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(54) **OXIDATION RESISTANT NIOBIUM BASED ALLOYS**

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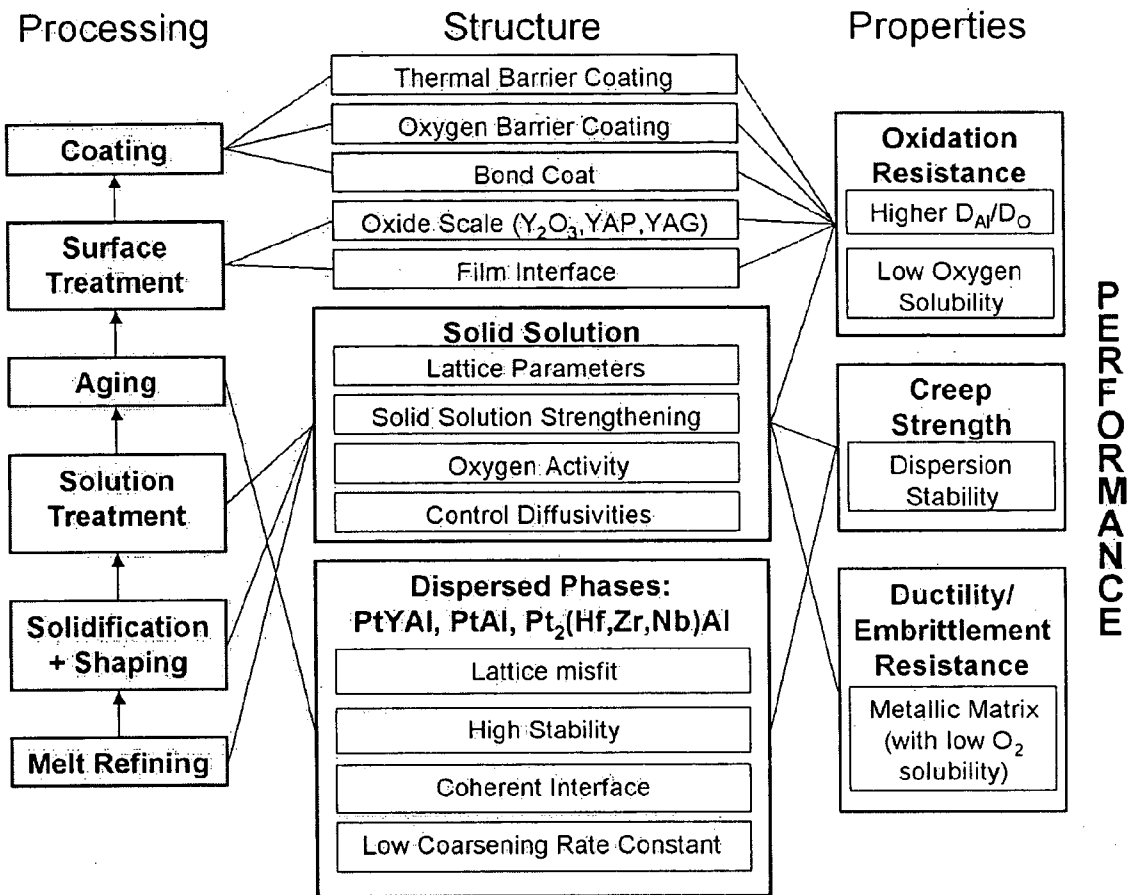
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(57) **ABSTRACT**

Oxidation resistant niobium based alloys have a composition to provide a stable ternary phase such as PtYAl or PdYAl, which supplies yttrium and aluminum to the system and forms a protective oxide such as Yttria-Aluminum-Garnet (YAG) scale at elevated temperature. These niobium based alloys further achieve an optimal combination of oxidation resistance and creep strength through a fine dispersion of a coherent second phase. The alloys, withstanding higher combustion temperatures, are useful for extreme-environment propulsion and power applications, including hot sections of gas turbine engines, aerospace turbine blades, and chemical and petroleum plants, where higher turbine efficiency and reduction of operating costs, by-products emissions, and global fuel reserves consumption are desired.

Processing   Structure   Properties

Thermal Barrier Coating

Oxygen Barrier Coating

Coating

Bond Coat

Surface Treatment

Oxide Scale (Y_2O_3,YAP,YAG)

Film Interface

Oxidation Resistance

Higher D_{Al}/D_O

Low Oxygen Solubility

Solid Solution

Lattice Parameters

Aging

Solid Solution Strengthening

Oxygen Activity

Solution Treatment

Control Diffusivities

Creep Strength

Dispersion Stability

Solidification + Shaping

Dispersed Phases:
PtYAl, PtAl, Pt_2(Hf,Zr,Nb)Al

Lattice misfit

High Stability

Melt Refining

Coherent Interface

Low Coarsening Rate Constant

Ductility/ Embrittlement Resistance

Metallic Matrix (with low O_2 solubility)

P E R F O R M A N C E

Figure 1

$-\triangle G_f$ AT 1300°C VS P-B RATIO

$-\triangle G$ (kJ/mole of O_2)

1500

1300°C

Y_2O_3

1400

YAG

1300

HfO_2

ZrO_2

1200

Al_2O_3

1100

NbO TiO_2 $NbAlO_4$

1000

SiO_2

Cr_2O_3 Nb_2O_5

900

1   1.5   2   2.5   3

PILLING -BEDWORTH RATIO

FIG. 2

MODEL ALLOYS   PROTOTYPES

NORMALIZED WEIGHT GAIN (mg/cm^2*hr)

