

013-275

NASA Case No. LEW #20,006-1

Print Figure 1

No. Of Pages in Claims 23

No. Of Pages in Abstract 1

NOTICE

The invention disclosed in this document resulted from research in aeronautical and space activities performed under programs of the National Aeronautics and Space Administration. The invention is owned by NASA and is, therefore, available for licensing in accordance with the NASA Patent Licensing Regulation (14 Code of Federal Regulations 1245.2).

To encourage commercial utilization of NASA-owned inventions, it is NASA policy to grant licenses to commercial concerns. Although NASA encourages non-exclusive licensing to promote competition and achieve the widest possible utilization, NASA will consider the granting of a limited exclusive license, pursuant to the NASA Patent Licensing Regulations, when such a license will provide the necessary incentive to the licensee to achieve early practical application of the invention.

Address inquiries and all applications for license for this invention to NASA Lewis Research Center, Patent Counsel, Mail Code Le-LAW, 21000 Brookpark Road, Cleveland, OH 44135-3195. Approved NASA forms for application for non-exclusive or exclusive license are available from the above address.

Serial Number 08/735,368

Filing Date October 21, 1996

NASA/LeRC

ABSTRACT

5 A diffusion barrier to help protect titanium aluminide alloys, including the coated alloys of the TiAl γ + Ti₃Al (α_2) class, from oxidative attack and interstitial embrittlement at temperatures up to at least 1000°C is disclosed. The coating may comprise FeCrAlX alloys. The diffusion barrier comprises titanium, aluminum, and iron in the following approximate atomic percent:

Ti-(50-55)Al-(9-20)Fe.

10 This alloy is also suitable as an oxidative or structural coating for such substrates.

Oxidation Resistant Ti-Al-Fe Diffusion
Barrier for FeCrAlY Coatings on Titanium
Aluminides

Michael P. Brady, NRC
James L. Smialke, LeRC
William J. Brindley, LeRC
08/735,368

Schematic Partial 1000°C Phase Diagram (Atomic Percent)

