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(54) **Method of forming a protective diffusion layer on nickel, cobalt and iron based alloys**

(57) The present invention is directed to a method for forming a protective diffusion layer on nickel, cobalt, and iron based alloy parts. The method has two steps. In a first step, a simple aluminide coating is formed on internal surfaces and any passageways (40) formed by the internal surfaces of the part. The simple aluminide coating forming step comprises providing a first source (16) of a gaseous aluminizing species, heating the source and the part, and maintaining a flow of an inert gas during the heating phase. Preferably, the inert gas is maintained at a critical forced flow rate to facilitate the formation of the coating in any passageways defined by the internal surfaces. The second step of the method comprises forming a $PtAl_2$ + NiAl, $PtAl_2$ + FeAl or $PtAl_2$ + CoAl coating on external surfaces of the part.

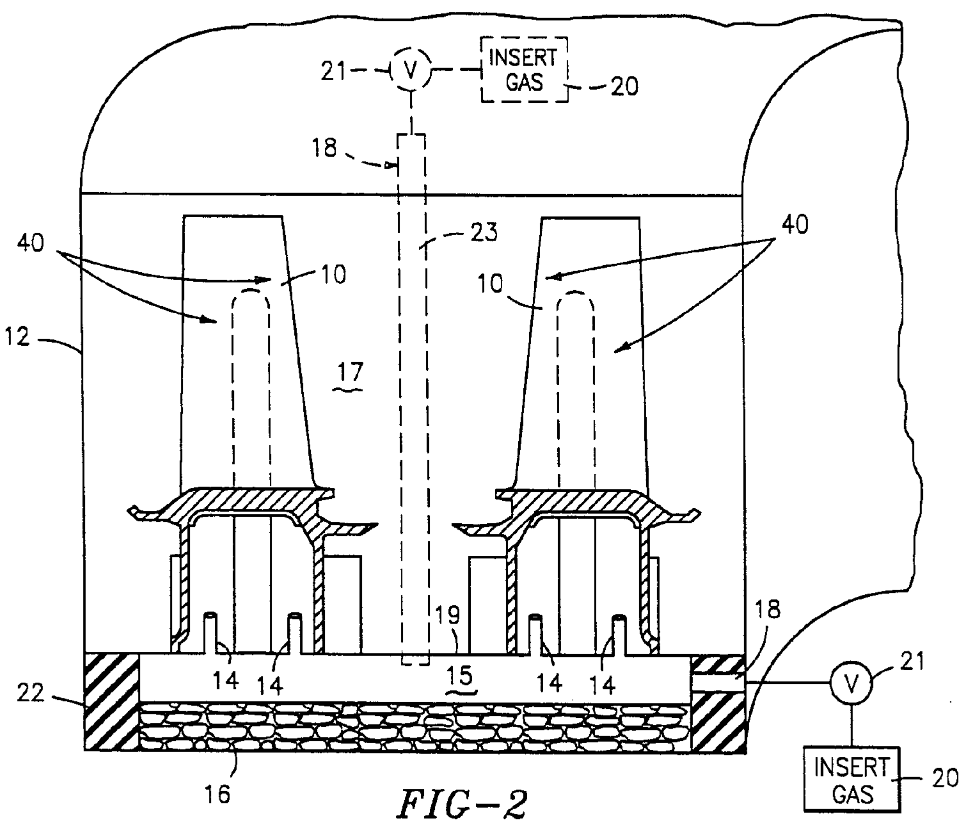

FIG-2

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Description

The present invention relates to a method for forming protective diffusion layers on nickel, cobalt, and iron base alloy parts and, more particularly, to a method for selectively applying a platinum aluminide coating on external surfaces of such parts and a simple aluminide coating on internal surfaces of such parts. The method of the present invention has particular utility in the formation of protective diffusion layers on gas turbine engine components.

Methods of forming protective diffusion coatings on nickel, cobalt and iron base alloy parts are known in the art. Such coatings are typically needed to enhance the resistance of parts, such as gas turbine engine components, to hot corrosion. In fact, most gas turbine engine manufacturers specify a $PtAl_2$ + NiAl outer zone coating microstructure for such parts made of a nickel-base superalloy. This type of platinum-aluminum coating is specified as a QC check to verify that an amount of platinum is present in the coating sufficient to assure adequate performance.