160

1HR   5 HR   1300 C

140

120

100

MULTI COMPONENT
MATRIX ALLOYS

80

60

BRITTLE, INTERMETALLIC
RICH   DUCTILE

40

20

IHPTET 5Hr
OBJECTIVE

0

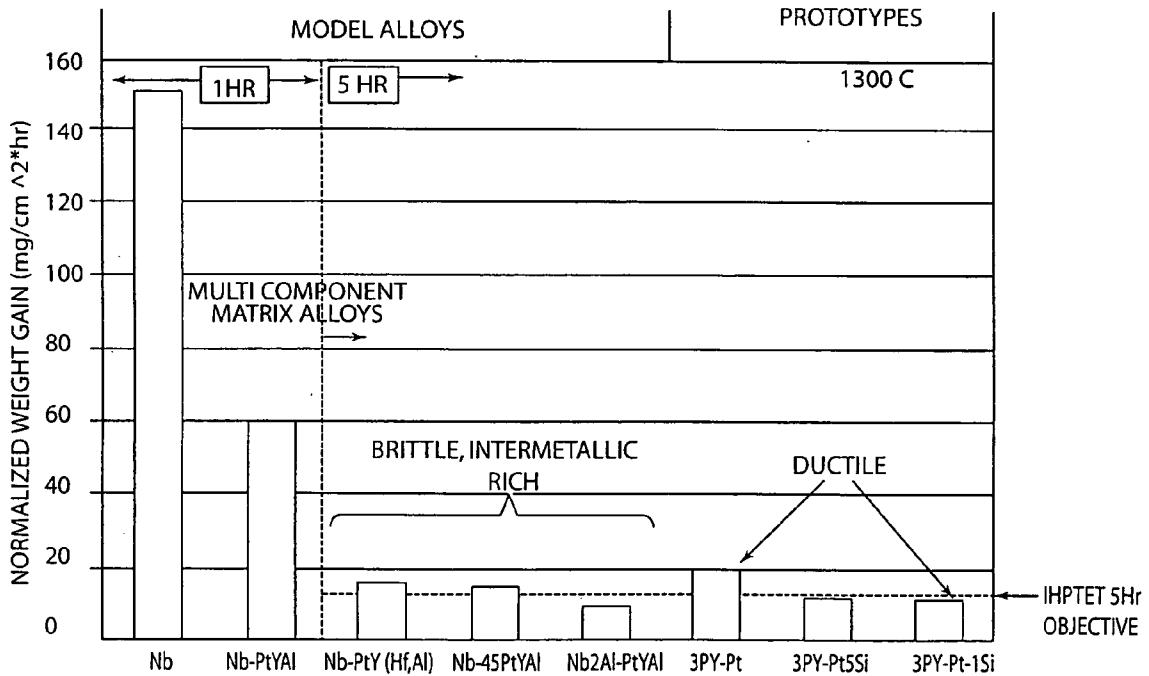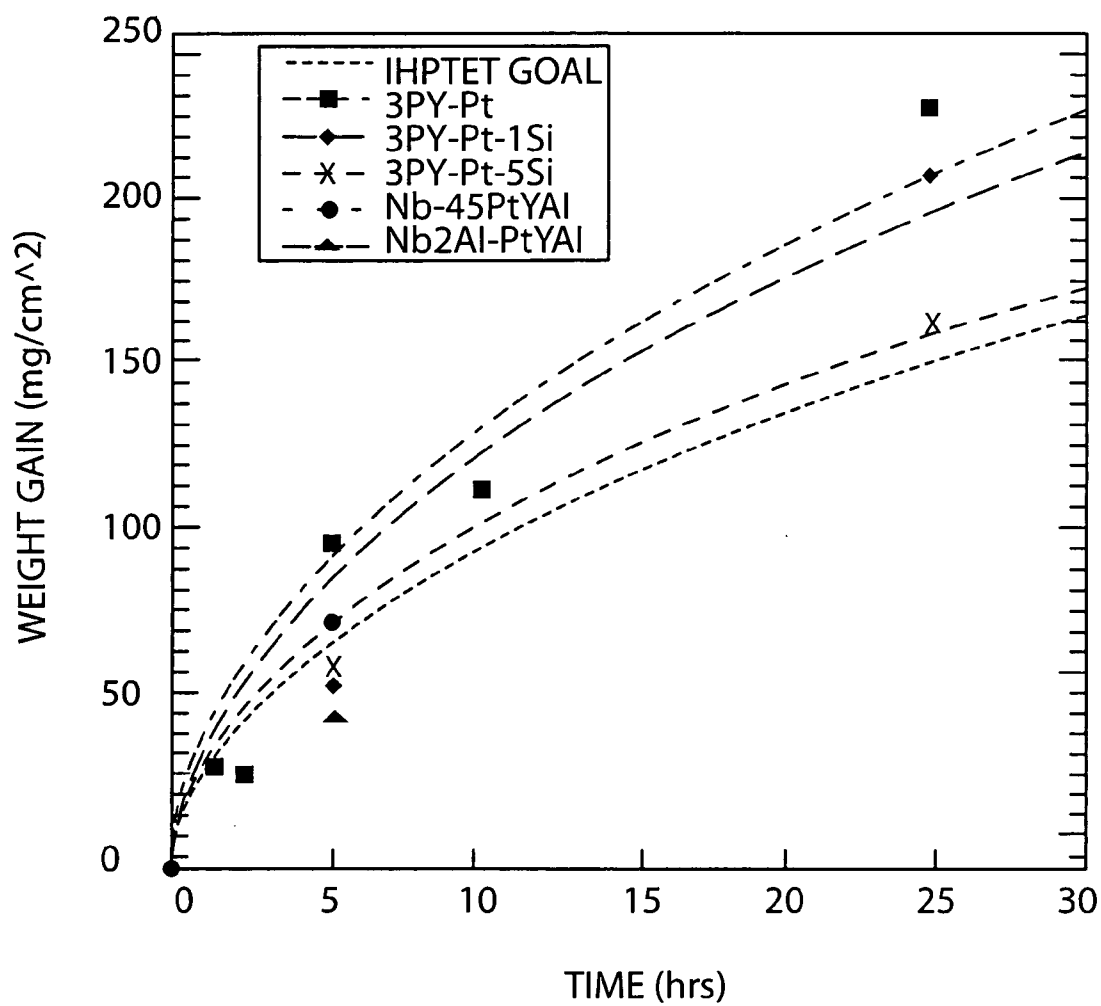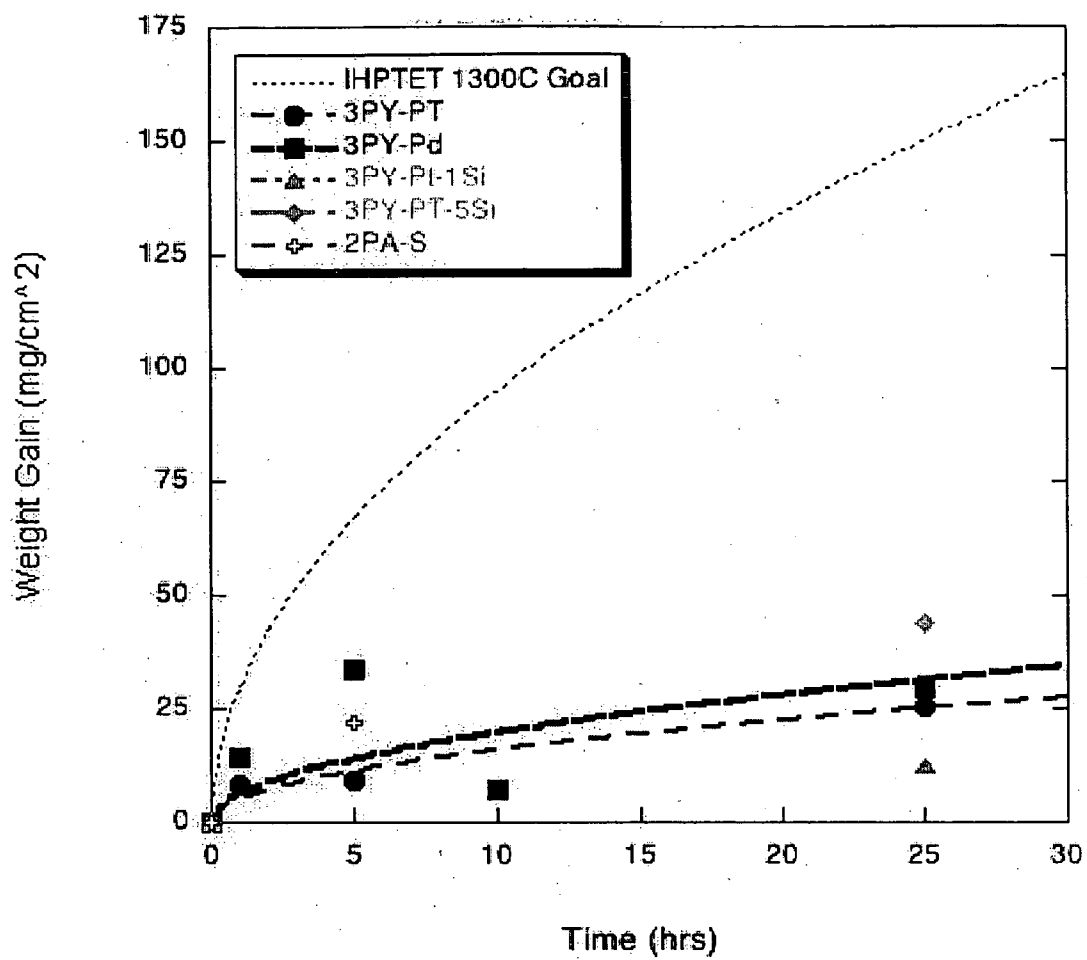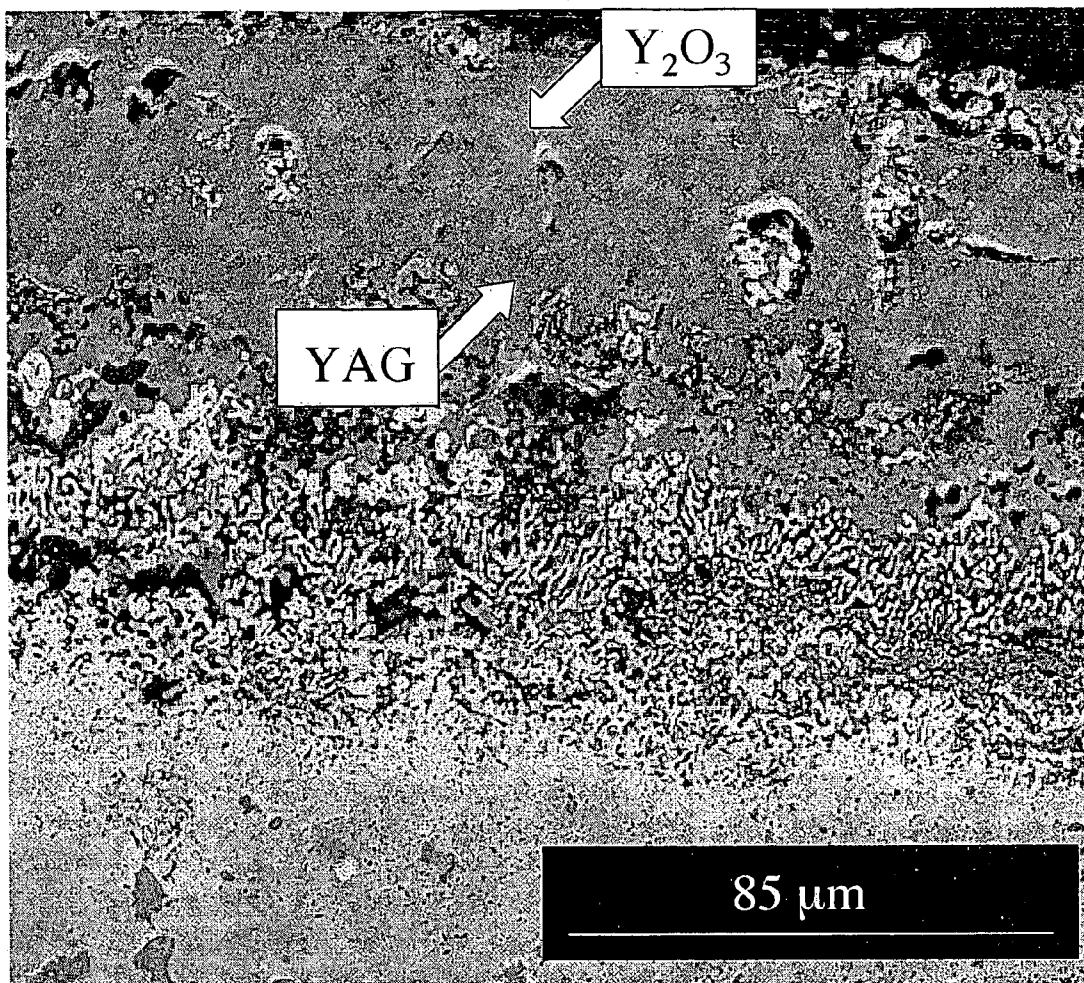Nb   Nb-PtYAl   Nb-PtY (Hf,Al)   Nb-45PtYAl   