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Thermal Barrier Removal Process

5 Background of the Invention

Gas turbine engines are widely used to propel aircraft, to generate electricity, and to pump fluids. There is an increasing requirement for higher performance and better fuel economy in such engines. At this point the most readily available approach to increase efficiency and power output is to increase operating temperature. However, 10 many gas turbine engine components currently operate very near their melting points, in fact many gas turbine engine components are internally cooled.

In recent years it has become fairly common to use ceramic insulating coatings on the external (heated) surfaces of gas turbine components, particularly air cooled gas turbine components, to permit operation at higher temperatures.

15 There is a wide variety of thermal barrier coatings used in gas turbines, they are all ceramic based, and most use yttria stabilized zirconia as the ceramic. Ceramic coatings can be applied by vapor deposition techniques (see for example US Patents 4,321,311; 5,238,752 and 5,514,482) or by thermal spray techniques (see for example US Patent 4,861,618).

20 With limited exceptions, ceramic thermal barrier coatings are applied to substrates which have previously received an intermediate, or bond coat. The bond coat provides

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- 5 enhanced adhesion and durability to the thermal barrier coating. The bond coat also affords a measure of environmental protection in the event that the ceramic thermal barrier coating is damaged in service.

Superalloys are alloys based on iron, nickel or cobalt having useful properties at temperatures in excess of 1,000 °F. Nickel superalloys are most widely used and Table I

10 lists several exemplary nickel base superalloys.

TABLE I
(wt % Exemplary Superalloy Compositions)

	Cr	Co	W	Cb	Ti	Al	B	Hf	C	Ni	Ta	Mo	Zr	Re
PWA1422	9	10	12	1	2	5	.015	1.6	.14	Bal	-	-	-	-
PWA1426	6.4	12.6	6.4	-	-	5.9	0.012	1.5	-	Bal	3.0	1.7	.08	.3
PWA1480	10	5	4	-	1.5	5	-	-	-	Bal	12	-	-	-
IN 792	12	9	3.8	-	4.1	3.5	.015	0.5	.12	Bal	3.9	1.9	.12	-

- 15 Two major types of bond coats are used. The first type is the overlay or MCrAlY bond coat. MCrAlY bond coats are alloys of nickel or cobalt combined with chromium aluminum and yttrium. Other minor alloy elements including tantalum, platinum, rhodium, silicon, hafnium, rhenium and others are also possible. In service, the MCrAlY forms an oxide surface layer of relatively pure the alumina.

20 Table II lists several exemplary MCrAlY compositions.

TABLE II
(wt % Exemplary MCrAlY Compositions)

	Ni	Co	Cr	Al	Y	Hf	Si
NiCrAlY	Bal	-	19.5	12.5	.45	-	-
CoCrAlY	-	Bal	18	11	.45	-	-
NiCoCrAlY	Bal	23	18	12.5	.3	-	-
NiCoCrAlY	Bal	22	17	12.5	.6	.25	.4

5 MCrAlY overlay coatings have typical thicknesses of 75-175 μ .

The second type of bond coat is the diffusion aluminide bond coat, which are formed by diffusing aluminum into the surface of the superalloy substrate material to form a surface layer enriched in aluminum to ensure that the surface oxide which forms will be mainly alumina. Typical aluminide coating thicknesses are 30-70 μ . A variety of
10 aluminide coatings are known, a principal variant is the platinum aluminide in which a layer of platinum is applied to the substrate surface prior to the diffusion of aluminum. Platinum aluminide coatings have superior properties to normal aluminide coatings in certain applications. See US Patent 5,716,720 for a discussion of Pt aluminides as bond coats.

15 It is also possible to combine the aluminide and MCrAlY and overlay coatings (see for example US Patents 4,897,315, and 4,005,989).

Both MCrAlY overlay coating and aluminide coatings form an alumina layer of relatively high purity to which the ceramic thermal insulating layer will adhere.

The ceramic layer can be applied using physical vapor deposition techniques or
20 by thermal spray techniques. Regardless of details of the bond coat and the ceramic application, the result is a gas turbine component comprising a superalloy substrate, a bond coat on the substrate, an alumina layer on the bond coat and a ceramic layer adhered to the bond coat.

