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DEPOSITION OF METAL CONTAINING COATING FROM VAPOR

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ABSTRACT OF THE DISCLOSURE

Disclosed is a method for forming a non-spalling coating upon a metal part by generating vapors from a pack containing a metal, metal oxide and ammonium halide and allowing the vapors to plate upon the metal part which is separated from the pack.

The present invention relates to a heat resistant, non-spalling ceramic coating for metal articles particularly parts having a relatively high percentage of chromium and/or nickel. Ceramic coating as defined herein refers to an essentially metal containing coating.

It is well known in the metallurgical field that the strength of alloys having a major percentage of steel diminishes with increase of temperature and walls off dramatically from 1400 to 1800 degrees F. This fact has limited the use of such materials to lower temperature applications and has required the development of alloys based on a major percentage of metals having better strength characteristics at higher temperatures such as columbium, nickel and chromium. Often metals having a relatively high heat resistance such as titanium have been used to coat less resistant metals. Such coatings tend to increase the heat resistance of the coated metal parts by 200–300 degrees F. or so but may be objectionable in certain applications because of their tendency to split away from the base metal and thus give the coated parts undesirable surface characteristics.

With the advent of jet and rocket engines where combustion chamber parts are heated to such levels that would cause unacceptable strength loss of steel alloy parts, the search for better coatings has been intensified, resulting in the development of many so-called ceramic coatings such as those which comprise chromium and iron as a solid solution on the surface of the parts being formed from a cementation pack mix of ferrochrome and kaolin. Surface roughness of the parts, alloying of the ferro-chrome with the metal of the part, as well as diffusion of the solution into the parts is relied on to adhere the coating to the parts.

A major drawback of ceramic coatings has been their low ductility which causes them to crack and to separate from thin sections of parts which flex during use, for instance due to vibration, and their tendency to spall when the part to which they are affixed undergoes high amplitude temperature cycling such as is the case with jet engine combustion chambers, rocket nozzles and the like. Such spalling tendency is especially pronounced where the coatings must be relatively thick in order to protect the parts to which they are affixed.

Many prior art ceramic coatings, such as those disclosed in the patent to Folliet et al., 1,943,171 are applied by embedding the part in a powdered mixture raising the temperature of the mixture and part in a container from which air is excluded. I have found that such coatings tend to be of uneven thickness and adherence and unacceptably rough for many applications absent additional surfaces finishing steps.

An important object of the present invention is to provide a ceramic coating which is highly resistant to spalling and which coats metal parts uniformly even adjacent the edges and on thin sections thereof.

Another object of the invention is the provision of a ceramic coating which has small grain size, is dense and uniform compared to prior art coatings.

A further object of the present invention is the provision of a ceramic coating which penetrates relatively deeply into the coated part so as to be strongly adherent especially on such materials as Inconel; International Nickel Co. Alloy 713; nickel, aluminum, chromium and columbium bearing metals and steels.

According to the present invention the parts to be coated are first degreased by immersion in a conventional degreasing solution, then are heated in a reducing atmosphere, for instance parts having a high chromium content may be heated in a hydrogen atmosphere. Alternatively, an exothermic gas such as dry, cracked illuminating gas or cracked ammonia gas could be utilized as the atmosphere.

The heating step is preferably carried out at about 2150 degrees F. ±100 degrees F. for about one-half hour for the purpose of opening up the grain structure of the parts adjacent the exterior thereof in order to facilitate diffusion of the coating into the parts and to relieve any stresses.

Following the heating step, the parts are cooled in the reducing atmosphere to below 400 degrees F. The parts are next placed on suitable supports in a retort having means to facilitate the exit of gas therefrom and means to prevent the flow of air into the retort. Exemplary apparatus which per se, forms no part of the present invention includes an inverted cup-shaped drum inverted in a shallow saucer-like tray with a bed of powdered glass or the like in the tray surrounding the outside of the base of the cup-shaped drum. The parts are mounted on suitable racks in the upper part of the drum and the coating composition in the form of a powdered mixture and a catalyst to be described is disposed on the tray within the drum, below the parts.

Upon heating the retort, the glass powder in the "moat" surrounding the drum starts to melt and the coating composition mixture within the drum begins to sublime, pushing air out of the drum through the molten glass. After the parts have been coated by the subliming mixture and heating of the retort is discontinued, the glass solidifies preventing entry of air into the retort as the parts cool. Thus, the parts cool in an air-free atmosphere.

According to the present invention, the mixture placed in the retort is composed of:

Constituent	Percent by weight	
	Useful range	Optimum point
Chromic oxide	40–75	60.0
Aluminum	60–25	38.0
Ammonium iodide	1–3	2.0

Preferably the mixture is present as a powder of about 200 mesh.

The coating of parts may be carried out at a temperature of 1700–2200 degrees F. and preferably is carried out at a temperature in the range between 1900 degrees F. and 2050 degrees F. inclusive. An increase in temperature and a lengthening of heating time increase the depth of the penetration. As an example, when parts of Inconel are being coated the coating increases in total depth by 0.002 inch per hour at 2000 degrees F.

Examination of the coatings produced by the present invention indicate that a reaction represented by the following equation predominates:

$$Cr_2O_3 + Al_2 \xrightarrow{NH_4I} Cr_2 + Al_2O_3$$

Substantial proportions of the metallic aluminum and of the metallic chromium diffuse into the surface region of the parts.

