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[54] **IMPACT RESISTANT COATINGS FOR
COBALT-BASE SUPERALLOYS AND
THE LIKE**

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[57] ABSTRACT

In the production of impact and oxidation resistant metal coatings on superalloy substrates, e.g., cobalt-base superalloys, by pack cementation, such as a nickel aluminide coating, the improvement wherein nickel is first diffusion coated onto the substrate from a pack containing a small but effective amount of sulfur as a metal transfer agent, following which the nickel coated substrate is then coated with another metal, such as aluminum.

16 Claims, No Drawings

IMPACT RESISTANT COATINGS FOR COBALT-BASE SUPERALLOYS AND THE LIKE

This invention relates to the pack-nickelizing of heat-resistant metal substrates and, in particular, to a method of producing a hot corrosion resistant metal coating in which the metal substrate is first nickelized to form a diffusion-bonded nickel coating thereon and thereafter aluminized in a separate coating step to provide an improved protective coating containing substantial amounts of nickel aluminide which coating exhibits markedly improved impact ductility.

Metallurgical developments in recent years have indicated the necessity of high-cobalt and/or high-nickel heat-resistant alloys (sometimes now referred to as "super alloys") having desirable physical properties for various high temperature uses, such as, for example, the manufacture of rotor blades and stator vanes for high-temperature gas turbines where operation without failure is desired of the part, such as during prolonged exposure to temperatures well above 1,500° F., and even substantially above the temperature range at which failure or diminution of the strength characteristics may be expected of even high temperature austenitic or nickel chromium steel.

The use of superalloys by themselves with nothing more have not always provided the necessary resistance to hot corrosion damage at such elevated temperatures. Thus, corrosion resistant coatings have been resorted to as one means of further augmenting the resistance of the substrate to high-temperature corrosion, particularly on complex-shaped components used in contemporary jet engines where handling and gauging damage have been known to cause premature failure of protective coatings which tend to be brittle in nature. With regard to cobalt-base superalloys, the most current coatings used in such applications are cobalt aluminides containing dispersions of MC, M₆C and M₂₃C₆ carbides. Coatings of this nature afford good oxidation resistance, but are too brittle for production assembly lines.

An attempt was made to evolve a two-step process for the independent deposition of nickel and aluminum on cobalt-base superalloys by using a nickel-alumina pack (40percent by weight nickel powder and 60percent by weight alumina) containing a halide energizer, e.g., one-quarter percent by weight of ammonium bifluoride. However, such packs were not successful to effect the transfer of nickel in that the energizer vapors tended to attack the component surface in preference to depositing nickel from the pack.

A method has now been found for effecting the transfer of nickel by pack cementation onto superalloy substrates, such as cobalt-base and nickel-base alloys, while avoiding the formation of chromium-containing embrittling phases at the interface. While the invention is particularly applicable to cobalt-base superalloys, it is also applicable to the coating of nickel-base alloys containing, for example, 10percent to 30 percent by weight of chromium where the deposit nickel dilutes the chromium at the interface to inhibit the formation of the aforementioned chromium-containing embrittling phases, such as the chromium carbides, nitrides and the like.

It is thus the object of the invention to provide a method whereby a high-impact and hot corrosion resistant coating may be produced on superalloys, such as cobalt-base and high-chromium-bearing nickel-base alloys.

Another object is to provide a method of nickelizing the substrate of cobalt-base and nickel-base superalloys preliminary to aluminizing said alloys for the production of hot corrosion resistant coatings based on nickel aluminide which exhibit markedly improved impact ductility.

Still another object is to provide a method of nickelizing chromium-containing superalloys whereby to avoid the formation of chromium-containing embrittling phases in the subsequent production of nickel aluminide coating by aluminizing the nickelized superalloys.

A further object is to provide a superalloy substrate, e.g., a cobalt-base superalloy, having a ductile impact and hot corrosion resistant coating diffusion bonded thereto.

These and other objects will more clearly appear from the following description and the appended claims.