The thermal barrier coated superalloy turbine component can be expected to
25 survive for thousands of hours in a gas turbine engine with gases at temperatures as high as 2700°F flowing over the superalloy coated articles at a rate of as much as 1000 feet per

5 second at pressures of as much as 400 psi. It will therefore be appreciated that the thermal barrier coating is durable and well adhered to the substrate.

Regardless of the initial durability, there will come a time in a life of a gas turbine component when repair or refurbishment of the coated part is necessary. It is then necessary to remove the ceramic coating and replace it with a new ceramic coating.

10 Conceptually the ceramic can be removed mechanically or chemically, but the real problem is to remove the ceramic without removing or adversely affecting the bond coat. When the bond coat is removed or is chemically attacked, and has its surface composition altered, it is usually necessary to replace the bond coat, to ensure that the new ceramic coating will be adherent, and have the same durability as the original coating. This is a
15 costly procedure which may not be economical.

Autoclaves are known in the superalloy industry, principally for use in removing ceramic molds and cores from superalloy castings. Shell molds can be .1-.25 inches in thickness and cores may extend 3-6 inches inside coatings. When used to remove molds and cores, autoclaves are operated with caustic solutions of sodium hydroxide and/or
20 sodium hydroxide at temperatures and pressures which cause aggressive attack and removal of the ceramic shells and cores in reasonable time periods. The emphasis in the prior use of autoclaves to remove shell and core ceramics from superalloys is on aggressive operation to remove large amounts of ceramics in reasonable times. The chemistry and quality of superalloy surfaces after the removal process is of little
25 consequence because shell and core removal occurs early in the blade production process and many other steps will be performed which will shape and size the blade for its final function, and because protective coatings will subsequently be applied.

5 The prior art has also made some use of autoclaves and caustic solutions for blade
cleaning, and for removal of thermal barrier coatings. See for example US Patent
5,685,917. These prior references of ceramic thermal barrier removal have been focused
on certain features such as the use of special coolants to produce super critical fluid
conditions in the autoclave process. The prior references have apparently not employed
10 mechanical abrasion processing.

Accordingly, it is an object of the invention to disclose the process by which the
ceramic portion of the thermal barrier coating can be removed without significantly
changing the thickness of the bond coat or the chemical composition of the bond coat.

It is a further object of the invention to describe a thermal barrier coating
15 refurbishment process.

Summary of the Invention

This invention is directed at a ceramic coating removal process including a wet
chemical ceramic removal step under carefully controlled conditions followed by a mild
20 abrasive surface cleaning step. The chemical step process parameters are selected to
remove the large majority if not all of the ceramic material without removing or
significantly attacking the bond coat. The mechanical abrasion step then removes any
remaining ceramic material, which will have been weakened and attacked by the
chemical removal step. The mild mechanical abrasion step also removes a thin layer
25 from the surface of the bond coat, a layer of a thickness equal to or greater than the
thickness of chemical attack of the bond coat.

5 According to the present invention a ceramic thermal barrier coating can be completely removed from the gas turbine engine component with a related removal of not more than about 15 microns of the bond coat material. Removal of this small amount of bond coat material has no practical effect on the subsequent functionality of the recoated article.

10 The wet chemical step of the invention is performed in a autoclave apparatus and uses a caustic chemical solution comprised of sodium hydroxide or potassium hydroxide or mixtures thereof. The caustic concentration is correlated with the temperature and pressure conditions in the autoclave to remove the ceramic portion of the thermal barrier coating in an economic amount of time, preferably less than about four hours total cycle
15 time, and preferably less than about one hour at the maximum process temperature.

 The consequence of the wet chemical caustic treatment when properly performed are that the majority, preferably more than about 80% on an area basis, of the ceramic thermal barrier coating is removed. Removal generally occurs by spalling of the ceramic material from the bond coat oxide layer. The remaining ceramic material, if any, is left in
20 a weakened condition and is easily removed by a subsequent mild mechanical abrasion step.

