloys which exhibit excellent resistance to oxidation and/or sulfidation. Typically, however, the degree of oxidation resistance is

proportional to the amount of Ni in the system with sulfidation resistance showing the same relationship to the Co content in the coating. Al is added in quantities from 4 to 15% to provide protection by Al_2O_3 formation. Cr is added to improve corrosion resistance and to increase the activity of Al thus permitting formation of Al_2O_3 at low Al levels.

The function of Y is not as clear. Recently, Golightly, et al. (44) and Pettit and Giggins (45) concluded that Y improves oxide adherence by prevention of void formation of the alloy-oxide interface by the provision of vacancy sinks and by keying or pegging the oxide scale to the metal matrix via oxidation of Y at grain boundaries. Golightly et al. (44) also believe that the incorporation of Y slows the outward diffusion of Al through the Al_2O_3 thus forcing planar oxide growth at the oxidemetal interface controlled by the inward diffusion of O_2 .

6.9 Slurry

A mixture of fine metallurgical powders and a solvent is applied via painting, spraying or dipping in this process. The solvent is driven off by low temperature drying in air. Subsequently, heat treatment in a controlled atmosphere fuses or sinters the coating, bonding it to the matrix via diffusion. (46)

Coatings of multiple elements have been attempted, but have not generally been successful. This process has been popular in aluminizing superalloys for use in gas turbines.

6.10 Sputtering

The bombardment of a target (cathode) of ionized gas molecules causes the release of target atoms. The target atoms are then electrically attracted to a biased substrate where they redeposit forming a very uniform coating. This process, known as sputtering, is very effective for

applying well controlled, thin films. Rates of deposition are extremely slow and therefore this process is not economical for the deposition of thick film coatings. A modification of this process, known as liquid phase sputtering, produces much faster deposition rates but is not fully developed at this time.

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7.0 DISCUSSION OF PROCESS APPLICABILITY

Coating process restrictions are varied for the four component systems considered in this review.

The turbine components for the DCHT will require coating only on the exterior surfaces. It is estimated that these components will range in length from less than 0.15 meters (six inches) to approximately 1.20 meters (four feet). Configurations will be complex with sharp corners, contours and edges.

Of the ten processes considered, four appear feasible for these sizes of DCHT turbine components. These are: HIP cladding, thermal spraying, pack cementation and slurry. Physical vapor deposition may also be used to coat the smaller DCHT components of up to 0.9 meters (47) feet) in length.

The primary coolant ducting for the NPH and DCHT applications may require coatings only on the inner diameter of the ducts. The ducts range in size from 0.9 meters (three feet) to 214 meters (eight feet) in diameter. Section length will be approximately 6 meters (20 feet). Surfaces should be smooth and of regular shape with the ducts, if metallic, probably constructed by welding roll formed sheet metal segments. Because of the brittle nature of most protective coatings, the coating process will probably be performed after roll forming and welding of the ducts. Because of the size of the ducting, only four coating processes; pack cementation, slurry, thermal spraying and electroplating, are currently commercially feasible. Cladding may be possible but vessels do not exist for HIPing sections of this length. Therefore, an alternate bonding technique such as that used by Lukens Steel would have to be employed. For ductile and weldable coatings or claddings it may be possible to clad prior to roll forming. Pack cementation appears best suited for this coating application. Currently, retort size restrictions limit the coatable component to a size of

0.8 meters (33 inches) in diameter by 13.7 meters (45 feet) in length;⁽⁴⁴⁾ however, larger retorts could be fabricated,

The interior and exterior surfaces of the primary system components (heat exchangers) for process heat applications are being considered for coating. Sections of tubing will be approximately 6-12 meters (20-40 feet) long. Interior diameters are expected to range from 0.025 to 0.127 meters (one to five inches) and will definitely pose severe restrictions on the number of coating processes useable. Economic considerations dictate that in some instances both inner and outer surfaces be coated simultaneously. The extremely small inner diameter severely limits the number of processes useable. Pack cementation is again the logical choice to deposit a uniform, controlled coating to this small diameter tubing. Another technique, which is co-extrusion, is capable of producing bimetallic tubes of small diameter. International Nickel Co. has developed the process for Alloy 800 and Inconel 671, currently marketing it under the name INCOCLADtm. If coated separately from the inner diameter, the outer diameter of this tubing may be coated by a variety of processes. Slurry, pack cementation, physical vapor deposition⁽⁴⁷⁾ and thermal spraying are all processes which are well suited for ducting of this size.