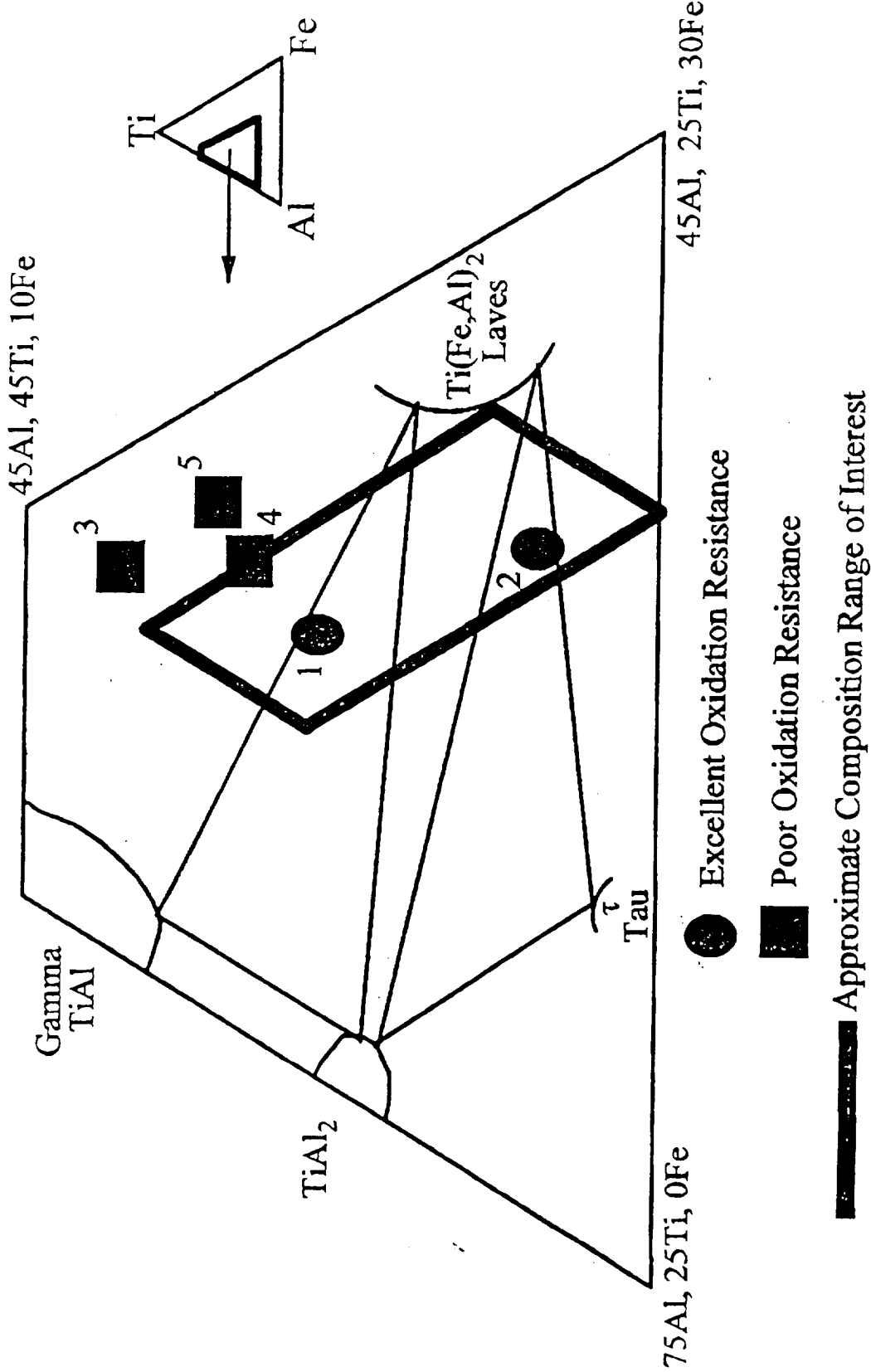


FIGURE 1

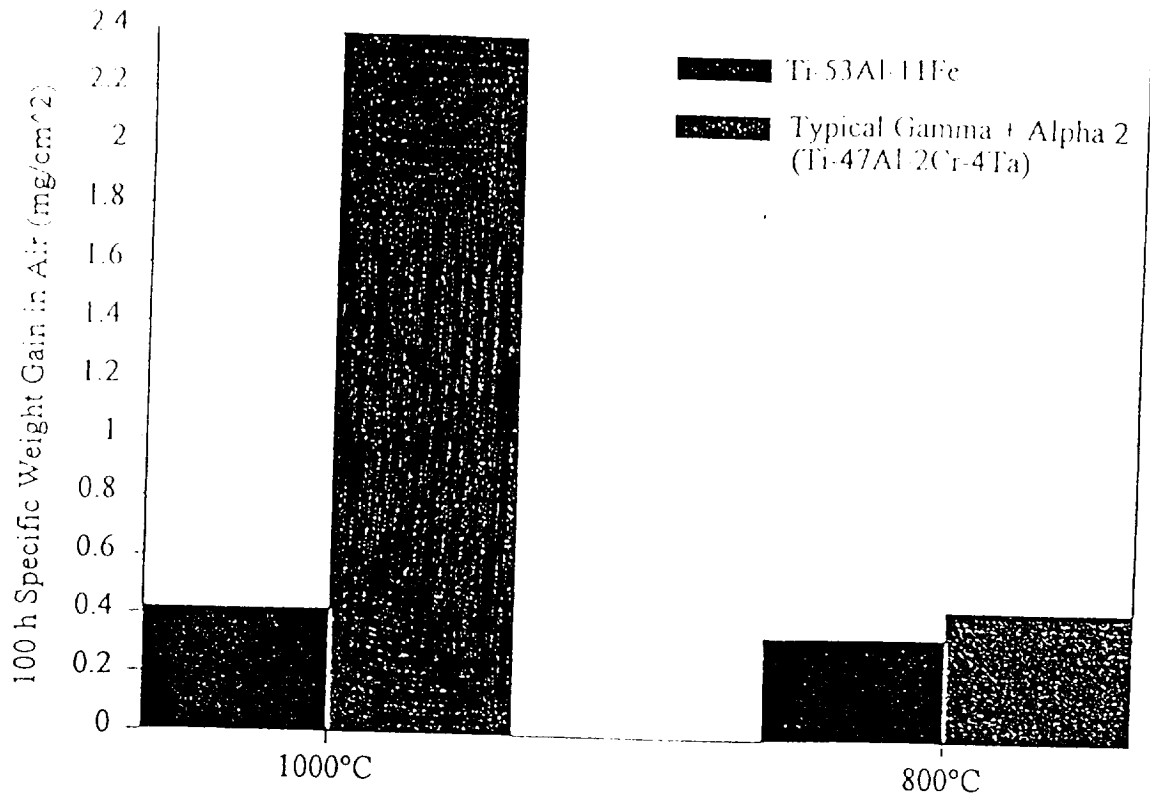
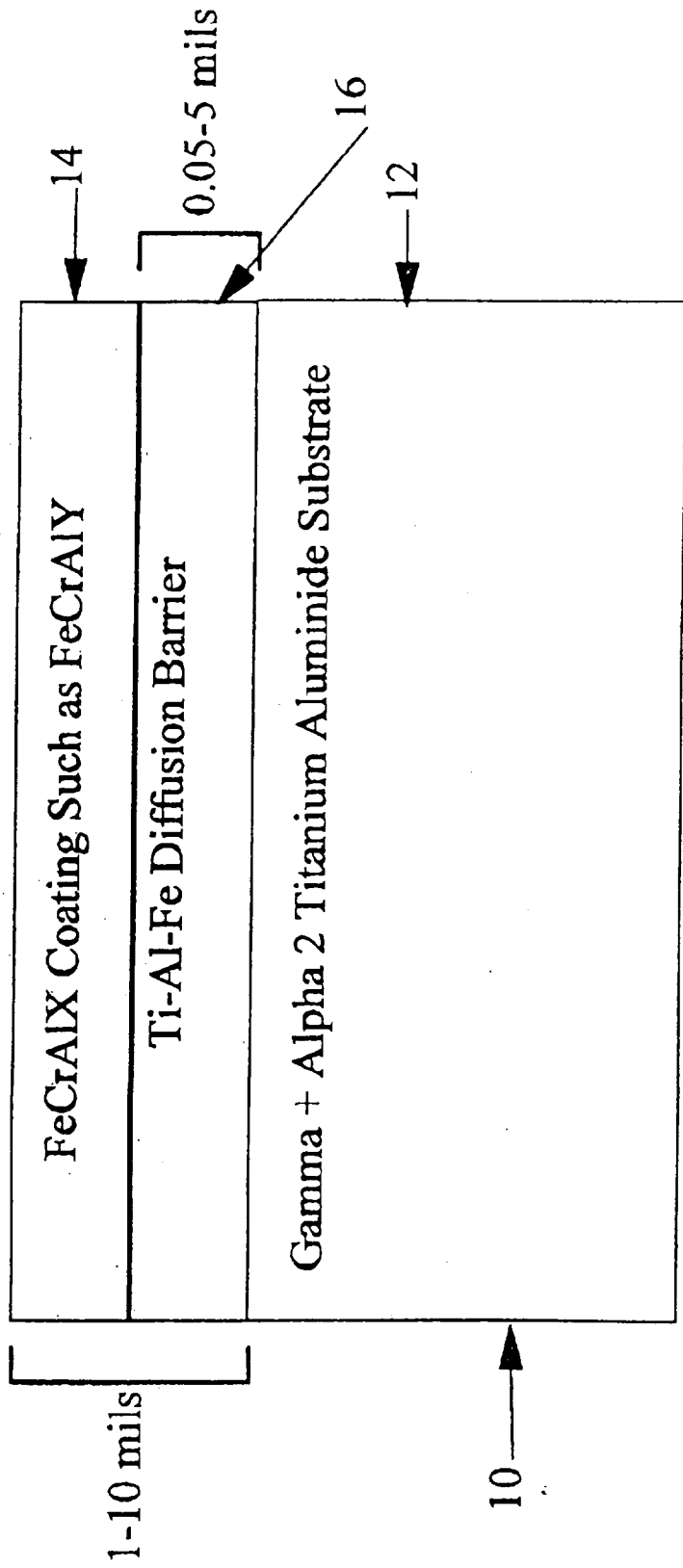