 It has been found that the chief deleterious effect of the wet chemical caustic step on the bond coat is to attack and preferentially remove aluminum from the surface of the bond coat. This can be deleterious to the subsequent use of the part because the surface
25 aluminum content is essential to developing the surface oxide layer which is in turn required to adhere the replacement ceramic thermal barrier coating to the substrate.

5 The subsequent mechanical abrasion process step removes all residual ceramic,
and an amount of the bond coat sufficient to expose a surface of the proper aluminum
composition to develop an adherent alumina layer, so that a replacement ceramic coating
will adhere to the bond coat.

10 Description of the Invention

 We employ an autoclave apparatus typical of that use in the industry comprised
of a pressure vessel made of corrosion resistant material such as monel, containing a
means for heating a liquid and a means for sealing the chamber to permit the buildup of
pressure. Using sealed vessel filled with the fluid which is heated will increase the
15 boiling of the fluid in the autoclave as the vapor pressure builds to above atmospheric
pressure, and the increased temperature substantially increases the rate of the chemical
attack of the caustic on the ceramic coatings on the parts.

 Preliminary experiments in which gas turbine components with ceramic thermal
barrier coatings were exposed to normal ceramic shell and core removal cycle used to
20 remove the molds and cores (typically 450 °F, 50% caustic for 24-48 hours) were
completely successful in removing the ceramic thermal barrier coatings, however they
also substantially attacked the bond coat reducing its surface aluminum level
significantly, to a depth of 30-50 microns. This depth of attack is too great to reliably
reuse the original bond coat. Thus the conventional autoclave shell and core removal
25 process cycle is not satisfactory.

 After extensive experimentation, process parameters were determined which can
remove the ceramic thermal barrier coatings without substantially changing the surface

5 bond coat composition to a deleterious depth. These conditions were combined with an auxiliary mechanical abrasion step provide the desired result, the complete removal of the ceramic thermal barrier coating without substantial change in the thickness and chemistry of the bond coat material.

The temperature and pressure that is used during treatment can be varied,
10 depending on the type of thermal barrier coating to be removed and the characteristics of the autoclave such as heat up and cool down rates.

The autoclave treatment may involve combinations of ultrasonication, mechanical mixing, and boiling (by varying the autoclave pressure).

We use a concentrated caustic solution comprising about 15-50% of weight
15 sodium hydroxide or potassium hydroxide, or mixtures thereof, preferably of about 25-50% by weight, and most preferably to about 35-50% by weight. We prefer to use a maximum operating temperature of from about 290-450°F, preferably from about 325-425°F, and most preferably from about 350-425°F.

We have used what we refer to as a spike procedure in which the parts are placed
20 in the autoclave, the autoclave is sealed and is then heated at the maximum rate possible to be the desired maximum temperature. Once that temperature is achieved the holding time at that maximum temperature is relatively minimal, less than one hour, and preferably less than 20 minutes. For the autoclave which we have used, which we believe is fairly typical of that found in the industry, this permits us to remove the bulk of
25 the ceramic thermal barrier material in a two or three hour cycle, about one hour to heat the autoclave to the desired maximum temperature, a hold at the maximum operating temperature of less to one hour, and a cool down step of approximately one hour

5 duration. The times and other operating conditions will vary slightly from autoclave to autoclave depending on such things as the size and thermal mass of the autoclave and the rate at which the autoclave can be heated to and cooled from the operating temperature.

Thermal barrier coatings are usually applied to turbine parts with internal cooling. The thermal barrier coating is applied to the surface exposed to the hot environment.

10 Cooling air is flowed through passages within the part, in some gas turbine applications cooling air may be as hot as 1,000° F. Because of the use of high temperature cooling air there is a trend to use protective coatings on the inside of the part to reduce internal oxidation by cooling air.

Internal coatings are aluminide coatings. In many applications cooling holes are
15 provided to allow the cooling air to flow through the part wall and to flow over the outside of the part to allow film cooling.

It is necessary to carefully control the wet chemical step to minimize attack of the internal aluminide coatings. Also, it will generally be appropriate to perform a thorough rinsing step after the wet chemical step to remove all caustic from within the blade.