8.0 RECOMMENDATIONS

8.1 Near Term

For purposes of this program, the evaluation of a wide range of coating processes which result in essentially the same final product (e.g., pack cementation and electron beam deposition of Al) is not recommended. The program should concentrate on evaluating several different alloy coatings using a proven deposition process to determine the feasibility of protecting alloys from carburization and internal oxidation in VHTR environments. Therefore, the following coating systems are recommended for testing in this program.

Aluminide	- Pack Cementation
Platinum-Aluminide	- Pack Cementation
NiCrAlY	- Physical Vapor Deposition
Silicide	- Pack Cementation

From earlier discussions, it is apparent that Al_2O_3 forming coatings may be protective in VHTR environments. Those coatings which form a protective Al_2O_3 scale can be divided into two classes: aluminides and MCrAlY's. Within the aluminide class, there are a number of alloy modifications which can be made; however, one that is particularly well known is the Pt-addition. Within the MCrAlY class, there are several modifications; some of the better known are: CoCrAlY, NiCrAlY, FeCrAlY, CoNiCrAlY and MCrAlHf.

The evaluation of the aluminides on components is strongly recommended because of the lowest cost and ease of application. In light of the improved oxide adherence provided by the addition of Pt to aluminides, the testing of Pt-aluminides also is recommended.

It is suggested that NiCrAlY and FeCrAlY systems be evaluated for use in the environment of the VHTR. Although Ni, Co or FeCrAlY systems can be applied by commercial vendors⁽⁴⁷⁾, NiCrAlY is best suited for applications where good diffusional stability is required. The FeCrAlY is recommended because of superior ductility compared to CoCrAlY and NiCrAlY. This increased ductility may permit roll forming of preclad sections of primary ducting. Welding of low Cr GE-1541 also may be successful.

The selection of coatings for Mo-Ti-Zr (TZM) DCHT components is based on the work performed over 10 years ago which is summarized well by Gibeaut and Bartlett⁽⁴⁹⁾. These results and the evaluation of others have shown the most effective barrier to oxidation for TZM to consist of MoSi_2 produced by slurry and pack cementation. Two coatings, produced by Chromalloy, Division of the Chromalloy American Corporation, W-2 and W-3, have received the most attention with W-3 being preferred. The W-3 coating is a proprietary, B modified silicide applied by the pack cementation process. B is added to lower the melting point of the coating promoting a self-healing liquid phase.

More recently, Climax Molybdenum Company of Michigan have initiated a program to evaluate coatings for Mo to reduce carburization in VHTR environments. However, to this date no results are available. Coatings of interest are reported to be Cu, Au and glass⁽⁵⁰⁾.

In light of the lack of data from the program by Climax, siliciding of TZM by pack cementation appears to be the most logical coating to evaluate. Facilities exist that are large enough to handle the full range of DCHT turbine components if this alloy/coating system is ultimately chosen for use. From tables one and three, the alloys to be considered for coating in the initial phases of the VHTR program are TZM, Alloy 800H, Inconel 617 and Alloy 713LC. The coatings/coating processes of immediate interest for these alloys are summarized in Table 6.

Either DCHT alloy, Alloy 800H or Inconel 617 is recommended for coating with a cladding alloy which is weldable and formable. Therefore, the low Al, low Cr version (GE-1541) or FeCrAlY is recommended for testing. Also, rather than subject the test to the additional variables of cladding, it is suggested that the FeCrAlY be deposited by physical vapor deposition (PVD). The NiCrAlY also should be deposited by PVD and should be a high Al content. The composition of PWA 267 (Ni-20Cr-12Al-0.4Y) would be a good choice. AIRCO-Temescal of California is licensed by United Technologies Corporation to apply both NiCrAlY and FeCrAlY by PVD. Chromalloy's Pt-aluminide (RT22) coating has been used extensively in heavy duty gas turbines by GE and is recommended for use in this program. The CODEP process is recommended for the unmodified pack aluminide coating as it can be performed in-house at GE or at several outside vendors. Chromalloy is qualified to apply CODEP and should be used to minimize, as much as possible, vendor to vendor coating process variables in the pack cementation coatings applied.