One method which has been used to form these types of coatings is a pack cementation technique in which the article to be protected is placed in contact with or embedded within a powder mixture of aluminum or an aluminum alloy, a chemical transfer agent, usually a fluoride or chloride salt, and an inert diluent such as alumina. The powder mixture used in this technique forms a source of aluminizing gas species. To create the coating, the powder mixture is heated while the part being coated is within or in contact with the mixture. The article "Pack Cementation Coatings for Superalloys: A Review of History, Theory and Practice" by G.W. Goward et al., Transactions of the ASME, Vol.110, January 1988, pp. 150 - 154, discusses such known pack cementation techniques. Other articles discussing pack cementation techniques include "Kinetics of Pack Aluminization of Nickel", by L. L. Seigle et al., NASA Contractor Report 2939, and "Interdiffusion and Intrinsic Diffusion In the NiAl Phase of the Al-Ni System" by S. Shankar et al., Metalluraical Transactions A, Vol. 9A, Oct. 1978, p. 1467. One of the problems associated with pack cementation techniques is that gaseous aluminizing species must travel through the powder packs and through the region where the substrate being coated contacts the pack. As a consequence, less than desirable coatings can be formed. For this and other reasons, it is desirable to coat the article using a technique wherein the part being coated is out of contact with the source of the gaseous aluminizing species.

Out-of-contact methods of forming protective diffusion layers on nickel, cobalt and iron base alloy parts are also known. U.S. Patent Nos. 4,132,816, 4,427,720 and 5,068,127 and French Patent Nos. 1,433,497, 2,134,220 and 2,181,512 describe such methods. In one such method exemplified by U.S. Patent No. 4,501,776 to Shankar, a platinum aluminide coating is formed by depositing a platinum group metal on the surface of the part to be protected and forming a diffusion layer of platinum and aluminum on the surface by gas phase aluminizing the surface out of contact with a source of gaseous aluminizing species at elevated temperature. The benefits of such out-of-contact methods are described in the prior art. The articles "Hot Corrosion Resistance of Chromium Modified Platinum Aluminide Coating," by M. W. Dust et al., ASME 86-GT-291, June, 1986, and "Structure and 700C Hot Corrosion Behaviour of Chromium Modified Platinum-Alumninide Coatings," by M. Dust et al, J. Vac. Sci. Technol. A 4(6), Nov/Dec. 1986 also illustrate out-of-contact methods for forming protective diffusion layers on nickel, cobalt, and iron base alloy parts.

It has been recognized that to get a $PtAl_2$ + NiAl outer zone coating microstructure on a nickel-based superalloy, a critical amount of platinum, believed to be at least 38 to 40 wt%, and aluminum, preferably about at least 22 to 25 wt%, should be present in the outer zone. However, this outer zone microstructure can be affected by subsequent heat treatments. The article "Platinum Modified Aluminides" by J. S. Smith and D. H. Boone, ASME 90-GT-319, June 1990 describe this phenomenon. From a commercial fabrication point of view, it is important to obtain the $PtAl_2$ + NiAl outer zone microstructure on nickel-based superalloy specified by the gas turbine engine manufacturers as this determines whether the coating is an acceptable coating or not, regardless of the fact that some other microstructure fabricated by an out-of-contact technique may also be adequate.

In addition to the foregoing, modern parts for gas turbine engines contain internal surfaces which must also be protected. One approach for protecting such internal surfaces is described in U.S. Patent No. 4,148,275 to Benden et al. In this patent, an apparatus is disclosed for depositing a coating on the internal surfaces of hollow articles by gas deposition. The apparatus includes a sheet metal enclosure having a manifold member which defines first and second chambers therein. The first chamber is adapted to contain a powder mixture for generating a coating gas whereas the second chamber is adapted to house the articles being coated. The manifold member includes hollow tubes or other connector means extending therethrough to connect the interior of the articles in gas flow relation to the first chamber where the coating gas is generated. A source external of the enclosure supplies carrier gas to the first chamber at a controlled flow rate via tube means. The carrier gas transports the coating gas generated in the first chamber through the manifold tubes and then into the internal passages of the articles to effect deposition. The positive flow of coating gas through the internal passageways provides a substantially uniform coating thickness over the entire internal surface area of each article.