20 Rinse water may be flowed under pressure through the internal cooling passages. Hot water rinses, jetting agents, and agitation may be employed.

Using the previously described ranges of parameters of caustic concentration and temperature, and taking into account autoclave variations, one skilled in the art can readily determine an operating cycle which will remove at least 80% of the ceramic
25 thermal barrier coating while not changing the aluminum content in the bond coat to a depth greater than about 10 μ and preferably not more than 5 μ in the case of aluminide bond coats. If the part has an MCrAlY bond coat, and does not have an internal

5 aluminide coating, up to about 20 μ , but preferably not more than 5 μ of the bond coat may
be depleted of aluminum, because of the greater MCrAlY thickness. If the part has an
internal aluminide coating, attack of such internal coating will control the process, and
such internal coating attack should not exceed 10 μ and preferably 5 μ .

 We have observed that the bond coat is generally attacked locally at first, and that
10 these localized attack sites grow in area. We prefer to operate the chemical removal step
to minimize the percentage of bond coat area undergoing localized attack to less than
about 20% based on area, preferably not greater than about 3 microns. The portion of the
bond whose composition is changed is called the depleted zone. The depletion zone can
be defined as the surface region of the bond coat where the original aluminum content
15 has been reduced by more than about 20% from its original level. By way of example, in
the case of a bond coat containing 15% Al, we would define the depletion zone as that
outer portion of the bond coat containing less than about 13% Al.

 Generally, using only a chemical caustic process not all the ceramic thermal
barrier coating material can be removed before the bond coat chemistry, (aluminum
20 content) is modified to its depth of more than about 5 microns. The invention relies on
chemical attack to remove most of the ceramic without excess bond coat attack, followed
by mechanical abrasion to remove the remaining ceramic and any of the bond coat which
has been attacked.

 The ceramic appears to spall or delaminate at the alumina surface layer on the
25 bond coat. We believe that the caustic attacks the bond coat alumina layer or the
interface between the bond coat alumina surface layer and the ceramic layer.

5 After the autoclave ceramic removal step, the parts are removed from the
autoclave, and rinsed and are then subject to a mechanical abrasion step to remove any
remaining ceramic material, and to remove that thin surface portion of the bond coat
whose chemistry has been modified by the caustic process. We have used mild grit
blasting. However we feel it is well within the scope of one skilled in the art to employ
10 other abrasive techniques. For example there are many techniques which are generally
referred to as mass media finishing in which parts to be processed are buried in a
vibrating or moving bed of large ceramic particles, usually with a fluid added.

Example

15 Turbine blades having an alumina bond coat (30-40 microns thick) and
approximately 125 microns of 7% Y stabilized zirconia, applied by vapor deposition, as
an insulating coating were chemically stripped under different conditions.

Stripping was performed in an autoclave (pressurized only by the natural vapor
pressure of the caustic solution). The caustic solution was a 50% solution by weight of
20 potassium hydroxide in water. Two temperatures and several treatment times were
evaluated.

The results are presented in Table III. While there is scatter in the data, due to
small sample sizes and probable bond coat variations, some trends are clear. At both
temperatures, short times were effective at ceramic removal with minimum bond coat
25 attack. The spike treatment, less than about 10 minutes at temperature was effective at
both temperatures.

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TABLE III

	Temp.	Time	Max Depth of Attack, μ	Qualitative Aluminum Depletion	Area of Attack	TBC Removal
1	425 °F	Spike	2.5	Slight	Isolated	Total
2	"	1 hr	3	Mild	Nearly cont.	"
3	"	2 hr	6.3	Moderate	Continuous	"
4	"	4 hr	10	Moderate	"	"
5	"	6 hr	19	Severe	"	"
6	"	8 hr	21	Extremely severe	"	"
7	"	24 hr	24	"	"	"
8	"	48 hr	26	"	"	"
9	350 °F	Spike	NIL	NIL	NIL	Slight residuc left
10	"	1 hr	7	Moderate	Continuous	Total
11	"	2 hr	6	Moderate	Nearly cont.	Total
12	"	4 hr	8	Moderate	Nearly cont.	Total

Even where total removal of ceramic coating is indicated, there is still a general need for a light abrasion step to remove some of the bond coat, and to remove the chemical smut left by the caustic treatment.