Broadly stated, the invention resides in a method of producing an impact resistant coating on a superalloy substrate by pack cementation wherein a layer of diffusion-bonded sulfur-activatable transfer metal e.g., nickel, is produced as a first step in the ultimate formation of the impact resistant coating. The improvement resides in providing an article of said superalloy having a solute metal, e.g., chromium, whose free energy of formation of the sulfide is higher than that of the transfer metal (e.g., higher than nickel), embedding the article in a particulate cementation pack consisting essentially of said sulfur-activatable transfer metal mixed with an inert refractory material (e.g., alumina), the bed containing a small but effective amount of sulfur for effecting the transfer of said sulfur-activatable metal to the substrate of said article at an elevated diffusion coating temperature, and then heating said pack and the embedded article to an elevated diffusion coating temperature, whereby to effect diffusion coating of that article with the transfer metal, the coating being carried out while maintaining the oxygen in the pack below the partial pressure at which oxidation of sulfur to sulfur dioxide is inhibited.

In carrying out the pack cementation process, the oxygen is maintained at the desired partial pressure by mixing with the pack a small but effective amount of an oxygen-scavenging metal (e.g., titanium) whose free energy of formation of the oxide is at least about 115,000 calories per gram atom of oxygen at about 25° C.

Where nickel is employed as the transfer metal, the particulate nickelizing pack has a composition ranging by weight from about 5 to 60% nickel, about one-eighth to 1% titanium, about 0.002 to 0.1% of sulfur, and the balance essentially an inert refractory material e.g., such refractory oxides as alumina, magnesia, silica and the like. A particular pack composition is one containing approximately 40% nickel, approximately 0.2% titanium, approximately 0.02% sulfur and the balance essentially aluminum oxide. Following the production of the diffusion bonded nickel coating, the substrate of the article is cleaned and the coated surface then aluminized, whereby an impact resistant coating containing nickel aluminide of improved ductility is produced.

As stated above, the method is applicable to both nickel-base and cobalt-base superalloys. In the case of nickel-base alloys, a typical alloy composition range is one containing by weight about 10 to 30% Cr, up to about 20% of a metal from the group consisting of Mo and W, up to about 10% of a metal from the group consisting of Nb and Ta, up to about 0.5% C, up to about 6.5 percent by weight of a metal from the group consisting of Ti and Al, the total amount of these metals not exceeding about 10%, up to about 20% Co, up to about 2% Mn, up to about 2% Si, up to about 0.1% B, up to about 1% Zr, and the balance at least about 45% nickel.

With regard to the cobalt-base alloys, a typical composition range is one containing by weight about 10 to 30% Cr, up to about 15% Ni, up to about 15% Fe, up to about 5% Nb, up to about 15% W, up to about 5% Ti and/or Al, up to about 1% Zr, up to about 1.5% C, up to about 1 or 2% of Si, up to about 2% Mn and the balance essentially at least about 45% Co.

A well-known commercial composition is a cobalt-base alloy referred to by the designation WI-52 containing by weight about 0.45% C, about 0.25% Mn, about 0.25% Si, about 21% Cr, about 11% W, about 2% Nb, about 2% Fe and the balance essentially cobalt.

The optimum processing cycle for nickelizing the aforementioned WI-52 alloy involves the deposition of nickel at about 9,925° F. ± 25° F., (about 1,050° C. ± 14° C.) by embedding an article of the alloy, e.g., an airfoil section, in a particulate pack containing by weight about 40 percent — 200 mesh electrolytic nickel and 60 percent — 325 mesh alumina, the mixture containing by weight about three-sixteenth percent of titanium, with the sulfur level ranging from about 0.015 to 0.05 percent. The primary source of the sulfur is the nickel

powder. With the foregoing pack, the thickness of nickel coating ranges up to about 0.002 inch.