Nb2Al-PtYAl   3PY-Pt   3PY-Pt5Si   3PY-Pt-1Si
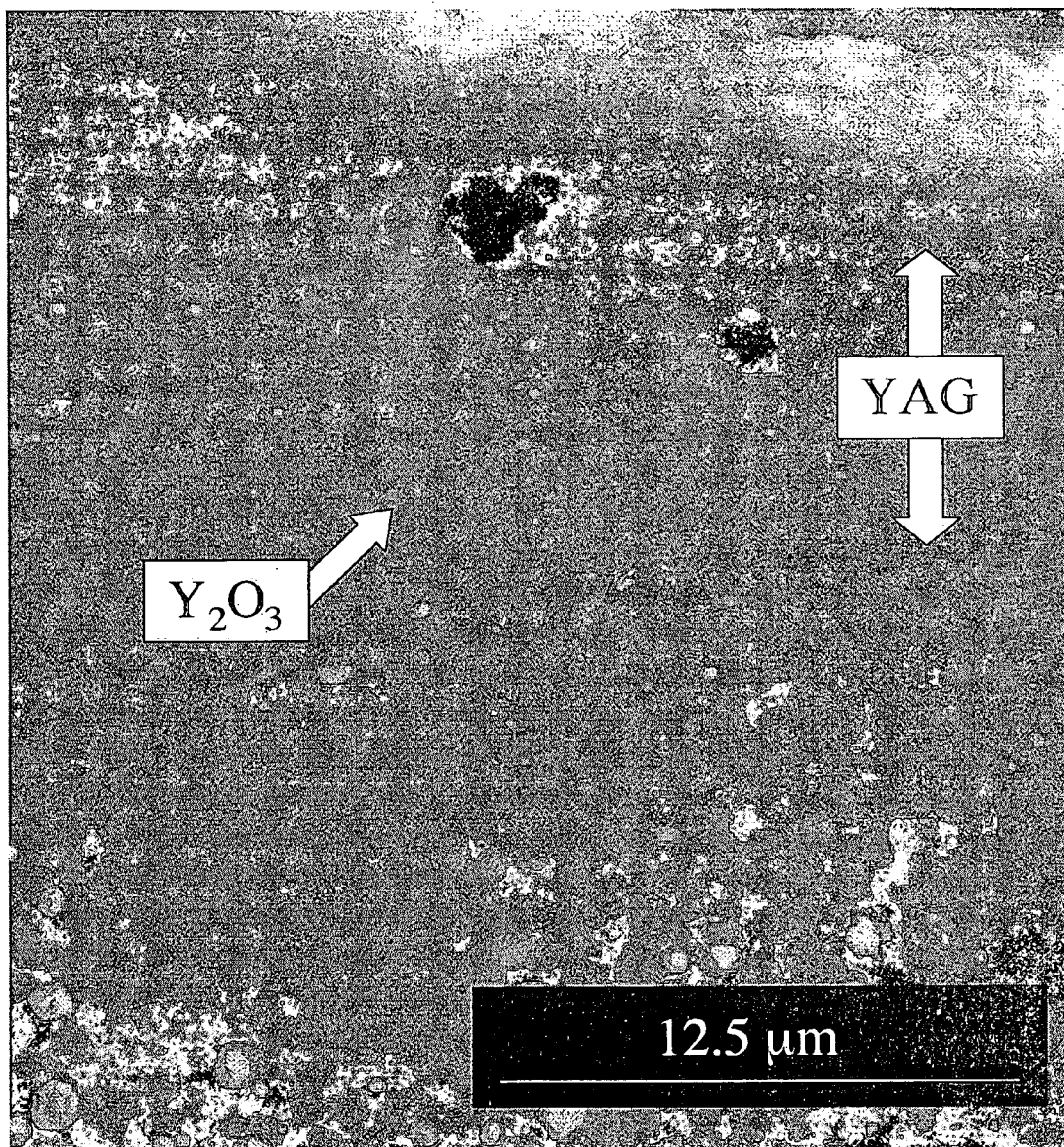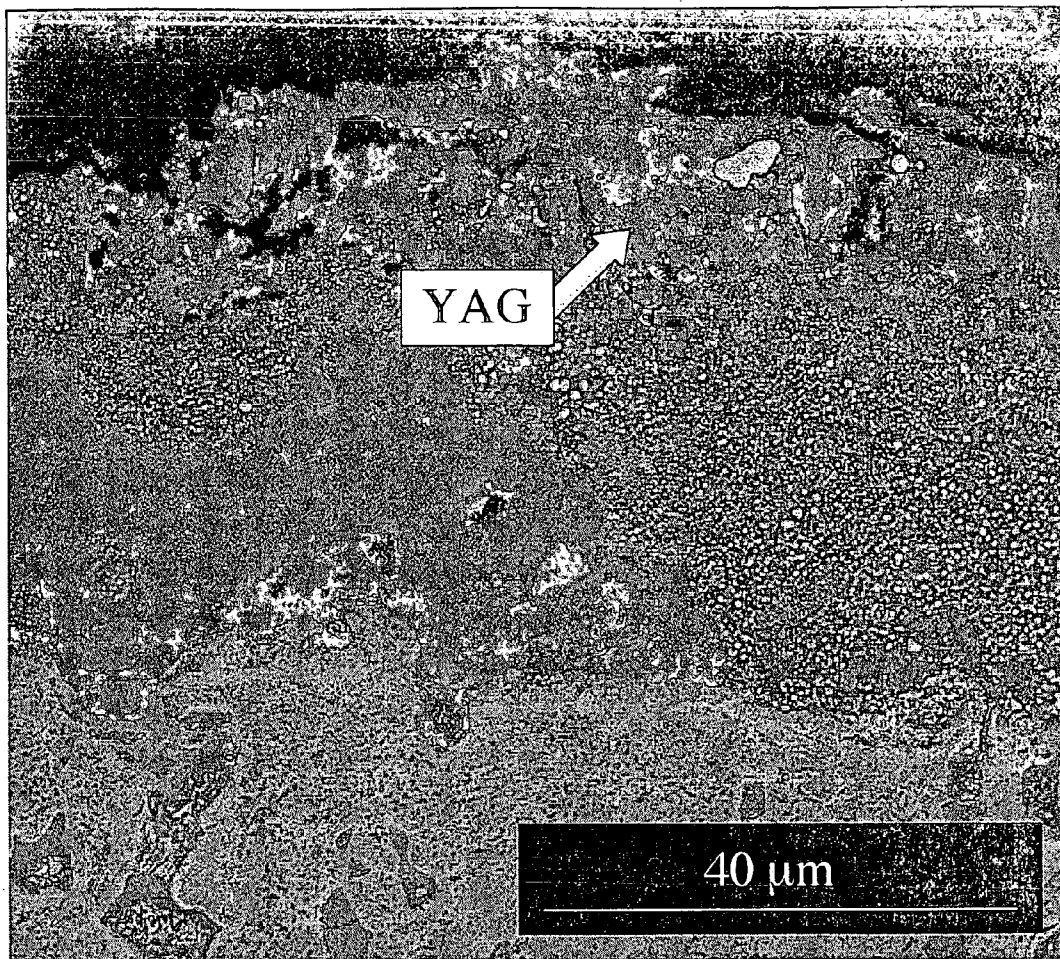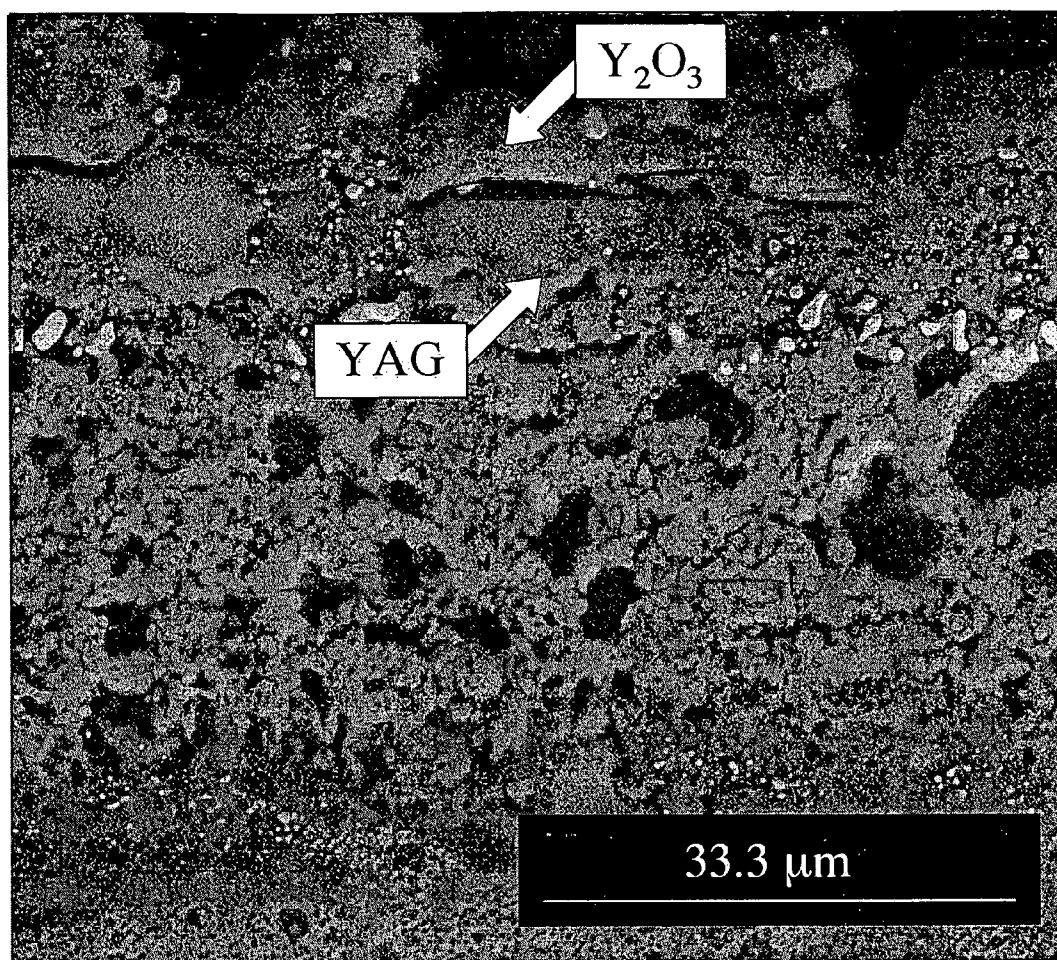
FIG. 3