- 10 Once the original ceramic layer is removed, a new ceramic layer may be applied to produce a refurbished coated part. The replacement ceramic layer will generally be substantially identical to the original ceramic layer. The bond coat may be treated to provide a desired surface finish and may then be treated to form the alumina surface layer. The details of the bond coat surface preparation, the alumina scale preparation and
- 15 the replacement ceramic will generally be the same as those used to apply the original ceramic thermal barrier layer.



5 In the Claims

1. Method for removal of ceramic thermal barrier coating from a superalloy substrate having a bond coat thereon which comprises:

a. immersing said coated substrate in a concentrated caustic solution at a pressure in excess of atmospheric and a maximum process temperature in excess of the atmospheric boiling point of said caustic solution for a time
10 sufficient to remove at least 80% of said ceramic coating without changing the chemical composition of the bond coat to a depth of more than about 15 microns.

b. mechanically abrading the bond coated substrate to remove any residual
15 ceramic material and to remove an amount of bond coat material greater or equal to the thickness of the bond coat whose chemical composition has been changed by the caustic chemical step.

2. A method as in claim 1 wherein the bond coat is an aluminide and less than 15
20 microns of bond coat is chemically changed.

3. A method as in claim 1 wherein the caustic solution comprises an aqueous solution of a material selected from the group consisting of KOH and NaOH and mixtures thereof in an amount of from 15-50% by weight.

25 4. A method as in claim 3 in which the caustic material is present in an amount of from 25-50% by weight.



- 5 5. A method as in claim 3 in which the caustic material is present in an amount of from 35-50% by weight.
6. A method as in claim 1 wherein the maximum temperature of the caustic solution is from about 290-450°F.
- 10 7. A method as in claim 1 wherein the maximum temperature of the caustic solution is from about 325-425°F.
8. A method as in claim 1 in which the time at the maximum time at temperature is less than about 1 hour.
- 15 9. A method as in claim 1 in which the time at the maximum temperature is from about 1 minute to about 20 minutes.
10. A method as in claim 1 wherein the maximum depth of chemical change in the bond coat is about 3 microns.
- 20 11. A method as in claim 1 wherein the abrasive process is selected from the group consisting of dry grit blasting, wet grit blasting and vibratory mass media finishing.
12. A method for replacing the ceramic portion of a thermal barrier coating on a gas turbine component including the steps of:



- 5 a. immersing said coated substrate in a concentrated caustic solution at a
 pressure in excess of atmospheric and a maximum process temperature in
 excess of the atmospheric boiling point of said caustic solution for a time
 sufficient to remove said ceramic coating without changing the chemical
 composition of the bond coat to a depth of more than about 15 microns.
- 10 b. mechanically abrading the bond coated substrate to remove any residual
 ceramic material and to remove an amount of bond coat material greater or
 equal to the thickness of the bond coat whose chemical composition has
 been changed.
- c. Reapplying a ceramic layer.
- 15 13. A method as in claim 1 wherein the caustic solution comprises an aqueous solution of
 a material selected from the group consisting of KOH and NaOH and mixtures
 thereof in an amount of from 15-50% by weight.
14. A method as in claim 2 in which the caustic material is present in an amount of from
20 35-50% by weight.
15. A method as in claim 1 wherein the maximum temperature of the caustic solution is
 from about 290-450°F.
- 25 16. A method as in claim 1 in which the time at the maximum temperature is less than
 about 1 hour.



5 17. A method as in claim 1 wherein the maximum depth of chemical change in the bond coat is about 3 microns.

18. A method as in claim 1 wherein the abrasive process is selected from the group consisting of dry grit blasting, wet grit blasting and vibratory mass media finishing.

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19. A method as in claim 11 wherein the reapplied ceramic layer contains more than about 80% zirconia by weight.

20. A refurbished gas turbine component produced by the method of claim 11.