In determining the positive effect of sulfur, or sulfur-containing compounds, as a metal transfer agent, the addition of small but effective amount of flowers of sulfur and such sulfur compounds as NiS, Cr₂S₃ and (NH₄)₂S was noted to increase the quantity and depth of nickel of transfer. However, the presence of too much sulfur may result in extensive attack of the grain boundary carbide phases and the deposition of sulfur-compounds in situ. Thus, the term "small but effective amount" is meant to cover that amount of sulfur conducive to forming the desired coating of nickel while avoiding the deposition of sulfur-rich compounds, except for the formation of chromium sulfide at the surface of the substrate which is easily removed by glass head honing. For advantageous results, the amount of sulfur in the pack, whether deliberately added, or whether present in the pack materials employed, e.g., nickel powder and/or the alumina, may range from about 0.002 to 0.1 percent by weight.

The sulfur is consumed in the formation of scale and reaction with titanium (scavenger) and oxygen. Thus, the reaction of sulfur with chromium in the alloy substrate may result in several kinds of chromium sulfide which form on the surface of the article following deposition of the nickel. The reaction with titanium in the pack may result in the formation of some

ly, other oxygen scavengers may be employed so long as the free energy of formation of the oxide is at least about 115,000 calories per gram atom of oxygen. As stated above, unless precautions are taken to maintain the oxygen partial pressure in the pack to desirably low levels, the transfer of nickel from the pack and onto the alloy substrate is adversely affected. This can occur if too little titanium is in the pack to avoid the formation of sulfur dioxide and even chromium oxide on the alloy substrate. For example, no titanium in the pack results in no nickel transfer and severe oxidation of the substrate being coated. Another method of maintaining the oxygen partial pressure to the desirable low level is to sweep out the oxygen occluded in the pack by means of a substantially oxygen-free inert gas, such as argon. Generally speaking, where titanium is employed as the oxygen scavenger, the amount in the pack may range from about 1/8 to about 1 percent. A typical pack for processing the alloy WI-52 is one comprising about 40% nickel powder, the pack mixture containing about three-sixteenth percent of titanium and about 0.015 to 0.05% of sulfur with the balance essentially inert refractory oxide, e.g., alumina. A particularly advantageous range of titanium is about three-sixteenth to about one-half percent.

As illustrative of the various superalloys that can be coated in accordance with the invention, the following are given in Table 1 by way of example:

TABLE 1

Alloy designation	Chemical composition, weight percent												
	C	Cr	Ni	Co	Mo	W	Cb	Fe	Ti	Al	B	Zr	Others
Mar-M-509	0.55-0.65	23-24.5	9-11	Bal.		6.5-7.5		max 2.0	0.15-0.25		max 0.01	0.1-0.6	3-4 Ta
SM-302	0.85	21.5		Bal.		10.0					0.005	0.20	9.0 Ta
AiResist 215	0.35	19.0	max 0.5	Bal.		4.5	Ta + Cb 7.5	max 0.5		4.3		0.13	0.13 Y
L-605	0.1	20.0	10.0	Bal.		15							1.5 Mn, 0.5 Si
WI-52	0.45	21.0		Bal.		11.0	2.0	2.0					0.25 Mn, 0.25 Si
X-40	0.5	25.5	10.5	Bal.		7.5							0.75 Mn, 0.75 Si
Udimet 500	0.08	18.0	Bal.	18.5	4.0				2.9	2.9	0.006	0.05	
Mar-M-432	0.15	15.4	Bal.	19.7		3.0	1.8		4.4	2.9	0.013	0.03	2.2 Ta
IN-713 C	0.12	12.5	Bal.		4.2		2.0		0.8	6.1	0.012	0.10	
Hastelloy X	0.1	22.0	Bal.	1.5	9.0	0.6		18.5					0.5 Mn, 0.5 Si
Inconel 600	0.04	15.8	Bal.					7.2					0.2 Mn, 0.2 Si

titanium sulfide. Residual oxygen in the pack can react with the sulfur dioxide and with the titanium to form titanium dioxide. The preference and degree to which these reactions occur is dependent upon the relative concentration of the elements in the pack.