Fig. 1-Oxidation weight gain data for a typical Ti-Al-Fe alloy, Ti-53Al-11Fe atomic percent. For comparison a typical gamma + alpha 2 titanium aluminide is also shown (data from reference 2). The Ti-Al-Fe alloy exhibits superior oxidation resistance to the gamma + alpha 2 titanium aluminide.

FIGURE 2



Schematic Drawing of Ti-Al-Fe Diffusion Barrier for FeCrAlY Coatings on Gamma + Alpha 2 Titanium Aluminide Substrates.

Figure 3

**OXIDATION-RESISTANT Ti-Al-Fe ALLOY
DIFFUSION BARRIER COATINGS**

ORIGIN OF INVENTION

5 The invention described herein was made in part by employees of
the United States Government and may be manufactured and used by the
Government for governmental purposes without the payment of any royalties
thereon or therefor.

10 FIELD OF INVENTION

This invention pertains to the art of alloys of titanium and
aluminum, and more specifically to an oxidation coating and/or a diffusion
barrier to limit the interaction between a titanium aluminide substrate and
MCrAlX (e.g., FeCrAlY) coatings which protect the titanium aluminide from
15 oxidation and interstitial embrittlement up to at least 1000°C. The diffusion
barrier comprises a titanium-aluminum-iron alloy which is of intermediate Fe
content, i.e., having an iron content between that of the FeCrAlY coating and
the titanium aluminide substrate. Suitable Ti-Al-Fe alloys fall primarily in the
 γ - τ -Laves composition range. The Ti-Al-Fe diffusion barrier can be used to
20 limit interaction between FeCrAlY coatings and titanium aluminide substrates,
and further is itself suitable as an oxidation and embrittlement-resistant coating
for titanium aluminides.