FIG. 4

Figure 5

Figure 6

Figure 7

Figure 8

Figure 9

OXIDATION RESISTANT NIOBIUM BASED ALLOYS

CROSS REFERENCE TO RELATED APPLICATIONS

[0001] This application claims benefits and priority of provisional application U.S. Ser. No. 60/592,924, filed Jul. 30, 2004, entitled, "Oxidation Resistant Niobium Based Alloys", which is incorporated herewith by reference.

CONTRACTUAL ORIGIN OF THE INVENTION

[0002] This disclosure was supported, at least in part, by Air Force Office of Scientific Research, Grant No. F49 620-01-1-0529 and may be subject to contract, license and other rights granted to the United States Government.

FIELD OF THE INVENTION

[0003] In a principal aspect, the present invention relates to oxidation resistant niobium based alloys, and, in particular, niobium based alloys with a protective oxide scale such as Yttrium-Aluminum-Garnet (YAG), enabling a myriad of practical applications including, but not limited to, turbine blades viable at temperatures in the range of 1100 to 1300° C., and structural and internal operating components in hot sections of nuclear reactors.

BACKGROUND OF THE INVENTION

[0004] Turbine blades in gas turbines and jet engines are typically nickel based alloys, which are in a single-crystal form and include various means to preclude melting and oxidation at high temperatures. The efficiency of gas turbines and jet engines could be significantly enhanced if the turbine blades could operate at higher temperatures. However, with peak use temperature of 1100° C. being greater than 90% of their melting temperatures, nickel based alloys are reaching the point where there is limited room to improve upon the operating efficiency of manufactured components. The Integrated High Performance Turbine Engine Technology (IHPTET) group has identified a set of performance objectives for turbine blade materials [Journal of the Minerals, Metals & Materials, 1996, vol. 48, pp. 33-38 (incorporated herewith)]. The key in this set of objectives is the peak use temperature of 1315° C. The next generation turbine blades should survive for at least 2000 mission hours. To meet this criterion, a target recession rate of less than 2.5 μm/hr at the operating temperature was specified in IHPTET Phase III.

[0005] Extensive research has been carried out on replacing nickel based superalloys with intermetallics, ceramics and metallic alloys. Of all these candidate systems, metal matrix based systems have an inherent advantage because they are more ductile than ceramics and intermetallics. Systems based on niobium are especially attractive, because niobium has a melting temperature of 2467° C. and also has a low density, making it an ideal candidate for replacement of nickel in rotating components. Niobium based superalloys, used at 1300° C., would improve the ideal Carnot efficiency from 0.745 to 0.788. Niobium also has a low modulus and coefficient of thermal expansion suitable for thermal stress tolerance. Furthermore, niobium based alloys have intrinsically good void swelling resistance with respect to irradiation impact, which makes them a viable candidate for use in hot sections of nuclear reactors.

[0006] However, conventional niobium based refractory alloys lack appropriate oxidation resistance at high temperatures. Nickel based alloys overcome the oxidation issue by forming a protective chromic oxide or alumina layer. A thermal barrier coating and bond coat system provide additional thermal and oxidation protection. However, conventional niobium based alloys form non-protective oxides that exhibit linear growth kinetics, unlike the protective oxide layer in nickel based alloys. A non-protective oxide is porous and allows oxygen to rapidly diffuse to the metal. Current commercial niobium silicide alloys suffer from limited ductility. Niobium based metallic alloys combining oxidation resistance, creep strength and ductility operating at 110° C. and above are much needed.

SUMMARY OF THE INVENTION

[0007] The invention comprises niobium based alloys having improved oxidation resistance at elevated temperatures, such as for example 1100 degrees C. and above. In an illustrative embodiment of the invention, the niobium based alloys include a composition that provides a stable ternary phase, such as $PtYAl$ or $PdYAl$, which supplies yttrium and aluminum to the alloy system for forming a protective oxide scale, such as for example Yttria-Aluminum-Gamet (YAG) scale, at elevated temperature.

[0008] In a particular illustrative embodiment of the invention, the oxidation resistant niobium based alloys include aluminum, platinum and/or palladium, yttrium and balance niobium.

[0009] In another illustrative embodiment of the invention, the niobium based alloys employing a protective YAG scale provide an oxidation rate constant equivalent to chromic oxide layers.

[0010] In still another illustrative embodiment of the invention, the oxidation resistant niobium alloys are provided with composition tolerance by incorporating a third multicomponent phase as a buffer for excess aluminum in the oxidation resistant niobium based alloy. The composition tolerance can be provided by incorporating a Nb_2Al phase as a buffer for excess aluminum in the oxidation resistant niobium based alloy.

[0011] These and other features and advantages of the present invention will be set forth in the following detailed description taken with the following drawings.

BRIEF DESCRIPTION OF THE DRAWINGS

[0012] In the detailed description that follows, reference will be made to the drawings comprising the following figures:

[0013] FIG. 1 is a flow block logic diagram that characterizes the design concepts of the alloys of the invention;

[0014] FIG. 2 shows parametric cross plots of atomic selection for oxide scale formation;

[0015] FIG. 3 is a plot that depicts normalized weight gain at 1300° C. due to oxidation of model alloys and prototypes;

[0016] FIG. 4 is a plot that depicts weight gain at 1300° C. as a function of oxidation time of model alloys and prototypes;

[0017] **FIG. 5** is a plot that depicts weight gain at 1100° C. as a function of oxidation time of model alloys and prototypes;

[0018] **FIG. 6** is a micrograph showing nearly continuous YAG formation, appearing as a dark phase, in 3PY-Pt-1Si oxidized at 130° C. for 5 hours;

[0019] **FIG. 7** is a micrograph showing nearly continuous YAG formation, appearing as a dark phase, in Nb-45PtYAl oxidized at 1300° C. for 5 hours;

[0020] **FIG. 8** is a micrograph showing discontinuous YAG formation, appearing as a dark phase, in 3PY-Pt oxidized at 1100° C. for 25 hours; and

[0021] **FIG. 9** is a micrograph showing a discontinuous mixed Y-Al oxide in 3PY-Pt oxidized at 130° C. for 5 hours.

DETAILED DESCRIPTION OF THE INVENTION

[0022] The present invention provides niobium (Nb) based alloys which have improved oxidation resistance. The alloys can have a multicrystalline microstructure, although the invention is not so limited since the alloys can have a single crystal or directionally solidified microstructure depending on the service application. In an illustrative embodiment of the invention, the Nb based alloy composition comprises at least about 25 preferably about 40 atomic % Nb together with aluminum (Al), platinum (Pt) or palladium (Pd) or a combination thereof, and yttrium (Y). The Nb concentration of the alloy more preferably is at least about 53 atomic % in certain illustrative embodiments described below. The Nb based alloys preferably include from about 10 to about 25 atomic % and more preferably about 10 to about 20 atomic % of Al. The Nb based alloys preferably include from about 5 to about 40 atomic % and more preferably about 5 to about 10 atomic % of Pt or Pd or a combination thereof. The Nb based alloys preferably include from about 5 to about 25 atomic % and more preferably from about 5 to about 15 atomic % of Y. The Nb based alloys optionally may include one or more of the alloying elements selected from the group consisting of Ti, Si, Hf, Cr, and W, and combination of two or more of such alloying elements where each element may be present in an appropriate amount. One or more of the Ti, Si, Hf, Cr, and W alloying elements may be provided in the alloy to enhance diffusivity ratio of aluminum to oxygen in the ductile Nb based matrix for surface oxide formation. For example, Ti may be present in an amount up to about 6 atomic % preferably about 3.5 to 6 atomic % of the alloy. Si may be present in an amount up to about 5 atomic % preferably about 1 to about 5 atomic % of the alloy. Hf may be present in an amount up to about 8 atomic % preferably about 2.5 to about 7.5 atomic % of the alloy. Cr may be present in an amount up to about 4 atomic % preferably about 2.5 to about 4 atomic % of the alloy. W may be present in an amount up to about 2 atomic % preferably about 1 to about 2 atomic % of the alloy.

[0023] A particular illustrative niobium base alloy pursuant to an embodiment of the invention comprises at least about 53 atomic % niobium, about 13 to 18 atomic % aluminum, about 2.5 to 4 atomic % chromium, about 2.5 to 6 atomic % hafnium, up to about 8 atomic % palladium, up to about 7.45 atomic % platinum, up to about 5 atomic % silicon, about 5 to 6 atomic % titanium, up to about 2 atomic

% tungsten, and about 7 to 9 atomic % yttrium, wherein the alloy is characterized by target recession rate less than 2.5 μm/hr at 1100° C. or high.

[0024] Another particular illustrative niobium based alloy comprises, in atomic percent, about 13 to about 25 parts aluminum, up to about 4 parts chromium, up to about 5 parts hafnium, about 5 to about 15 parts platinum, up to about 5 parts silicon, up to about 6 parts titanium, up to about 2 parts tungsten, about 7 to about 15 parts yttrium, and the balance niobium.