In nickelizing the cobalt alloy identified hereinbefore by the designation WI-52, the sulfur content of the pack at the low-range results in a nickel zone in the substrate of about 0.5 mils thick (0.0005 of an inch), with about 2 to 10% nickel diffused into the surface. Generally, the lower the sulfur level in the pack over the small but effective range, the less is the nickel transfer and the smaller the depth of diffusion. Usually, a nickel zone is obtained on the substrate of the alloy containing up to about 20 percent by weight of nickel as determined by microprobe analysis.

In the normal process cycle, the parts as removed from the nickelizing pack are covered with light scale which is removed by low-pressure glass bead honing. The scale is composed of distinct phases of chromium sulfide with entrapped powder from the pack, the chromium sulfide ranging in composition from Cr₂S₃ to Cr₅S₈. The scale thickness usually averages 0.3 mils, the thickness increasing with sulfur additions and increased nickel transfer.

It is important that the oxygen partial pressure in the pack be maintained below a level at which oxidation of sulfur is substantially inhibited. A titanium level of about three-sixteenth percent has been determined to be particularly advantageous in providing improved nickel transfer while minimizing oxidation damage during the nickelizing process cycle. Alternative-

The SM-302 and AiResist 215 alloys nickelized in a pack composition containing by weight about 40% electrolytic nickel powder (-200 mesh), about three-sixteenth percent titanium about 0.03 sulfur and the balance essentially alumina (-325 mesh) at a temperature of about 1,925° F.±25° F. for 30 hours resulting in a deposited nickel zone ranging in nickel content from about 20 to 22 percent by weight according to microprobe analysis.

Following the nickelizing of the alloys in Table 1, nickelized alloys are then aluminized in a prereacted pack containing by weight 20% Cr, 3% Al, 1/4% NH₄FHF and the balance essentially alumina (-325 mesh) to yield a corrosion resistant coating of substantially improved impact ductility. In the case of the cobalt-base alloys, the 0.002 to 0.0025 inch coating produced comprises nickel-cobalt aluminides containing chromium in solid solution.

In the case of Hastelloy X (comprising 0.1% C, 22% Cr, 1.5% Co, 9% Mo, 0.6% W, 18.5% Fe, 0.5% Mn, 0.5% Si and the balance essentially nickel), the substrate is similarly nickelized in a pack containing by weight 20% electrolytic nickel powder (-200 mesh), about 0.3% titanium, about 0.02% of sulfur and the balance essentially -325 mesh alumina at a temperature of 1,925° F.±25° F., for about 10 hours, following which the surface of the alloy substrate is cleaned by glass bead honing and then aluminized in the aforementioned prereacted pack at 1,900° F.±25° F. for 20 to 30 hours to yield a corrosion resistant nickel aluminide coating (0.0025 to 0.003 inch thick) which is very highly impact and spall resistant.

The treatment in the nickel pack causes chromium depletion in the substrate which allows for the formation of a ductile aluminide coating during the second diffusion bonding. Apparently, the improved ductility of the coating compared to the more brittle coatings currently used on such alloys is attributed to less chromium-rich phases within the coating and the absence of porosity at the coating substrate interface.

In the case of the alloy designated WI-52, the improved impact resistant coating provides a resistance to at least about 17 inch lbs. impact as compared to one-fourth inch lb. impact for the conventionally produced single step aluminide coating.

A simple test devised to simulate the stress and temperature environment of actual turbine hardware during engine service comprises a simple bending load test in which the load is applied to a coated test bar which is subjected to an end to end temperature gradient developed by a concentrated oxyacetylene flame which is applied to the center of the test bar and the heat allowed to dissipate to the opposite ends of the bar. Each testpiece is cycled from maximum temperature (e.g., 2,000° F.) to black heat during a 10 minute period. As the specimen is being cooled, the simple beam load is lifted and dropped three times to reproduce foreign object impact damage during service. Results have shown that the coating produced in accordance with the invention exhibits at least a 3 to 1 improvement over the conventional aluminized coating mentioned hereinabove. With regard to the conventional single step aluminide coating, chipping and spalling of the coating occurred after 45 cycles, while in the improved coating produced in accordance with the invention, the coating was still intact after 135 cycles.