BACKGROUND OF THE INVENTION

25 Titanium aluminides are intermetallic compounds known to be
candidate materials for use in advanced structural applications because they
offer a desirable combination of low density and high temperature strength. In
particular, substrates which are mixtures of TiAl (γ) and Ti₃Al (α_2) are being
examined for high-temperature, structural applications including, for example,
30 aircraft and automotive engines and exhaust systems. However, these materials
are currently limited to applications below approximately 700°C-800°C because
of inadequate oxidation resistance. They are also susceptible to environmental
embrittlement by interstitial diffusing species which may severely degrade their
mechanical properties and limit their use as structural materials.

In the art, it is known that providing a metallic substrate with a coating may serve to enhance a substrate's structural properties. Such coatings are required to provide sufficient oxidative resistance without degrading the substrate's structural properties because of brittleness and chemical or thermal incompatibility.

5

MCrAlX-type coatings, where M is typically iron, nickel, or cobalt, and X is typically an active element such as Y, Zr, Hf, Yb, and similar reactive elements have been proposed to protect titanium aluminide substrates from oxidation and interstitial embrittlement. For example, FeCrAlY coatings have been shown to be effective in protecting titanium aluminides. However, the system has the disadvantage of diffusion over time between the titanium aluminide substrate and the FeCrAlY coatings which can lead to embrittled interlayers and coating failure. Consequently, these systems may require the use of a diffusion barrier to limit interaction between the coatings and the substrate.

10

There have been diffusion barriers proposed for MCrAlX coatings on titanium aluminide substrates. For example, the use of tungsten as a diffusion barrier to limit the interaction between a FeCrAlY coating and a titanium aluminide substrate is discussed in a paper entitled "Oxidation and Protection of Ti₃Al-Based Intermetallic Alloys" (D.W. McKee, Mat. Res. Soc. Proc., Vol. 288, Materials Research Society, p. 953; 1993).

15

20

In general, the diffusion barriers known in the art have traditionally been nonoxidation-resistant materials such as tungsten. While diffusion barriers such as tungsten have successfully allowed coatings such as FeCrAlY to protect titanium aluminides from oxidation and interstitial embrittlement due to elevated temperature exposure in air, they are not practical because of poor oxidation resistance. Cracking of the outer FeCrAlY coating such as may occur during use due to mechanical or thermal loading would consequently result in rapid oxidation of the tungsten diffusion barrier; this would result in catastrophic failure of the coating. The titanium aluminum iron alloys of the present invention solve this problem since they are highly oxidation resistant.

25

30

SUMMARY OF THE INVENTION

In accordance with the present invention, alloys of Ti-Al-Fe are provided for use as an oxidation-resistant diffusion barrier between MCrAlX-type coatings and substrates such as titanium or titanium aluminide substrates, and further for use as coatings to protect titanium and titanium aluminide substrates from oxidation and interstitial embrittlement.

More particularly in accordance with the invention, an oxidation-resistant diffusion barrier is comprised primarily of Ti-Al-Fe Alloys of the $Ti(Fe,Al)_2$ Laves phase and the τ (L_{12}) phase or the γ (TiAl) phase. This diffusion barrier is sufficiently oxidation-resistant that it can also be used without an MCrAlX overlay coating to protect titanium and titanium aluminide alloys from oxidation and interstitial embrittlement.

In accordance with the invention, studies of oxidation behavior of titanium aluminides with significant quantities (5-30 atomic percent) of ternary alloying additions led to the identification of ternary Laves-type phases as a major source of excellent oxidation resistance. In particular, ternary Laves-type phases which are low in aluminum content have been found to exist in equilibrium with the γ (TiAl) and τ (L_{12}) phases which are of much higher aluminum content. Additionally, the orientation of the phase fields is such that the γ or τ phases act as an aluminum reservoir for the Laves phase during oxidation. This is believed to contribute to the ability of the alloy to initiate and maintain a protective alumina-based scale, which provides the excellent oxidation resistance of the alloys. Thus, in accordance with the invention, alloys in the τ + Laves and γ + Laves Ti-Al-Fe composition range have been selected for use as oxidation-resistant coating(s), in particular for use as an oxidation-resistant diffusion barrier between FeCrAlY coatings and titanium aluminide and/or titanium substrates. The composition range is approximately Ti-(50-55)Al-(9-20)Fe atomic percent. The format of atomic percent used herein specifies the percent of aluminum and iron, the remainder from 100 being titanium. More particularly, compositions of Ti-53Al-11Fe and Ti-54Al-17Fe (atomic percent \pm 2 atomic percent each) have been found to exhibit protective

alumina scale formation at 1000°C in air. Thus according to one aspect of the present invention, an iron-modified titanium aluminum alloy consists essentially of iron, titanium, and aluminum, in the following approximate atomic percent:



5 These oxidation-resistant coatings can be used with an MCrAlX outer coating having superior mechanical properties. In this case, the titanium aluminum iron alloys act as a diffusion barrier. They are of "intermediate" iron content insofar as they have an iron content between that of a preferred FeCrAlY coating and a titanium aluminide substrate, i.e., 9-20 atomic percent.
10 The diffusion barrier has the effect of limiting inward diffusion between the FeCrAlY coating and titanium aluminide substrates.