[0025] Another illustrative niobium based alloy comprises in atomic percent about 13 to about 23 parts aluminum, up to about 3 parts chromium, up to about 8 parts hafnium, about 5 to about 38 parts palladium, up to about 6 parts titanium, up to about 2 parts tungsten, about 8 to about 25 parts yttrium, and the balance niobium.

[0026] Still another illustrative niobium based alloy comprises, in atomic percent, about 13 to about 18 parts aluminum; about 2 to about 4 parts chromium; about 2 to about 5 parts haffnium; about 5 to about 8 parts platinum; up to about 5 parts silicon; about 5 to about 6 parts titanium; up to about 2 parts tungsten; about 7 to 9 parts yttrium; and the balance niobium.

[0027] A further particular illustrative niobium alloy comprises, in atomic percent, about 13 to about 15 parts aluminum; about 2 to about 3 parts chromium; about 2 to about 6 parts hafnium; about 5 to about 8 parts palladium; about 4 to about 6 parts titanium; up to about 2 parts tungsten; about 8 to about 9 parts yttrium; and the balance niobium.

[0028] The Nb based alloys form a protective oxide layer that includes aluminum oxide (Al_2O_3) and/or (Y_2O_3) or their reaction products (e.g. some reaction products described in the Examples below) upon exposure in air or other oxygen bearing atmosphere at elevated temperatures, such as for example, from 1100 degrees C. and above. Preferably, the Nb based alloys form an oxide layer having a combination of yttrium oxide (Y_2O_3) and aluminum oxide (Al_2O_3) also known as YAG (yttrium aluminum garnet). Such alloys exhibit long term stability enabling use and fabrication of component parts from the alloys.

[0029] The Nb based alloys can be cast and/or heat treated to provide certain microstructural features that involve providing a ductile Nb-based metallic matrix alloy solid solution, strengthened by a fine dispersion of coherent aluminide phases or precipitates such as the PdYAl and/or PtYAl. As mentioned above, the presence of certain alloying elements (e.g. one or more of Ti, Si, Hf, Cr, and W) in the matrix may be used to provide a beneficial diffusivity ratio of aluminum to oxygen in the matrix for surface oxide formation. The invention also envisions making the Nb based alloys using other processes such as rapid solidification of powders, ribbon or the like followed by consolidation (e.g. cold or hot isostatic pressing) and heat treatment to develop the desired microstructural features. The dispersion of PdYAl and/or PtYAl phases in the ductile Nb based matrix contribute both to strength and a source of Al and Y for oxidation resistance via Al_2O_3 and Y_2O_3 formation. Moreover, the invention envisions including other phases, such as including but not limited to, PtAl, Pt_2(HfZr,Nb)Al [e.g. Pt_2HfAl where some of the Hf may be substituted by Zr and where Nb may be substituted as well] together with the PdYAl and/or PtYAl phases in the ductile Nb based matrix

[0030] **FIG. 1** is a systems flow-block diagram which illustrates the processing/structure/properties/performance relationships for alloys of the invention. The desired performance for the application (e.g. turbine blades in gas turbines and jet engines, structural and internal operating components in hot sections of nuclear reactors, etc.) determines the set of required alloy properties. Alloys of this invention exhibit the structural characteristics that can achieve the desired combination of properties and can be accessed through the sequential processing steps shown on the left of **FIG. 1**.

[0031] Employing the concepts reflected by **FIG. 1**, oxidation resistance equivalent to or better than chromic oxide layers is targeted. The physical properties and microstructural characteristics for the designed alloys are described below. This is followed by the applications of the alloys, the experimental results relating to the discovery and examples of the alloys that define, in general, the range and extent of the elements, and the physical characteristics of the present invention.

[0032] To achieve improved oxidation resistance, alumina would be an ideal protective oxide for niobium based alloys; however it has not been achieved to date. Alumina is stable at high temperatures, and has the lowest Pilling-Bedworth (P-B) ratio V_{oxide}/V_{metal} among stable oxides, which enables the protective oxide to adhere to the metal surface. Alumina also exhibits parabolic oxidation kinetics, and is already being used in nickel based alloys. In order to obtain this external oxide scale in niobium based systems, the aluminum content must follow Wahl's extension of Wagner's second criterion to two-phase alloys:

$$N_{Al}^{tot} N_{Al}^{Matrix} = \left[\frac{f}{\upsilon} N_o^{(s)} \frac{D_o V_m}{D_{Al} V_{ox}} \right]$$

[0033] where f and υ are constants (f~1 and υ=1.5) and $N_{Al}^{tot} = v^P N_{Al}^P + (1-v^P) N_{Al}^{Matrix}$. Here, v^P is the phase fraction of the second phase. $N_O^{(s)}$ is the oxygen solubility in the metal matrix, D_O the oxygen diffusivity in the matrix, D_{Al} the intrinsic diffusion coefficient of Al in the alloy matrix for dilute alloys, V_m the molar volume of the alloy, and V_{ox} the volume of the alumina per mole of aluminum. For stable alumina film formation on a niobium alloy at 1300° C. at a reasonable aluminum content, the quantity

$$N_o^{(s)} \frac{D_o}{D_{Al}}$$

must be reduced by five orders of magnitude, which is challenging.

[0034] In order to predict the parameters in the above quantity, mobility and thermodynamic databases were developed as a part of a doctoral research project at Northwestern University described by Misra, A. in Doctoral Thesis, Department of Materials Science and Engineering, Northwestern University, Evanston, Ill., **2005**, which is incorporated herein by reference, under the AFOSR-MEANS initiative. Using the databases, the effect of alloying elements on the above parameters were calculated and prototype alloys were designed that achieved the 5 orders of magnitude reduction in the design parameter. However the

alloys failed to form alumina due to the formation of competing phases such as HfO_2 and $NbAlO_4$. Although the databases and calculations described above and below were used in designing the Nb based alloys, Applicants do not intend that the invention be limited in any way to any databases or calculations since the invention involves the Nb based alloys themselves described and claimed herein to provide improved oxidation resistance.

[0035] Since alumina formation is difficult to achieve in niobium based alloys, a broader survey of components and phases was conducted. YAG is identified as the preferred oxide scale to enhance the intrinsic alloy oxidation resistance and overcome the thermodynamic stability of the competing rutile-type $NbAlO_4$ oxide. Thermodynamic and kinetic atomic selection criteria were devised to this end.

[0036] For the thermodynamic atomic selection criterion of oxide scale, the oxide free energy of formation and P-B ratio relative to niobium were used. The four-dimensional survey is summarized by the Ashby-type selection cross plots in **FIG. 2**. The plot at the left represents the equilibrium thermodynamic parameters of oxide free energy of formation and P-B ratio relative to niobium, while the plot at the right represents 1300° C. kinetic parameters of oxide scale parabolic rate constant and relative diffusivity in niobium of the corresponding metal solute. As indicated by the arrows, preferred properties in the left plot lie at the upper left, while preferred properties in the right plot lie at the lower right. Using a quantum mechanical estimate of the free energy of formation for $NbAlO_4$ relative to alumina and niobium pentoxide, it was found that yttria offers the desired high stability with the same P-B ratio as rutile oxides, and mixed alumina-yttria oxides such as YAG offer a good compromise between stability and P-B ratio.

[0037] For the kinetic atomic selection criteria, the parabolic rate constant and relative diffusivity in niobium of the corresponding metal solute at 1300° C. is used. Bracketing relative component diffusivities of mixed oxides by their corresponding atomic constituents, the kinetic plot at the right shows that yttria also offers the advantage of the high diffusivity of yttrium in niobium while providing a low oxidation rate constant comparable to chromic oxide. The well-known low transport properties of YAG offer promise of exceptionally low oxidation rate constant, but the relative diffusivity will be compromised by the slower diffusion of aluminum. These considerations identify yttria and YAG as preferred oxide scales with the prospect of alloys that could take advantage of the high diffusivity of yttrium to initially passivate with yttria followed by longer time passivation by slower growing YAG.