Despite the existence of this technology, there remains a need for an effective, commercial method for forming a $PtAl_2$ + NiAl, $PtAl_2$ + FeAl or $PtAl_2$ + CoAl outer zone microstructure on the external surfaces of gas turbine engine components formed from nickel, iron or cobalt based alloys respectively and for forming a simple aluminide coating on internal surfaces of the same components. Some have suggested that such coatings could be obtained in a single operation. This is not believed to be possible. One of the fundamental aspects of "out-of-contact" processes, a form of CVD process, is the fact that if one wants a coating to be relatively high in aluminum content, one has to use a high activity source. When one wants to coat complex internal passages simultaneously with a high activity external surface coating, the gas flows needed for applying the internal coating may dilute the activity of the external source. As a result, a microstructure such as a (PtNi)Al microstructure on a nickel-based superalloy may be formed. While this type of coating is adequate from a protection standpoint, it does not meet the specification requirements of gas turbine engine manufacturers.

Accordingly, it is an object of the present invention to provide a method for forming an outer zone microstructure of $PtAl_2$ + NiAl, $PtAl_2$ + FeAl or $PtAl_2$ + CoAl, depending upon the superalloy being used for a particular component, and a simple aluminide internal surface coating.

It is also an object of the present invention to provide a method as above which is simple to perform and economically practical.

Still other objects and advantages to the method of the present invention are set out in the following description and the accompanying drawings wherein like reference numerals depict like elements.

The foregoing objects are attained by the method of the present invention.

The method of the present invention has two steps. In the first step, a simple aluminide coating is formed on internal surfaces of a part, such as a gas turbine engine component, by providing a first source of aluminum, heating the source of aluminum to obtain a gaseous aluminum species, and then flowing the gaseous aluminum species against, and through any passageway(s) defined by, the internal surfaces. The flowing step comprises providing and maintaining a flow of an inert gas at a critical rate and at a pressure preferably of at least about 12.5 psi so as to cause said gaseous aluminum species to flow in the desired manner and form the simple aluminide coating. In a preferred embodiment of the present invention, the first source comprises a granular material containing from about 25 to about 50 wt% aluminum, and the balance consisting essentially of at least one material selected from the group consisting of iron, cobalt, nickel and chromium with at least about 1.0 wt% of a halide activator sprinkled on or in contact with the granules.

The second step of the method of the present invention comprises forming a $PtAl_2$ + NiAl, $PtAl_2$ + FeAl or $PtAl_2$ + CoAl coating on the outer surfaces of the part depending upon the composition of the superalloy used to form the part. The coating is preferably formed by providing a second source of aluminum and heating the part and the second source to form a gaseous aluminizing species that coats the external or outer surfaces. Prior to coating the external surfaces, and preferably prior to coating the internal surfaces, a coating of a platinum group metal is deposited on the external surfaces of the part. The external coating step is performed in the absence of any flow of inert gas. The second source preferably comprises from about 45 to about 50 wt% of aluminum, the balance essentially cobalt with less than 1.0 wt.% of a halide activator sprinkled on or in contact with the granules.

Figure 1 is a flow chart illustrating the method of the present invention;

Figure 2 is a cross sectional view of a heating chamber during the step of applying the internal coating to the part to be protected;

Figure 3 illustrates a cross sectional view of the heating chamber of Figure 2 during the external coating forming step;

Figure 4 is a photomicrograph illustrating a $PtAl_2$ + NiAl external coating formed on a DS-Mar M-200 + Hf material substrate by the method of the present invention; and

Figure 5 is a photomicrograph illustrating a simple aluminide internal coating formed by the method of the present invention on the substrate of Figure 4.

As previously mentioned, the present invention relates to a method for coating a metal based alloy part, such as a gas turbine engine component, having internal surfaces defining at least one passageway and external surfaces. The part may be formed from a nickel-based alloy, a cobalt-based alloy, or an iron-based alloy.

Figure 1 provides an overview of the method of the present invention. As shown therein, a part to be treated or coated is first inspected, prepared, masked, plated with platinum, optionally heat treated to diffuse the platinum, and optionally remasked to protect areas not to be coated. These steps are all preferably carried out prior to the commencement of the actual coating operations. If desired, the part may be prepared by degreasing it, blast cleaning it, and then rinsing it. Any suitable degreasing, blast cleaning and rinsing techniques known in the art may be used to prepare the part.