Pack cementation to form a silicide is the sole recommended coating for TZM. Based on the available information, Chromalloy's W-3 coating should be used. Coating thickness should be maintained between 0.025-0.050mm (0.001-0.002 inches) for optimal performance (50).

Under the constraints of the program, a total of four preselected alloys are to be tested initially, including one coating on TZM. The selection of recommended alloys and coatings are shown in Table 7. This evaluation, which includes four coatings on four different alloys, does not permit the separation of coating and base alloy effects. Identification of coating effects without substrate effects could be accomplished by evaluating one alloy with three different coatings. Of the three alloys in Table 7, the best choice for coating would be Inconel 617 as it is probably more susceptible to carburization than Alloy 713LC. This matrix while still staying within the total coating constraint of four alloys, shown in Table 8, should enable identification of coating influence without including the variable of substrate composition.

A much more thorough test would be established if the number of alloy/coating combinations to be evaluated were increased to six. This would permit the head-on-head comparison of the three high Al coatings on Inconel 617, while permitting evaluation of NiCrAlY on two substrates, Inconel 617 and Alloy 713LC (either of these two coating/alloys may be tested in the preoxidized condition). Also permitted would be the evaluation of a low Al content FeCrAlY on the NPH alloy, Alloy 800H. This matrix is shown in Table 9 and is recommended over the previous programs, if the funding permits.

8.2 Coating Development and Evaluation Program

Longer term coating development and evaluation programs should approach the problem of carburization in a more systematic manner. There are three probable means by which the interaction of carbon with the substrate may occur. These are: (1) penetration of the coating oxide by carbon through cracks or areas of spallation, (2) direct diffusion of carbon through the oxide films and (3) loss of oxide forming capability which facilitates the self-healing of films, by diffusion of the oxide forming elements from the coating into the base metal.

In view of the probable slow rate of oxide formation and the potential for carburization in the VHTR environment, it is possible that in the event of oxide defoliation or cracking, carburization of the substrate may initiate before the oxide can reform. In this case the sole means of providing protection from carburization will be to preoxidize the coating, maintaining this continuous scale without cracking or spallation at all times.

It follows then, that the maximization of coating ductility and adherence should, therefore, be pursued by the incorporation of elements such as Hf, Y and Pt, which have been shown to improve oxide retention in simple and complex systems.

Assuming a continuous oxide film can be maintained, the rate of carburization will be determined by the diffusion of C through the oxides. At this time, little is known concerning C diffusion through oxides, in fact no data could be found dealing with the subject. It is known, however, that certain simple and complex oxides⁽⁵¹⁾, especially spinels, possess reduced diffusion rates for O_2 . It is logical, then, that these same oxides may also reduce the diffusion of C.

Complex oxide systems to reduce C diffusion must be based on the stable oxides of Al, Ti, Si, Hf and Y. It is recommended that the oxides of Al and/or Si be used as the primary protective oxides, with Ti, Hf and Y being minor additions to these two, since evaluations have shown these two oxides to perform well in both oxidizing⁽⁵¹⁾ and sulfidizing⁽⁵¹⁾ atmospheres. Multi-step pack cementation deposition of these elements is ideally suited for the simple systems. PVD is suggested for the more complex MCrAlY type systems.

The third possible mechanism is degradation of the coating by diffusion of the oxide forming elements into the base material. Barriers to diffusion have been sought by many investigations, but to date no proven barriers exist. Recently, the incorporation of Pt in aluminides and the generation of an alleged diffusion barrier has been shown to increase the corrosion resistance of these coatings. The validity of this diffusion barrier has yet to be proven. However in light of the excellent performance of Pt modified aluminides, which includes improved oxide performance, this coating is recommended for extensive testing.

The protection of TZM will require the development of a more ductile coating. The current silicide coatings such as W-2 and W-3 are known to undergo excessive strain on refractory alloys on cooling which causes cracking, thus exposing the substrate to direct attack by the environment. Monitoring of the Climax coating program and testing of the most promising candidates identified in their evaluation is recommended.