After the coating step, the parts are allowed to cool in a reducing atmosphere are then removed from the retort. No further processing of the coating is necessary.

A specific example of a coating produced according to the present invention is on a part composed of, approximately 85% chromium and 15% aluminum. The mixture in the retort comprised chromic oxide 60 percent, aluminum 38 percent and ammonium iodide 2.0 percent. The coating step was carried out in the gas phase at 2050 degrees F. for five hours.

It appears that the uniform coating produced according to the present invention results in part because the coating is carried out by nascent attack in the gas phase wherein the iodide transports metal ions to the parts and the ammonia cracks to provide a reducing atmosphere. Unlike the more reactive halides, iodine will not cause burning of the parts or the coating at temperature above the coating range abovementioned and its low toxicity relative to the more reactive halides allows the ammonium iodide to be employed in a retort of the type described above whereas the use of chlorides, bromides or fluorides would necessitate using elaborate ventilation and accident prevention techniques.

In the coating mixture according to the present invention the chromic oxide can be replaced in whole or in part by oxides of tungsten, cobalt, columbium, molybdenum, nickel, silicon, tantalum, titanium, vanadium or zirconium and combinations thereof. Heating a mixture of berryllium fluoride and magnesium according to the conditions of the process described hereinabove will deposit a coating of beryllium and magnesium on the part that will withstand temperatures of about 2200 degrees F.

In use, the chromium and aluminum grains on the surface of parts coated according to the present invention tend to oxidize to form chromic and aluminum oxides. Because of the refractory character of these oxides, further burning is inhibited. Because of the extremely small grain size and spheroid shape of the coating, adherence is good, since expansion and contraction are allowed for. The brittle oxides, although adjacent to each other are not continuous and so cracking is prevented.

I claim:

1. A process for forming a nonspalling coating on a metallic part containing at least one constituent selected from the group consisting of chromium, nickel, aluminum, columbium and steel comprising:

placing the part to be coated and a powdered mixture in a container, said powdered mixture comprising chromic oxide, aluminum and ammonium iodide and wherein the part is so disposed as to be out of physical contact with the said powder mixture;

heating the part and the powdered mixture to a temperature in the range between 1700 and 2200 degrees F. whereby the mixture sublimes and condenses on the part forming a coating on said part,

allowing said part to cool in said container; and

removing said part from said container.

2. The process of claim **1** wherein the mixture is essentially composed of 60 weight percent chromic oxide, 38 weight percent aluminum and 2.0 weight percent ammonium iodide.

3. The process of claim **1** wherein said temperature is in the range between 1900 and 2050 degrees F.

4. The process of claim **1** further comprising degreasing the part before the initial heating of the part in a reducing atmosphere.

5. The process of claim **1** wherein a reducing atmosphere is chosen from the group consisting of hydrogen, cracked illuminating gas or cracked ammonia.

6. The process of claim **1** wherein the ammonium iodide cracks during the said heating step and the said heating step and cooling step of the coated part are substantially carried out in the resulting reducing atmosphere.

7. The process of claim **1** wherein the said heating step and said cooling step of the coated part are carried out in a reducing atmosphere.

8. The process of claim **1** wherein the said coating step and said cooling step of the coated part are carried out in a substantially air-free atmosphere.

9. A process for forming a non-spalling coating on a metallic part containing at least one constituent selected from the group consisting of chromium, nickel, aluminum, columbium and steel comprising:

heating the part in a reducing atmosphere sufficiently to open the grain structure of the part adjacent the exterior thereof, and subsequently cooling the part

placing the part to be coated and a powdered mixture in a container, said powdered mixture comprising at least one oxide of a metal selected from the group consisting of chromium, tungsten, cobalt, columbium, molybdenum, nickel, silicon, tantalum, titanium, vanadium, zirconium and mixtures thereof, a member selected from the group consisting of beryllium, magnesium and aluminum and a halogen containing sublimating agent and wherein the part is so disposed as to be out of physical contact with the said powder mixture;

heating the part and the powdered mixture to a temperature in the range between 1700 and 2200 degrees F. whereby the mixture sublimes and condenses on the part forming a coating on said part,

allowing said part to cool in said container; and

removing said part from said container.

10. The process of claim **9** wherein the said coating step and said cooling step of the coated part are carried out in a substantially air-free atmosphere.

11. The process of claim **9** wherein the sublimating agent is ammonium iodide.

12. A metal part coated by the process of claim **9**.

13. A powdered mixture for forming a coating on parts containing at least one of a constituent from the group consisting of chromium, nickel, aluminum, columbium and steel, said mixture consisting essentially of chromic oxide; aluminum and ammonium iodide.

14. The mixture of claim **13** wherein the aluminum is finely divided being of at least 200 mesh.

15. The mixture of claim **13** wherein the chromic oxide constitutes about 60 percent by weight of the mixture, aluminum about 38 percent by weight of the mixture and ammonium diode about 2.0 percent by weight of the mixture.

16. A powdered mixture for sublimation coating of metal parts, said powdered mixture consisting essentially of at least one metal oxide selected from the group consisting of chromium, tungsten, cobalt, columbium, molybdenum, nickel, silicon, tantalum, titanium, vanadium, zirconium and mixtures thereof, a member selected from the group consisting of beryllium, magnesium and aluminum and ammonium iodide.

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