Platinum may be deposited on the part using any suitable technique known in the art. For example, platinum may be electroplated onto external surfaces of the part to a thickness of about 0.0003 inches. Thereafter, the part may be heat treated at about 1900°F for about three hours in an argon atmosphere to diffuse the platinum into the external surfaces of the part.

After a number of parts 10 to be coated have been prepared and platinum has been deposited thereon, they are moved into a heating chamber or furnace 12 such as that shown in Figure 2. The heating chamber 12 has an upper chamber 17 and a lower chamber 15 separated by a wall 19. It also has one or more pins 14 upon which each of the parts 10 to be coated is mounted. When mounted on the pins, the parts 10 are positioned within the upper chamber 17. However, any internal passageways (40) in the parts are in communication with the lower chamber 15 via suitable passageways (not shown) in the pins 14. The internal passageways (40) in the parts are for the cooling air. In some components the cooling air is fed from the bottom and in this case the components are positioned vertically on the pins as indicated in Figure 3. In some other components the cooling air is fed from the side. In this case the components are positioned horizontally on the pins (14). Said pins may take the form of hollow tubes. Seals, such as seals 22, are provided to prevent the gaseous aluminizing species from leaking out of the bottom coating chamber.

A first source 16 of gaseous aluminizing species is positioned beneath the parts 10 in the lower chamber 15. The source 16 is preferably a granular material having particle sizes in the range of from about 1/4 inch to about 1/2 inch with at least 1.0 wt% of a halide activator sprinkled on or in contact with the granules. The granular material forming the source preferably has a composition of from about 25 to about 50 wt% aluminum and the balance consisting essentially of at least one material selected from the group consisting of iron, cobalt, nickel, chromium, and mixtures thereof. The halide activator may be a fluoride, chloride, iodide or bromide such as aluminum fluoride, ammonium chloride, ammonium iodide, etc.

The heat chamber 12 also has an inlet 18 for allowing an inert gas to be introduced into the lower chamber 15 from an external source 20. Suitable valve means 21 may be provided to regulate the flow rate of the inert gas entering the lower chamber 15. If desired, the inlet 18, source 20 and valve means 21 may be arranged in an alternative location as shown in dotted lines in Figure 2. In this alternative arrangement, the inlet is connected to the lower chamber via conduit 23.

In order to coat the internal surfaces of the parts and any passageway(s) fully and adequately with the gaseous aluminizing species so as to form a simple aluminide coating, good throwing power is needed. This throwing power is determined by the flow rate of the gaseous aluminizing species and the potency of the activator. It has been found that to obtain the desired throwing power and the desired coating, a critical flow of an inert gas, such as argon, is needed. The quantity of this critical flow to take the gaseous aluminizing species through any internal passageway(s) formed by the internal surfaces of the parts 10 depends on part geometry. This critical flow is directly proportional to the volume of the internal passageways calculated by measuring the volume of water that is held by the passageways. Preferably, the critical flow is from about 0.5 cfh to 60 cfh at a pressure of 12.5 psi. For one type of part formed from a nickel base alloy, it is preferred to use a flow rate of at least about 12.0 cfh.

The actual process for coating the internal surfaces and/or passageway(s) involves initiating a flow of inert gas into the chamber 15 at the critical flow rate and a pressure of 12.5 psi and applying heat to the chamber 12 so as to cause the generation of a gaseous aluminizing species from the source 16. The heating step comprises heating the source to a temperature of about 1750°F to about 2150°F for a time period of one to fourteen hours. While the heat is being applied, the flow of the inert gas under the above conditions is maintained.

When the heating cycle has been completed and the internal coating has been applied, the flow of inert gas is stopped. The chamber 12 is then opened and a second source 24 of gaseous aluminizing species is inserted into the upper chamber 17. The first source 16 is left in place during this external coating step. This second source is used to form the $PtAl_2$ + NiAl, $PtAl_2$ + FeAl, or $PtAl_2$ + CoAl coating on the exterior surfaces of the parts. As shown in Figure 2, the second source 24 is positioned intermediate the parts 10. If desired, the second source may comprise one or more source modules of material for creating the gaseous aluminizing species.