As stated hereinbefore, the nickelizing pack may range by weight from about 5 to 60% nickel powder, about 1/4 to 1% titanium, about 0.002 to 0.1% sulfur and the balance an inert refractory material, such as particulate refractory oxides, e.g., Al_2O_3 , MgO , SiO_2 and the like. Examples of other oxygen scavengers are thorium, cerium, yttrium and other rare earth metals. The nickelizing temperature may range from about 1,500° to 2,000° F. for about 5 to 40 hours.

A cementation pack which may be employed in the aluminizing step comprises about 10 to 30 percent of a buffering metal (e.g., chromium), about 1 to 5% of aluminum, a small but effective amount of a halide energizer, e.g., one-quarter percent of NH_4FHF (such as 1/4 to 1 percent energizer) and the balance a particulate inert refractory material as mentioned hereinabove. The buffering metal aids in controlling the transfer and deposition of the aluminum. Examples of other buffering metals are nickel, iron and cobalt. Generally speaking, the pack is mixed and prereacted at an elevated temperatures of, for example, 1,750° to 2,050° F. for about 1 to 20 hours prior to use for coating and the nickelized article then aluminized at a temperature of about 1,750° to 2,050° F. for about 1 to 30 hours.

As illustrative of a preferred embodiment of the invention, the following example is given:

EXAMPLE

An airfoil section made of an alloy (WI-52) comprising about 0.45% C, about 0.25% Mn, 0.25% Si, about 21% Cr, about 11% W, about 2% Cb, about 2% Fe and the balance essentially cobalt is embedded in a nickelizing pack containing by weight about 40% electrolytic nickel powder (-200 mesh), about 0.2% titanium powder, about 0.02% sulfur and the balance essentially alumina (-325 mesh) in a retort. The retort is sealed with low-melting silicate glass composition and the retort then heated in a muffle furnace to a temperature of about 1,925° F. $\pm$ 25° F. and held at temperature for about 30 hours. The retort is thereafter cooled to room temperature and the airfoil section cleaned by glass bead honing at low pressure to remove chromium sulfide scale at the surface. A diffused layer of nickel is obtained having an enriched zone of about 0.002 inch thick containing about 20% nickel.

Following the cleaning of the airfoil element, the element is

similarly embedded in an aluminizing pack containing by weight 20 percent chromium (-100 mesh powder) as a buffering agent 3 percent aluminum powder (-325 mesh), about one-quarter NH_4FHF and the balance essentially -325 mesh alumina. The aluminizing was carried out for 20 hours in a sealed retort to produce an extremely ductile mixed nickel-cobalt aluminide coating containing chromium in solid solution.

Although the present invention has been described in conjunction with preferred embodiments, it is to be understood that modifications and variations may be resorted to without departing from the spirit and scope of the invention as those skilled in the art will readily understand. Such modifications and variations are considered to be within the purview and scope of the invention and the appended claims.

What is claimed is:

1. In a method of producing a highly impact resistant coating by pack cementation on a substrate of a heat resistant superalloy article in which nickel is diffused into the substrate as a first step in the ultimate formation of said impact resistant coating, the improvement which comprises,

providing a chromium-containing superalloy article, embedding said article in a particulate cementation pack consisting essentially of nickel powder mixed with an inert refractory material, the bed containing a small but effective amount of sulfur for effecting the transfer of said nickel to the substrate of said article at an elevated diffusion coating temperature, and

then heating said pack and the embedded article to an elevated diffusion coating temperature whereby to effect diffusion coating of said article with nickel, said coating being carried out while maintaining the oxygen in said pack at a partial pressure below which oxidation of sulfur to sulfur oxide compounds is substantially inhibited.

2. The method of claim 1, wherein the oxygen is maintained at the desired partial pressure by mixing with said pack a small but effective amount of an oxygen-scavenging metal whose free energy of formation of the oxide is at least about 115,000 calories per gram atom of oxygen at about 250° C.

3. The method of claim 2, wherein the oxygen-scavenging metal is titanium.

4. The method of claim 3, wherein the pack cementation bed has a composition ranging from about 5 to 60% Ni, about 1/4 to 1% Ti, about 0.002 to 0.1% S and the balance essentially the inert refractory material.