 Particularly preferred alloys have phases in the τ + Laves and/or in the γ + Laves composition ranges. Because the Ti-Al-Fe alloys are titanium and aluminum based and of intermediate iron content between FeCrAlY coatings and titanium aluminide substrates, they can be used as a diffusion
15 barrier to limit interaction between a FeCrAlY coating and titanium aluminide and titanium substrates.

 The Ti-Al-Fe alloys of the present invention are also suitable as an oxidation-resistant diffusion barrier for other MCrAlX-type coatings, such as
20 NiCrAlY and CoCrAlY, on titanium aluminide and titanium substrates. The Ti-Al-Fe alloys of the present invention are also suitable as an oxidation and interstitial embrittlement-resistant coating for titanium aluminide and titanium substrates. The Ti-Al-Fe alloys of the present invention also have uses as an oxidation-resistant structural material. The Ti-Al-Fe alloys of the present
25 invention are also suitable for coating alumina-based fibers to prevent matrix-fiber interactions in titanium-based metal matrix composites.

 In accordance with the invention, a particular use of the Ti-Al-Fe alloys is as a diffusion barrier between FeCrAlY oxidation-resistant coatings and
 $\gamma + \alpha_2$ titanium aluminide substrates, for example Ti-47Al-2Cr-4Ta and Ti-48Al-
30 2Cr-2Nb. The advantage of this Ti-Al-Fe diffusion barrier is that it is oxidation resistant.

In another embodiment, the Ti-Al-Fe coatings of the invention can act as a diffusion barrier for MCrAlX-type coatings such as NiCrAlY or CoCrAlY.

5 In yet another embodiment, the Ti-Al-Fe coatings of the invention can be used with other possible titanium aluminide substrates: α_2 -based titanium aluminides, orthorhombic-based titanium aluminides, and α or β titanium aluminides and pure titanium.

Thus the titanium aluminum iron alloy of the present invention can be used as:

- 10 a) a diffusion barrier for MCrAlX-type coatings on titanium aluminides;
- b) an oxidation and interstitial embrittlement-resistant coating for titanium aluminides;
- c) an oxidation-resistant structural material; and
- 15 d) a diffusion barrier between alumina-based fibers and titanium-based matrices in titanium metal matrix composites.

BRIEF DESCRIPTION OF THE DRAWINGS

20 The detailed description of the invention which follows will be understood with greater clarity if reference is made to the accompanying drawings in which:

FIGURE 1 is a phase diagram indicating the preferred composition range of Ti-Al-Fe alloys of the present invention;

25 FIGURE 2 is a bar graph showing oxidation weight gain for a typical Ti-Al-Fe alloy (Ti-53Al-11Fe) compared to a typical gamma + alpha 2 titanium aluminide alloy at both 800°C and 1000°C; and

FIGURE 3 is a schematic drawing of a Ti-Al-Fe diffusion barrier in accordance with the invention.

DETAILED DESCRIPTION OF THE INVENTION

Studies of the oxidation behavior of titanium aluminides with significant quantities (5-30 atomic percent) of ternary alloying additions led to the identification of multiphase Ti-Al-Fe alloys, consisting primarily of a γ + Laves or τ + Laves microstructure, as holding the potential for excellent oxidation resistance. Air oxidation screenings were conducted and evaluated at 1000°C in air for the Ti-Al-Fe alloys listed in Table I. The Ti-Al-Fe alloys were produced by arc-melting and casting techniques as are known in the art. Oxidation behavior was evaluated by visual inspection and/or cross-sectional analysis of the oxidized specimens using a scanning electron microscope equipped with energy-dispersive X-ray analysis.

The alloys Ti-53Al-11Fe (1) and Ti-54Al-17Fe (2) were found to exhibit excellent oxidation resistance due to the formation of an alumina-based oxide scale. Alumina-based scales are protective due to their very low rate of growth, and are also an effective barrier to the transport of interstitials such as oxygen and nitrogen into the alloy, which can result in embrittlement.

The Ti-Al-Fe alloys of Table I are mapped on the schematic 1000°C phase diagram (atomic percent) shown in Figure 1. The alloys Ti-53Al-11Fe (1) and Ti-54Al-17Fe (2) exhibited excellent oxidation resistance. The microstructures of these alloys were examined in detail by electron microprobe and X-ray diffraction. The results of this analysis were used to create the partial schematic phase diagram shown in Figure 1. Based on the composition range defined by the tie-lines of Ti-53Al-11Fe (1) and Ti-54Al-17Fe (2), and the relatively poor oxidation resistance of alloys 3-5 (Table I), the composition range of Ti-(50-55)Al-(9-20)Fe atomic percent was identified as oxidation-resistant (capable of alumina-based scale formation).