The second source 24 is also preferably a granular material having particle sizes in the range of from about 1/4 inch to about 1/2 inch with less than about 1.0 wt% of a halide activator sprinkled on or in contact with the granules. Preferably, the granular material forming the second source has a composition comprising from about 45 to about 50 wt% aluminum and the balance consisting essentially of cobalt. The halide activator may be a fluoride and/or chloride such as aluminum fluoride. For the source 24, as well as the source 16, the amount of halide activator within the material is determined by the aluminization time. For longer aluminization times, more activator is required.

Application of the external coating is accomplished by raising the temperature in the heat chamber back to a temperature in the range of about 1750°F to about 2150°F for a time in the range of from about 1 to about 14 hours. During the external coating step, there is no forced flow of inert gas into the coating chamber 12; however, an inert gas atmosphere is maintained within the chamber 12. Since there is no flowing inert gas to dilute the gaseous aluminizing species, the amount of activator needed in the source 24 to effect coating is very low.

To demonstrate the method of the present invention, the following example was performed.

<u>EXAMPLE</u>

A test was performed using a part fabricated from a DS Mar-M-200 + Hf material whose nominal composition was 9.0% Cr, 10.0% Co, 0.14% C, 2.0% Ti, 5.0%

Al, 12.5% W, 0.015% B, 1.0% Cb, 1.6% Hf and the balance nickel. The part had a number of internal surfaces forming a passageway.

The internal surfaces were coated using a source comprising 4 lbs of CoAl granules and 0.12 lbs of aluminum fluoride activator. Argon was caused to flow into a heat chamber at a rate of 15 cfh at a pressure of 12.5 psi. The part and the source were then heated, while the flow of argon was maintained, to a temperature of about 1900°F + 25°F for 3 hours.

After the internal coating had been applied, a second source was introduced into the heat chamber. The second source consisted of 8 lbs of CoAl granules and 0.008 lbs of aluminum fluoride activator. Argon was caused to flow into the chamber to maintain an inert gas atmosphere in the chamber; however, there was no forced flow of argon during this step. The part and the second source were heated to a temperature of about 1900°F + 25°F for 4 hours.

Figures 4 and 5 illustrate the coatings which were obtained. Figure 4 clearly shows the formation of a $PtAl_2$ + NiAl protective layer. Figure 5 illustrates the internal coating which is a simple aluminide coating.

The method of the present invention is advantageous in that it allows the formation of a highly desirable simple aluminide internal coating and the formation of a desirable $PtAl_2$ + NiAl, $PtAl_2$ + FeAl or $PtAl_2$ + CoAl external coating. The method is further advantageous that it is economically viable and simple to perform.

Claims

1. A method for coating a metal based alloy part (10) having internal surfaces (40) and external surfaces, said method being characterized by the steps of:

   forming a simple aluminide coating on the internal surfaces of said part;
   said aluminide coating step comprising providing a first source (16) of gaseous aluminum, heating said first source to obtain a gaseous aluminum species, and then flowing said gaseous aluminum species to said internal surfaces;
   said flowing step comprising providing and maintaining a critical force flow of an inert gas so as to cause said gaseous aluminum species to flow against said internal surfaces and into any passageway formed by said internal surfaces and thereby form said aluminide coating; and
   thereafter forming a coating on said external surfaces, which coating has a different microstructure than said simple aluminide coating on said internal surfaces.

2. The method of claim 1 wherein said heating step comprises heating said part and said source of aluminum to a temperature between about 1750°F and 2150°F for a time period between about 1 and 14 hours.

3. The method of claim 1 wherein said first source providing step comprises providing a granular material consisting essentially of from about 25 to about 50 wt% aluminum and the balance consisting essentially of at least one material selected from the group consisting of iron, cobalt, nickel, chromium and mixtures thereof and providing at least 1.0 wt% of a halide activator.

4. The method of claim 3 wherein said granular material is formed from granules having a size in the range of from about 1/4" to about 1/2" and said first source is out of contact with said part.