The outline of a more comprehensive program is shown in Table 10. In this program, four alloys have been chosen to represent the classes of materials which are candidates for use in the VHTR. Uncoated, these materials are not expected to perform well under carburizing environments.

TZM is the only refractory alloy under consideration and is recommended for testing with both modified W-3 and the most promising candidate emerging from the Climax testing program.

Alloy 800H is typical of the wrought Fe-base candidates having high Cr and Ni with low Al and Ti. It is recommended for testing with three modified aluminides, Al + Pt, Al + Si, Al + Ti, and with FeCrAlY and FeCrAlHf.

Hastelloy X is representative of wrought Ni-base alloys having high Cr and Mo. All of the coatings recommended for testing on Alloy 800H, with the exception of FeCrAlHf plus an unmodified aluminide and NiCrAlY, are recommended for testing on Hastelloy X.

Rene' 100 was chosen to represent the cast nickel base superalloys since it contains high Ti and Al plus considerable amounts of Cr and Mo; a combination found in most cast Ni-base superalloys. Both Hf and Y modified NiCrAl is recommended for testing to determine the relative effects of these two elements. A wide range of diffusion coatings are suggested including Al, Al + Pt, Al + S, Al + Ti and Si + Al.

This program, although larger in the number of specimens tested compared to the original program, does not attempt to deal in any depth with the effects of combined elemental additions to base metals. In fact, the simpler alloys were chosen to eliminate as much as possible these effects on coating performance. This program should provide an insight into the types of coatings that will provide protection in VHTR environments. However, final testing of the particular alloy and coating chosen for use must be performed to accurately determine the performance of the combination.

TABLE 6

COATINGS/COATING PROCESSES
OF INTEREST FOR VHTR APPLICATION

Alloy	COATING				
	Pack Aluminide (CODEP)	Pack Al+Pt (RT-22)	PVD NiCrAlY (PWA 267)	PVD FeCrAlY (GE-1541)	Pack Silicide (W-3)
Alloy 800H	X	X	X	X	
Inconel 617	X	X	X	X	
Alloy 713LC	X	X	X		
TZM					X

TABLE 7

COATINGS/COATING PROCESSES
RECOMMENDED FOR VHTR TESTING

(To Comply with Preselected Alloys and
the Number of Coatings Permitted)

Alloy	COATING				
	Pack Aluminide (CODEP)	Pack Al+Pt (RT-22)	PVD NiCrAlY (PWA 267)	PVD FeCrAlY (GE-1541)	Pack Silicide (W-3)
Alloy 800H		X			
Inconel 617	X				
Alloy 713LC	X				
TZM					X

TABLE 8

COATINGS/COATING PROCESSES
RECOMMENDED FOR VHTR TESTING

(To Comply Only with Total Number
of Coating Specimens Predicted)

Alloy	COATING				
	Pack Aluminide (CODEP)	Pack Al+Pt (RT-22)	PVD NiCrAlY (PWA 267)	PVD FeCrAlY (GE-1541)	Pack Silicide (W-3)
Alloy 800H					
Inconel 617	X	X	X		
Alloy 713LC					
TZM					X

TABLE 9

COATINGS/COATING PROCESSES
RECOMMENDED FOR VHTR TESTING

(Four Alloys and Six Specimens)

Alloy	COATING				
	Pack Aluminide (CODEP)	Pack Al+Pt (RT-22)	PVD NiCrAlY (PWA 267)	PVD FeCrAlY (GE-1541)	Pack Silicide (W-3)
Alloy 800H				X	
Inconel 617	X	X	X		
Alloy 713LC			X		
TZM					X

TABLE 10

SUMMARY OF EXPANDED COATING EVALUATION

	Al	Al-Pt	Al-Si	Al-Ti	Si-Al	FeCrAlY	FeCrAlHf	NiCrAlY	NiCrAlHf	Si-B	Climax Candidate
TZM										X	X
Alloy 800H		X	X	X		X	X				
Hastelloy X	X	X	X	X		X		X			
Rene' 100	X	X	X	X	X			X	X		

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