TABLE I

ALLOYS (Atomic %)	1000°C/100 Hour Air Oxidation Screening
Ti-53Al-11Fe (1)	Alumina Former (Excellent Oxidation Resistance)
Ti-54Al-17Fe (2)	Alumina Former (Excellent Oxidation Resistance)
Ti-48Al-10Fe (3)	Poor Oxidation Resistance
Ti-50Al-12Fe (4)	Poor Oxidation Resistance
Ti-48Al-13Fe (5)	Poor Oxidation Resistance

5

10

Oxidation resistance data after 100 h at 1000°C and 800°C in air for Ti-53Al-11Fe and a typical $\gamma + \alpha_2$ alloy, Ti-47Al-2Cr-4Ta, is shown in Figure 2. The Ti-53Al-11Fe alloy exhibits superior oxidation resistance to the $\gamma + \alpha_2$ alloy especially at 1000°C.

15

20

25

The Ti-(50-55)Al-(9-20)Fe atomic percent alloys of the present invention are ideal for use as a diffusion barrier to limit interaction between FeCrAlY coatings and titanium aluminide substrates. They are of intermediate Fe content between FeCrAlY coatings (which typically contain greater than 30-50 atomic percent Fe) and $\gamma + \alpha_2$ titanium substrates (which typically contain between 0-2 atomic percent Fe) and exhibit excellent oxidation resistance. In the event of cracking of the outer FeCrAlY layer, such as may occur during use due to mechanical or thermal loading, the Ti-(50-55)Al-(9-20)Fe atomic percent diffusion barrier would remain intact, while a nonoxidation-resistant diffusion barrier such as tungsten would be rapidly consumed by oxidation. Rapid oxidation of the diffusion barrier would lead to catastrophic failure of the FeCrAlY coating.

Figure 3 shows a schematic drawing of a Ti-Al-Fe diffusion barrier for FeCrAlY coatings on $\gamma + \alpha_2$ titanium aluminide substrates. In this Figure, an article such as, for example, a turbine blade, is shown generally at 10. This article includes a $\gamma + \alpha_2$ titanium aluminide substrate 12 which is coated on at

least one surface, and more preferably coated on all exposed surfaces with an oxidation protective coating 14 of about 1 to 10 mils total, comprising an outer layer of about 1 to about 9.95 (10) mils of FeCrAlY, and an intermediate layer of from about 0.05 to about 5 mils of a Ti-Al-Fe diffusion barrier 16. The coatings can be applied by coating techniques known in the art such as thermal spray, plasma spray, sputtering, physical vapor deposition, chemical vapor deposition, slurry processing, and other well known techniques.

In an alternate embodiment, the Ti-Al-Fe alloys of the present invention are also suitable oxidation-resistant coatings and/or for diffusion barriers for other titanium aluminide substrates such as α_2 -based or orthorhombic-based alloys such as Ti-24Al-11Nb or Ti-22Al-23Nb, respectively.

In still another use, the Ti-Al-Fe alloys are also suitable for coating alumina-based fibers to prevent matrix/fiber interactions in titanium-based metal matrix composites.

It will be apparent to those skilled in the art that the above methods may incorporate changes and modifications without departing from the general scope of this invention. It is intended to include all such modifications and alterations insofar as they come within the scope of the appended claims or the equivalents thereof.

Having thus described the invention, it is now claimed:

Schematic Partial 1000°C Phase Diagram (Atomic Percent)