5. The method of claim 1 wherein said internal and external surface coating steps are performed sequentially.

6. The method of claim 1 wherein said external surface coating step comprises:

   providing a second source (24) of aluminum; and
   heating said part and said second source of aluminum to a temperature in the range of from about 1750°F to about 2150°F for a time period in the range of from about 1 hour to about 14 hours to coat said external surfaces.

7. The method of claim 6 wherein said internal surface coating step is performed in the absence of the second source of aluminum and wherein said external coating step is performed in the absence of any internal forced flow of said inert gas.

8. The method of claim 6 wherein said second source of aluminum providing step comprises providing a material consisting essentially of from about 45 to about 50 wt% of aluminum and the balance consisting essentially of cobalt and further providing less than about 1.0 wt% of a halide activator and said external surface coating step comprising forming a $PtAl_2$ + NiAl, $PtAl_2$ + FeAl or $PtAl_2$ + CoAl coating on said external surfaces.

9. The method of claim 1 further comprising:
   depositing a coating of a platinum group metal on said external surfaces of said part prior to coating said internal surfaces.

10. A method of forming a protective diffusion layer on nickel, cobalt and iron base alloy part (10) characterized by the steps of:

depositing a platinum coating on external surfaces of said part;
placing said part into a heating chamber;
placing a first source (16) of a gaseous aluminizing species in said heating chamber;
coating internal surfaces of said part by heating said part and said first source to a temperature sufficient to create said gaseous aluminizing species while maintaining a critical forced flow of an inert gas, said coating step creating a simple aluminide coating on said internal surfaces;
discontinuing said flow of inert gas and said heating;
inserting a second source (24) of gaseous aluminizing species into said heating chamber; and
coating external surfaces of said part by heating said part and said second source to a temperature sufficient to create a gaseous aluminizing species and thereby forming a coating having a $PtAl_2$ + NiAl, $PtAl_2$ + FeAl or $PtAl_2$ + CoAl microstructure.

11. The method of claim 10 wherein:

said part placing step comprises mounting said part on a tube (14); and
said first source placing step comprises placing said first source in a first chamber (15) separate from a second chamber (17) in which the part is located.

12. The method of claim 11 wherein said second source inserting step comprises placing said second source in said second chamber and said external surface coating step is carried out in the absence of any forced flow of an inert gas.

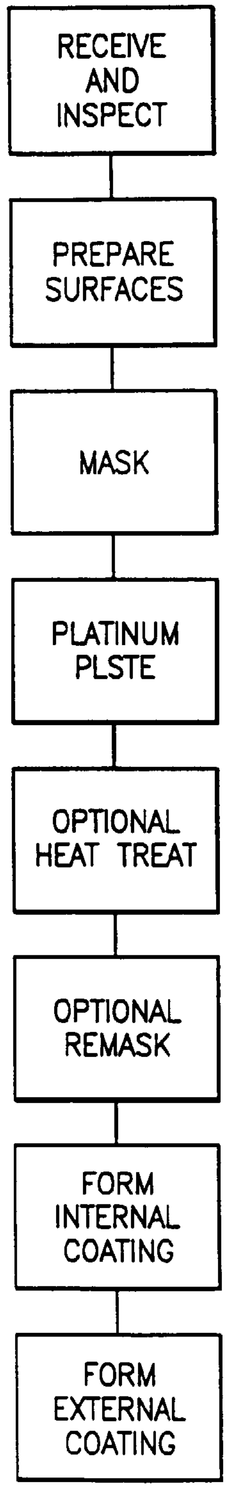
RECEIVE AND INSPECT
PREPARE SURFACES
MASK
PLATINUM PLSTE
OPTIONAL HEAT TREAT
OPTIONAL REMASK
FORM INTERNAL COATING
FORM EXTERNAL COATING