5. The method of claim 4, wherein the bed comprises approximately 40% nickel, approximately 0.2% Ti, approximately 0.02% S and the balance essentially aluminum oxide.

6. The method of claim 4, wherein following the production of the diffusion-bonded nickel coating, the substrate of the article is cleaned, and the coated surface then aluminized, whereby a highly impact and spall resistant coating containing nickel aluminide is produced.

7. The method of claim 6, wherein the nickel-coated article is aluminized by embedding it in a cementation pack containing by weight about 10 to 30% Cr, about 1 to 5% Al, a small but effective amount of a halide energizer and the balance a particulate inert refractory material, said article being then aluminized at a temperature of about 1,750° to 2,050° F. for 1 to 30 hours.

8. The method of claim 4, wherein the superalloy is selected from the group consisting of cobalt-base alloys containing by weight about 10 to 30% Cr, up to about 15% Ni, up to about 15% Fe, up to about 5% Cb, up to about 15% percent W, up to about 5% Ti and/or Al, up to about 1% Zr, up to about 1.5% C, up to about 1 to 2% Si, up to about 2% Mn and the balance essentially 45% Co; and nickel-base alloys containing by weight about 10 to 30% Cr, up to about 20 percent of a metal from the group consisting of Mo and W, up to about 10 percent of a metal from the group consisting of Cb and Ta, up to about 0.5% C, up to about 6.5% of a metal from the group consisting of Ti and Al, the total amount of these metals not exceeding about 10%, up to about 20% Co, up to about 2%

Mn, up to about 2% Si, up to about 0.1% B, up to about 1% Zr and the balance at least about 45% nickel.

9. In a method of producing a highly impact and spall resistant coating by pack cementation on a substrate of a cobalt-base superalloy article containing about 10 to 30% Cr, up to about 15% Ni, up to about 15% Fe, up to about 5% Co, up to about 15% W, up to about 5% Ti and/or Al, up to about 1% Zr, up to about 1.5% percent C, up to about 2% Si, up to about 2% Mn, and the balance essentially at least about 45% cobalt in which a layer of diffusion-bonded nickel is produced as a first step in the ultimate formation of said impact resistant coating, the improvement which comprises,

embedding the article in a particulate cementation pack consisting essentially of said nickel mixed with an inert refractory material, the bed also containing a small but effective amount of sulfur for effecting transfer of nickel from the pack to the substrate of the article, and then heating said pack and the embedded article to an elevated diffusion coating temperature whereby to effect diffusion coating of said article with nickel,

said coating being carried out while maintaining the oxygen in said pack at a partial pressure below which the oxidation of sulfur to sulfur oxide compounds is substantially inhibited.

10. The method of claim 9, wherein the oxygen is maintained at the desired partial pressure by mixing with said pack a small but effective amount of an oxygen-scavenging metal

whose free energy of formation of the oxide is at least about 115,000 calories per gram atom of oxygen at about 25°C.

11. The method of claim 10, wherein the oxygen-scavenging metal is titanium.

12. The method of claim 11, wherein the pack cementation bed has a composition ranging from about 5 to 60% Ni, about 1/2 to 1% Ti, about 0.002 to 0.1% and the balance essentially the inert refractory material.

13. The method of claim 11, wherein the bed comprises approximately 40% nickel, approximately 0.2% Ti, approximately 0.02% S and the balance essentially aluminum oxide.

14. The method of claim 11, wherein following the production of the diffusion-bonded nickel coating, the substrate of the article is cleaned, and the coated surface then aluminized, whereby a highly impact resistant coating containing nickel aluminide is produced.

15. The method of claim 14, wherein the nickel-coated article is aluminized by embedding it in a cementation pack containing by weight about 10 to 30% Cr, about 1 to 5% Al, a small but effective amount of a halide energizer and the balance a particulate inert refractory material, the article being then aluminized at a temperature of about 1,750° to 2,050° F. for 1 to 30 hours.

16. An article of manufacture produced in accordance with the method of claim 1.

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