[0038] A challenge to the incorporation of yttrium is the low solubility of yttrium in niobium and the relatively low melting point of yttrium compounds. Of the binary yttrium-aluminum compounds, Al_2Y offers the highest melting point (1485° C.) and the nearest Al/Y stoichiometry to that of YAG. Our experiments show however that it reacts with niobium to form a niobium aluminide and AlY with a lower melting point. A literature survey of yttrium compounds identified those with platinum group metals to be the most stable. An experimental study was undertaken to measure the melting points. As seen in Table 1, the equiatomic PtYAl is uniquely distinguished by our measured melting point above 1500° C. meeting a primary requirement for our high temperature alloys. PdYAl has the next highest melting point, and can be used in applications requiring a maximum operating temperature of 1100° C.

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TABLE 1

Phase	Crystal Structure	Measured Melting Point (° C.)
PdYAl	TiNiSi	1160
Pd₂YAl	Na₃As	890
PtYAl	TiNiSi	1580
Pt₂YAl	Multi-Phase	1120

[0039] Inspired by those melting point measurements, energy of formation values for relevant compounds were calculated using the Full-potential Linearized Augmented Plane Wave (FLAPW) method with local-density approximation. Promising predictions were followed by high-temperature differential thermal analysis. As seen in Table 2, the predicted energy of formation ΔH_f is in a good agreement with experimental values, and PtYAl shows the highest stability, which promotes thermodynamic compatibility with niobium. ΔH_f of PdYAl is also largely negative, indicative of high stability. Therefore, the present invention incorporates PtYAl for 1300° C. applications, and lower cost PdYAl for 1100° C. applications to supply both yttrium and aluminum to the system while maintaining desired high compound melting points.

TABLE 2

	PdYAl	PtYAl	Pt₂HfAl
Crystal Structure	TiNiSi	TiNiSi	Na₃As
Predicted ΔH_f (LDA, kJ/mol)		−111.8	−94.4 (L2₁)
Measured ΔH_f (kJ/mol)	−87.4	−111.3	−107.2

[0040] To provide composition tolerance, a multicomponent Nb₂Al phase is incorporated as a buffer for excess Al in the oxidation resistant niobium based alloy. In order to promote YAG, aluminum and yttrium should ideally be present in the alloy in nearly the 5:3 ratio. However YAG is a line compound and favors eutectic formation with other oxides such as alumina or yttrium aluminate. Since yttrium aluminate has a higher melting point than alumina, it is beneficial to be slightly rich in yttria. To increase the composition tolerance in manufacturing and promote robust alloy production, alloys of present invention incorporate a multicomponent niobium aluminide phase, which would be in equilibrium with the niobium matrix and equiatomic PtYAl or PdYAl in the matrix. Variations in excess alumi-

num would be absorbed in small composition variations in the niobium aluminide based buffer phase, which would be kept at a sufficiently low phase fraction not to degrade physical properties.

[0041] Among many, the following applications could be considered as possible applications for oxidation resistant niobium based alloys pursuant to the invention.

[0042] For example, the present invention targets a market of extreme-environment propulsion and power applications, including hot sections of gas turbine engines, aerospace turbine blades, and chemical and petroleum plants since niobium based alloys, withstanding higher combustion temperatures, will raise the turbine efficiency and reduce operating costs, by-products emissions, and global fuel reserves consumption. Furthermore, niobium based alloys have intrinsically good void swelling resistance with respect to irradiation impact, which makes them a viable candidate for use in hot sections of nuclear reactors. With appropriate oxide scale formation for niobium based alloys, Generation IV reactor designs could achieve higher operating temperatures and more efficient energy production. Construction of more efficient reactors will also allow for the use of less nuclear fuel and less nuclear waste, thereby increasing public safety.

[0043] As a potential NASA application, the NASA Solar Electric Propulsion Technology Application Readiness thruster, or NSTAR thruster, can be considered. The NSTAR thruster is typically used in high specific impulse/low thrust applications that require longer lifetimes and higher efficiency than state-of-the-art chemical propulsion systems. A revolutionary niobium based superalloy combining oxidation and erosion resistance, creep strength and ductility, operating at 1100° C. and above will greatly improve the overall system efficiency of the thruster and enhance the spacecraft performance on space missions.

[0044] EXAMPLES: Experimental results and examples related to the subject invention are described as follows. A series of model alloys and design prototypes were prepared. The alloys were arc melted and cast in water-cooled copper molds to form sample buttons. The buttons were subjected to a high temperature anneal such as at 1000 to 1300 degrees C. The model alloys were designed primarily to allow experimental measurement of important phase relations, while the prototypes were designed to meet oxidation resistance criteria. The compositions of these are given in Table 3.

TABLE 3

	Alloy	Nb	Ti	Hf	Cr	W	Pd	Pt	Y	Al	Si
Model Alloys	Nb—Pd—Y—Al 1	44	—	—	—	—	16	—	25	15	—
	Nb—Pd—Y—Al 2	44	—	—	—	—	18.5	—	15	22.5	—
	Nb—Pd—Hf—Y—Al	25	—	7.5	—	—	37.5	—	11.25	18.75	—
	Nb—PtYAl	61	—	—	—	—	—	13	13	13	—
	Nb—45PtYAl	38	3.5	3	2.5	—	—	14	15	24	—
	Nb2Al—PtYAl	42.55	3.5	3	2.5	—	—	14.45	9	25	—
Proto-types	3PY—Pt	53.55	6	3	3	—	—	7.45	9	18	—
	3PY—Pd	59.63	6	3	3	1	5.45	—	8.23	13.69	—
	3PY—Pt—1Si	53.55	6	3	3	—	—	7.12	8.66	17.67	1
	3PY—Pt—5Si	53.55	5	2.5	2.5	—	—	6.45	8	17	5

Note:
All values in at %

[0045] In calculating Wahl's criterion, the oxygen solubility is strongly dependant on the oxide scale that is in equilibrium with the underlying metal alloy. Calculations relative to niobium monoxide or niobium pentoxide indicate that insufficient aluminum is present in the alloys to form continuous YAG and that better performance would be expected at 1300 than 1100° C. However, experimentally, samples tested at 1100° C. outperformed equivalent samples at 1300° C. The reason for the increased oxidation resistance is that at 1100° C. the ternary oxide $NbAlO_4$ forms preferentially over niobium pentoxide as the transient oxide. The presence of $NbAlO_4$ greatly reduces the oxygen solubility in the metal and thus performance equal to or better than 1300° C. is predicted by Wahl's criterion. Similarly, through proper alloying, $NbAlO_4$ should be able to be stabilized over niobium pentoxide at 1300° C. Under these conditions, Wahl's criterion is exceeded for our prototype alloys and hence continuous YAG formation would be expected as shown in Table 4.

At 1300° C., a high volume fraction of pores in the niobium pentoxide leads to a short circuit diffusion path that circumvents the protection mechanisms described by Wahl's criterion. **FIG. 9** shows discontinuous mixed Y-Al oxide in 3PY-Pt oxidized at 130° C. for 5 hours.

[0049] While certain embodiments of the invention have been described in detail above, those skilled in the art will appreciate that changes and modifications can be made therein within the scope of the invention as set forth in the appended claims.