FIG-1

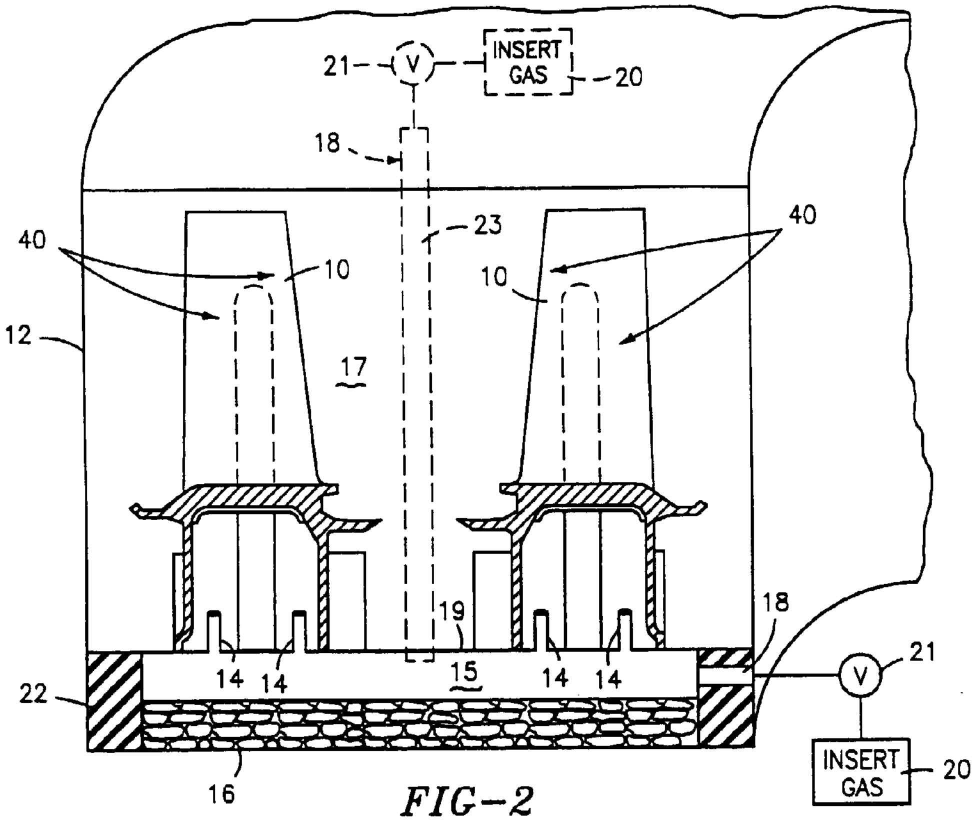

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FIG-2

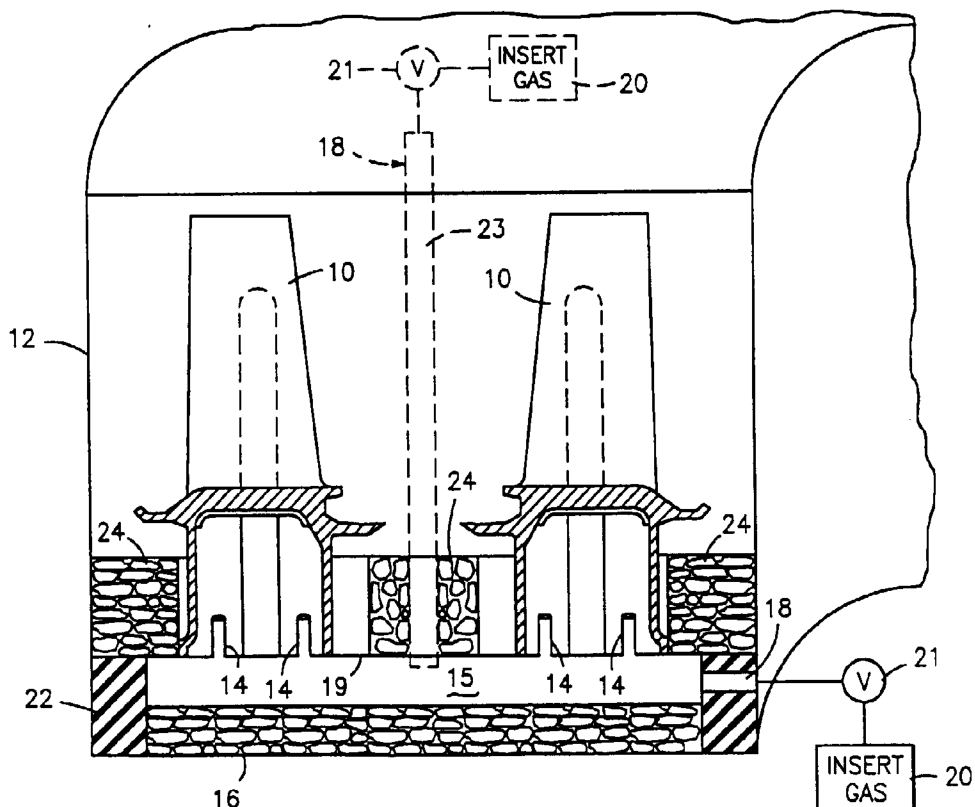

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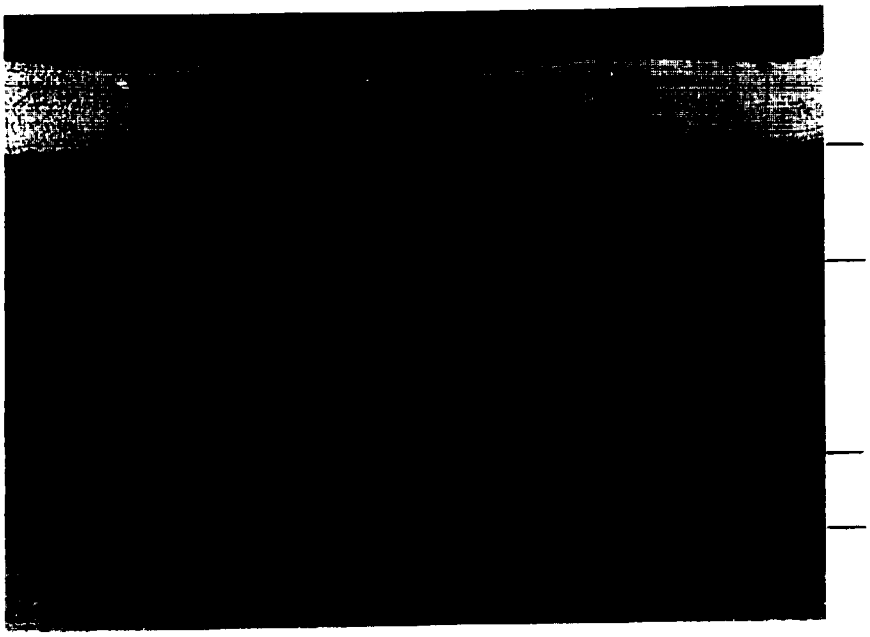
FIG-3


$PtAl_2$ + NiAl
NiAl
Diffusion Zone
Substrate

FIG–4


NiAl
Diffusion Zone
Substrate

FIG–5

European Patent Office

EUROPEAN SEARCH REPORT

Application Number
EP 96 30 1522

DOCUMENTS CONSIDERED TO BE RELEVANT

Category	Citation of document with indication, where appropriate, of relevant passages	Relevant to claim	CLASSIFICATION OF THE APPLICATION (Int.Cl.6)
Y,D	US-A-4 148 275 (ROBERT S. BENDEN) * column 2, line 56 - column 3, line 65; claims 1-4; figure 1 *	1-4,6-8	C23C10/08 C23C10/02
Y	DE-C-41 19 967 (MTU MOTOREN-UND TURBINEN-UNION) * claims 1-11; figure 2 *	1-4,6-8	
A	US-A-5 071 678 (EDWARD J. GRYBOWSKI) * column 5, line 32 - column 9, line 22; claims 1-16; figure 2 *	1-4,6-12	
A	EP-A-0 349 420 (S.N.E.C.M.A.) * claims 1-5; figure 1 *	1-4,6-12	
A	FR-A-1 433 497 (S.N.E.C.M.A.) * page 2, column 2, line 30 - page 3, column 1, line 4 *	3,4	
A,D	US-A-4 501 776 (SRINIVASAN) * claims 1-15 *	9	TECHNICAL FIELDS SEARCHED (Int.Cl.6)
A	FR-A-2 306 276 (LE SECRETAIRE D'ETAT A LA DEFENSE DU ROYAUME UNI DE GRANDE-BRETAGNE)		C23C

The present search report has been drawn up for all claims

Place of search	Date of completion of the search	Examiner
THE HAGUE	7 June 1996	Elsen, D

CATEGORY OF CITED DOCUMENTS

X : particularly relevant if taken alone
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D : document cited in the application
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& : member of the same patent family, corresponding document

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