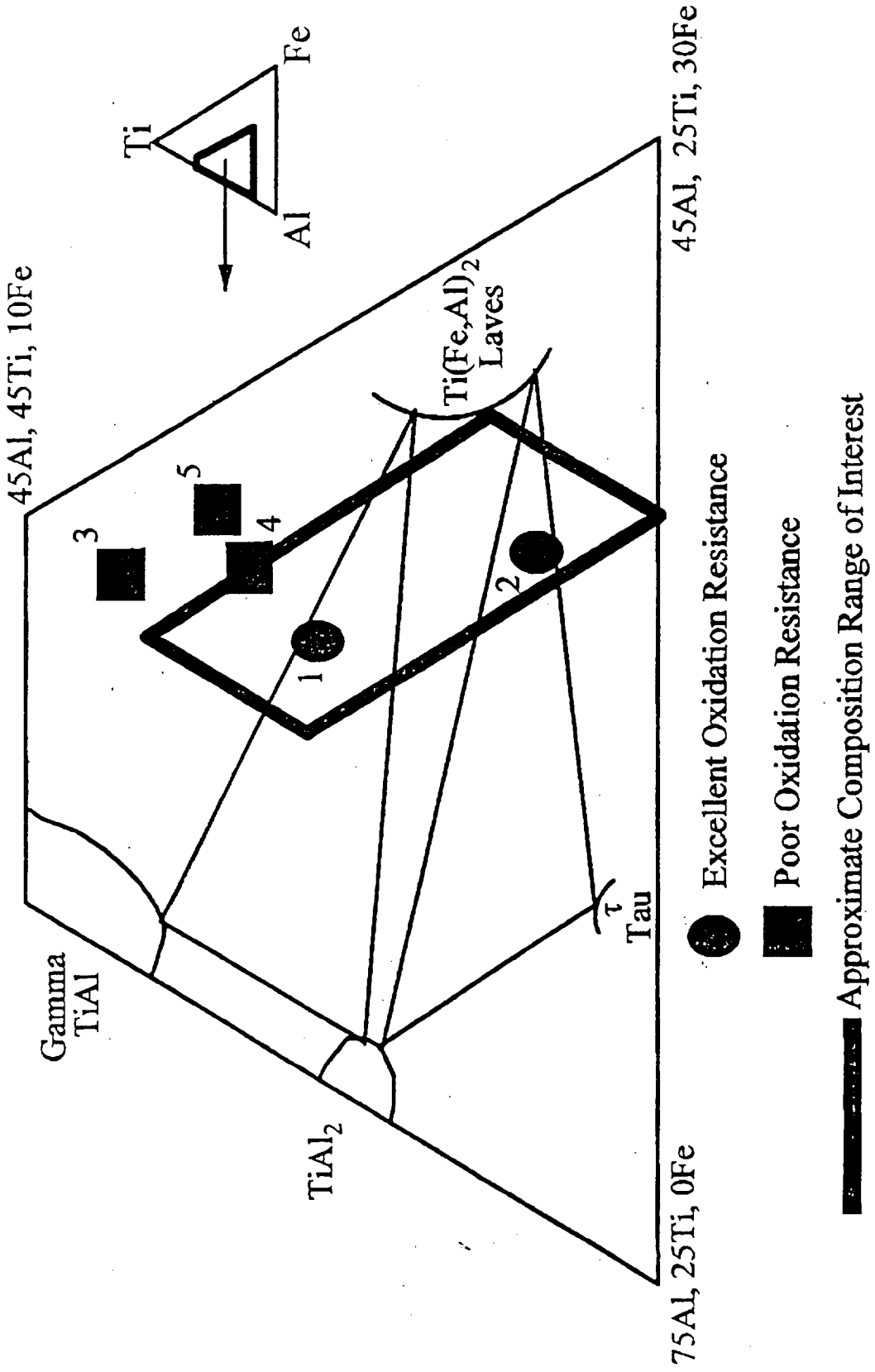


FIGURE 1

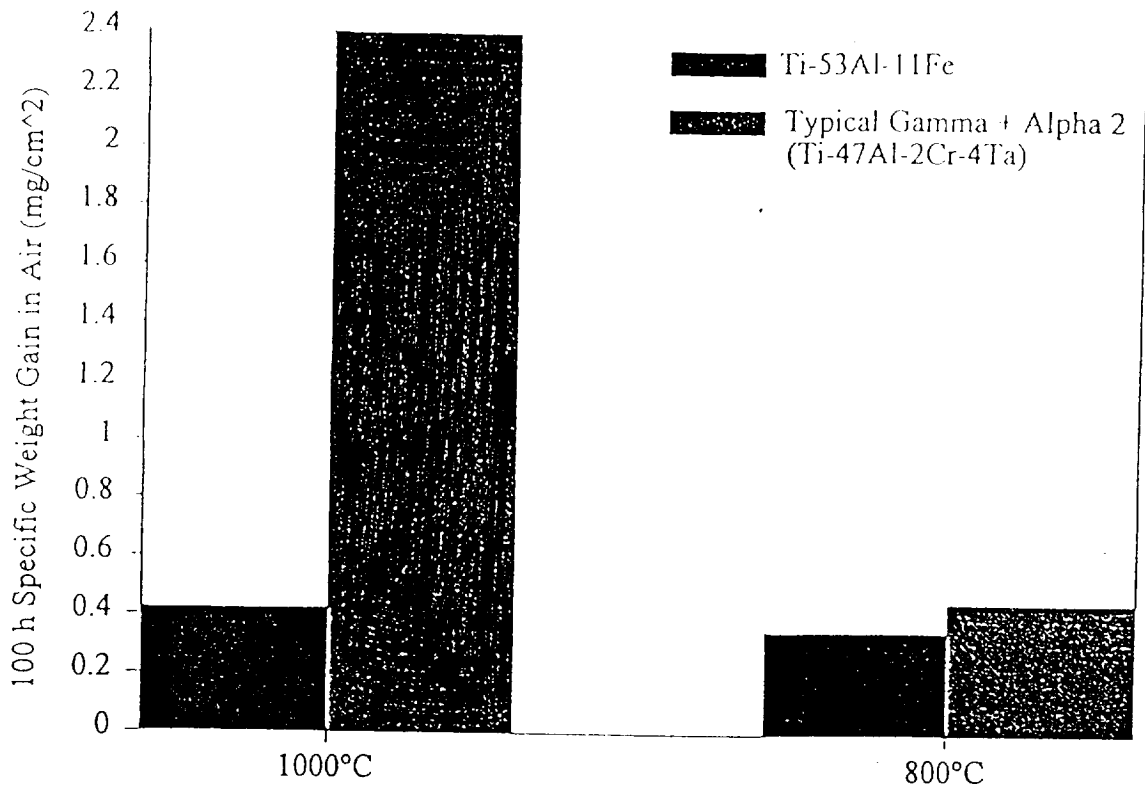
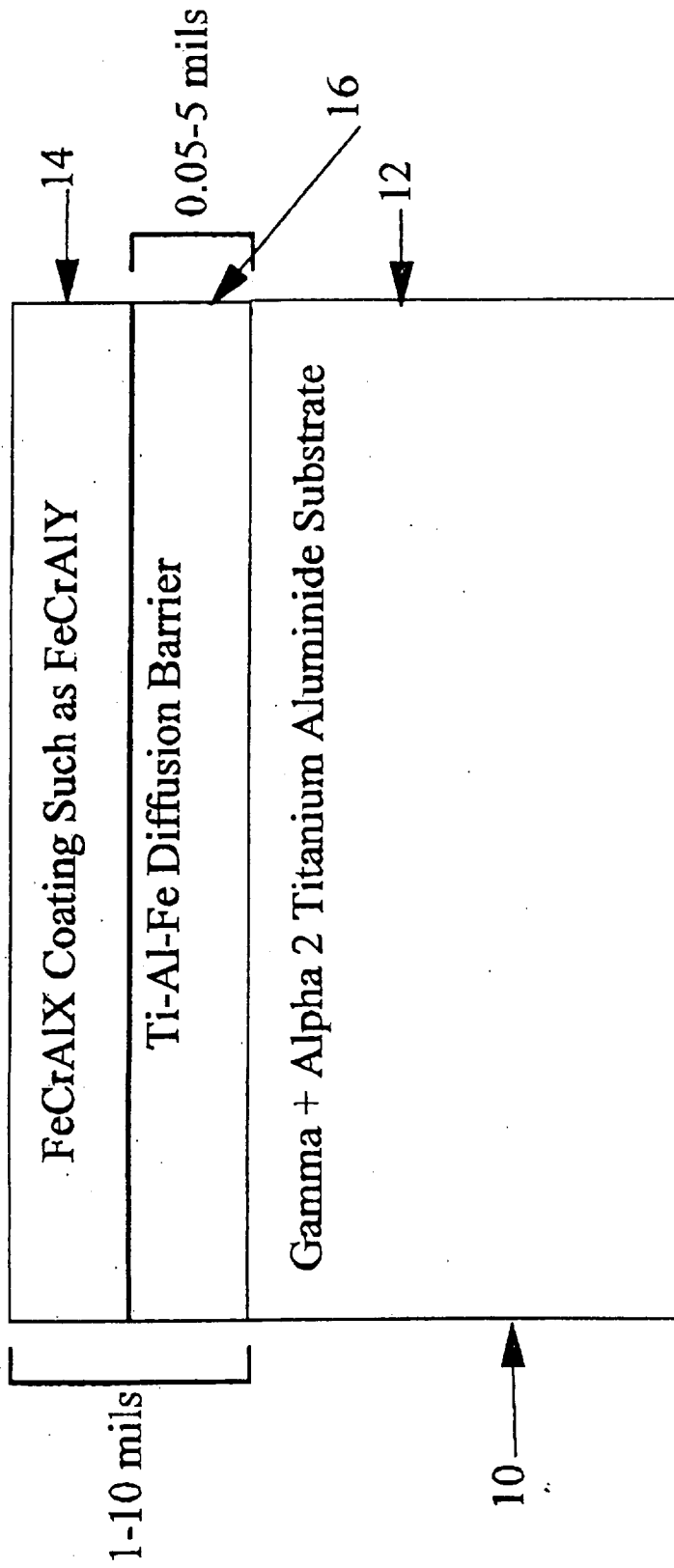


Fig. 1-Oxidation weight gain data for a typical Ti-Al-Fe alloy, Ti-53Al-11Fe atomic percent. For comparison a typical gamma + alpha 2 titanium aluminide is also shown (data from reference 2). The Ti-Al-Fe alloy exhibits superior oxidation resistance to the gamma + alpha 2 titanium aluminide.

FIGURE 2



Schematic Drawing of Ti-Al-Fe Diffusion Barrier for FeCrAlY Coatings on Gamma + Alpha 2 Titanium Aluminide Substrates.

Figure 3