What is claimed is:

1. Niobium base alloy, comprising Al, Pt or Pd or a combination thereof, Y, and balance Nb.

2. The alloy of claim 1 wherein Al is present in an amount of about 10 to about 25 atomic % of the alloy.

3. The alloy of claim 1 wherein Pt or Pd is present in an amount of about 5 to about 40 atomic % of the alloy.

TABLE 4

1300° C.		N_O	D_O	D_{Al}	N_{Al}^{Matrix}	N_{Al}^{tot}	N_{Al}^{crit}
Model Alloys	Nb—PtYAl	1.47×10^{-5}	1.28×10^{-11}	4.69×10^{-16}	0.044	0.130	3.8
	Nb—45PtYAl*	4.21×10^{-7}	7.70×10^{-12}	3.81×10^{-14}	0.087	0.240	4.09×10^{-4}
	Nb2Al—PtYAl*	7.03×10^{-7}	1.62×10^{-12}	2.10×10^{-14}	0.107	0.250	2.11×10^{-4}
Proto-types	3PY—Pt	3.97×10^{-5}	1.55×10^{-11}	2.13×10^{-14}	0.101	0.180	0.12
	3PY—Pt—1Si	3.96×10^{-5}	1.55×10^{-11}	1.98×10^{-14}	0.100	0.177	0.13
	3PY—Pt—5Si	4.10×10^{-5}	1.55×10^{-11}	1.14×10^{-14}	0.091	0.170	0.3

*indicates that the phase equilibrium predicted by Thermo-Calc is different than the experimentally observed equilibrium

[0046] The oxidation results of the model alloys and prototypes at 1300° C. are presented in **FIG. 3**. The prototype 3PY-Pt comes close to the IHPTET Phase III objective for 5 hours corresponding to a target recession rate less than 2.5 μm/hr over 2000 hrs at the operating temperature. The prototype 3PY-Pt-1Si meets the 5 hour-goal while maintaining ductility, while both 3PY-Pt-5Si and Nb_2Al-PtYAl were brittle. As seen in **FIG. 4**, alloys of subject invention are very near to meeting the criterion at 1300° C. As seen in **FIG. 5**, these alloys exceed the criterion at 1100° C. The prototype 3PY-Pt-1 Si exhibits the best performance.

[0047] The microstructures of alloys oxidized at 130° C. for 5 hours were analyzed in detail, confirming the formation of the predicted stable yttria outer scale. **FIG. 6** shows nearly continuous YAG formation, appearing as a dark phase, in 3PY-Pt-1Si. Nb-45PtYAl also forms nearly continuous YAG at the surface, as seen in **FIG. 7**. The scale thickness corresponds to a reduction in oxidation rate constant by two orders of magnitude. Below the light gray yttria scale is a mixed layer of alumina+yttria with a dispersion of platinum. It is expected that at longer times the alumina+yttria layer will be converted to the desired stable YAG layer.

[0048] Despite the failure to meet Wahl's criterion, 3PY-Pt oxidized at 1100° C. for 25 hours shows continuous YAG formation near the surface, as in **FIG. 8**. While $NbAlO_4$, YAG, yttrium aluminum perovskite, and alumina all show signs of forming dense oxide scales even in mixed scales, niobium pentoxide forms a porous scale. The discontinuous YAG formation at 1300° C. could be due to niobium pentoxide, or yttria, which forms compact scales that crack after reaching a significant thickness due to a poor P-B ratio.

4. The alloy of claim 1 wherein Y is present in an amount of about 5 to about 25 atomic %.

5. The alloy of claim 1 further comprising an element selected from the group consisting of Cr, Hf, Si, Ti, and W and combination thereof.

6. The alloy of claim 1 having PtYAl phase and/or PdYAl phase disposed in a ductile Nb based matrix.

7. The alloy of claim 6 where the matrix includes an element to enhance diffusivity ratio of aluminum to oxygen in the matrix.

8. The alloy of claim 7 wherein said element is selected from the group consisting of Cr, Hf, Si, Ti, and W and combination thereof.

9. The alloy of claim 1 wherein the alloy forms an oxide layer comprising at least one of Al_2O_3, Y_2O_3, yttrium aluminum garnet, or reaction products of Al_2O_3 and Y_2O_3.

10. The alloy of claim 1 comprising Al, Pt, Y, an element selected from the group consisting of Cr, Hf, Si, Ti, and W and combination thereof, and balance Nb and having a ternary phase PtYAl.

11. The alloy of claim 1 comprising Al, Pd, Y, an element selected from the group consisting of Cr, Hf, Ti, and W and combination thereof, and balance Nb and having a ternary phase PdYAl.

12. The alloy of claim 1 having an oxidation resistance with a target recession rate less than 2.5 μm/hr at 130° C.

13. The alloy of claim 1 comprising at least about 53 atomic % niobium, about 13 to about 18 atomic % aluminum, about 2.5 to about 4 atomic % chromium, about 2.5 to about 6 atomic % hafnium, up to about 8 atomic % palladium, up to about 7.45 atomic % platinum, up to about 5

atomic % silicon, about 5 to about 6 atomic % titanium, up to about 2 atomic % tungsten, and about 7 to about 9 atomic % yttrium.

14. The alloy of claim 13 which is characterized by target recession rate less than 2.5 μm/hr at 1100° C. or higher.

15. The alloy of claim 1 comprising, in atomic percent, about 13 to about 25 parts aluminum, up to about 4 parts chromium, up to about 5 parts hafnium, about 5 to about 15 parts platinum, up to about 5 parts silicon, up to about 6 parts titanium, up to about 2 parts tungsten, about 7 to about 15 parts yttrium, and the balance niobium.

16. The alloy of claim 1 comprising, in atomic percent, about 13 to about 23 parts aluminum, up to about 3 parts chromium, up to about 8 parts hafnium, about 5 to about 38 parts palladium, up to about 6 parts titanium, up to about 2 parts tungsten, about 8 to about 25 parts yttrium, and the balance niobium.

17. The alloy of claim 1 comprising, in atomic percent, about 13 to about 18 parts aluminum; about 2 to about 4 parts chromium; about 2 to about 5 parts hafnium; about 5 to about 8 parts platinum; up to about 5 parts silicon; about 5 to about 6 parts titanium; up to about 2 parts tungsten; about 7 to about 9 parts yttrium; and the balance niobium.

18. The alloy of claim 1 comprising, in atomic percent, about 13 to about 15 parts aluminum; about 2 to about 3 parts chromium; about 2 to about 6 parts hafnium; about 5 to about 8 parts palladium; about 4 to about 6 parts titanium; up to about 2 parts tungsten; about 8 to about 9 parts yttrium; and the balance niobium.

19. The alloy of claim 1 comprising the alloy of claim 15 exposed to air or other oxygen bearing atmosphere at an elevated temperature such that said oxide layer comprising at least one of Al_2O_3, Y_2O_3, yttrium aluminum garnet, or reaction products of Al_2O_3 and Y_2O_3 is present on the component.

20. A turbine blade or vane made of the alloy of claim 1.

21. The oxidation resistant niobium based alloy of claim 1 further including a third multicomponent phase as a buffer for excess aluminum.

22. The alloy of claim 21 further including an additional, multi-component Nb_2Al phase as a buffer for excess aluminum in the oxidation resistant niobium based alloy.

23. Niobium base alloy, comprising a platinum-series element and balance Nb and having a yttrium aluminum garnet layer on the alloy.

24. The alloy of claim 23 comprising the platinum-series element selected from Pt or Pd or a combination thereof and an additional element selected from the group consisting of Al, Y, Cr, Hf, Si, Ti, W, and combination thereof.

25. The alloy of claim 23 further including a third multicomponent phase as a buffer for excess aluminum.

26. The alloy of claim 23 further including an additional, multi-component Nb_2Al phase as a buffer for excess aluminum in the oxidation resistant niobium based alloy.

27. A turbine blade or vane comprising the alloy of claim 23.

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