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METAL-CERAMIC LAMINATED SKIN SURFACE

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The present invention relates to protective coatings. More particularly, it relates in one embodiment to a distinctive form of outer surface for a laminated coating which enables the latter to better resist intense heat and/or the corrosive effects of high-velocity gases.

In a co-pending U.S. patent application of William L. Aves, Serial No. 848,477, filed concurrently herewith, there is disclosed a protective coating which combines the erosion resistance and excellent bonding properties of a metal such as molybdenum with the good thermal shock resistance and insulating properties of a ceramic such as aluminum oxide. These two substances are applied to a base member as a multi-layer coating, of a total thickness and with a number of laminations governed by the particular environmental conditions to be encountered. Such a multi-layer coating possesses excellent erosive, thermal shock and temperature resistance when employed to contain a rocket motor blast, for example, where temperatures in the neighborhood of 5,000° F. are developed in conjunction with high-velocity gases. By utilizing the invention set forth in this co-pending application, it is possible to work within the strict space, weight and fabrication limitations imposed by the design requirements of many types of guided missiles and other super- and hyper-sonic space flight vehicles.

One important feature contributing to the satisfactory results obtained from the material set forth in the co-pending application above referred to is that each metallic layer of the laminated coating acts both as a cementing agent and as a surface to which further ceramic material can readily adhere. Furthermore, each ceramic layer performs the function of an insulator, so that the temperature of a base member protected by such a laminated coating levels off at a figure as low as approximately 520° F. after 30 seconds' exposure to a 5,000° F. blast. This is due at least in part to the inherent porosity of the material, the entrapped air not only raising the insulating quality of the coating but also increasing its thermal shock resistance.

It has been indicated in the mentioned co-pending application that relatively high-melting-point metals are preferred for the multi-layer coating, some representative examples being boron, chromium, iridium, molybdenum, tantalum, and tungsten. It has now been found that the properties of a laminated material such as set forth in the co-pending application can be materially improved in several important respects without changing the basic character of the coating or the method by which it is applied.

In accordance with a feature of the present invention, a multi-layer coating of the type disclosed in application Serial No. 848,477 is further treated to yield the following additional advantages:

(1) Protection at temperatures well above the respective melting points of all of the materials used in the coating's fabrication.

(2) Extension of the period during which protection is afforded at high temperatures.

(3) Increased corrosion resistance for long shelf life.

In a broad sense, this is accomplished by adding vaporization or sublimation material to the laminated coating in some suitable manner as by diffusion or post-impregnation. Such an outer surface covering is chosen for the

specific protective property possessed thereby, such, for example, as high heat reflectivity or degree of corrosion resistance, or its ability to control the rate of cooling of the base member following the latter's elevation to relatively high temperature.

One object of the present invention, therefore, is to provide an improved form of multi-layer coating designed to protect the member upon which it is applied from heat and/or the corrosive effects of high-velocity gases, and to provide a process for making such a coating.

Another object of the invention is to provide a laminated form of protective coating for a base member in which layers of metallic material alternate with layers of an insulating substance having high thermal shock resistance, and then to provide an outer layer for such a laminated coating which not only protects the base member at temperatures well above the respective melting points of all of the materials used in the coating's manufacture, but also extends the life of such protection and increases the resistance of such member to the effects of corrosive fluids and gases.

Other objects and many of the attendant advantages of the invention will be readily appreciated as the latter becomes better understood by reference to the following detailed description.

Protection of a multi-layer metal-ceramic coating at temperatures well above the respective melting points of the substances used therein can be achieved, in a preferred embodiment of the present invention, by impregnating the coating with a vaporization or sublimation material. Examples of such a material include tin, zinc, nickel, cobalt, and certain of the halides, silicones, furenes, phenols and epoxies. They may be introduced by some preferred method such as post-impregnation or controlled dual application, according to the conditions under which the process is carried out and by the results desired. It is essential, however, that the material employed pass directly from a solid to a gaseous state without apparent liquification.

In a preferred embodiment of the invention, the relationship between the protective coating, the base member, and the outer surface covering of the article may be expressed by means of the following symbolic diagram

Zn, Sn, Ni, Co
Al_2O_3, MgO, HfO_2, SiC, TiC
B, Cb, Ir, Mo, Ta, W
Base Member

A final surface coating of the nature described above protects the base member at temperatures well in excess of the respective melting points of all of the materials incorporated therein. Furthermore, if the substance employed should be a silicone, halide, or one of the metallic compounds of higher vaporization point, impregnation of the coating thereby can be carried out so that subsequent cooling of the base member will proceed along essentially predetermined lines.

Such a coating also extends the base member's life at high temperatures. This results from the fact that many B.t.u.'s are needed to vaporize or sublimate the impregnating material, and obviously the B.t.u.'s so utilized take no part in heating the base member itself.

Finally, corrosion protection essential for long shelf life can be readily attained. Metals such as zinc and cadmium offer such corrosion resistance to most base materials in a sacrificial manner, and they need not be dense to protect the latter under the usual storage conditions. Chromizing, siliconizing, aluminizing (and in some cases nitriding) of the laminated coating also provides a high degree of corrosion resistance. When chromium and silicon are diffused into the surface of molybdenum or ferrous alloys, both elements greatly enhance the metal's resistance to corrosion at all temperatures in both oxidizing and reducing environments. Furthermore, chromium, silicon, nitrogen, and in some cases carbon will increase substantially the resistance of the metallic layers to hot gas erosion and particle abrasion.

Employing a coating with high heat-reflective properties as the top or final layer extends the life of base members subjected to elevated temperatures from an outside source. While the particular type of reflective coating selected should, of course, be determined by the character of the environmental conditions and by the magnitude of the temperatures to be encountered, it has been found that such materials as aluminum, gold, silver, platinum and rhodium (protected by silicon monoxide) are especially suitable for this purpose.

It should be noted that in the case of space vehicles, a highly emissive top coating (such, for example, as chromium oxide and certain carbides) can reduce the heat caused by atmospheric friction on re-entry.

Obviously many modifications and variations of the present invention are possible in the light of the above teachings. It is therefore to be understood that within the scope of the appended claims the invention may be practiced otherwise than as specifically described.

I claim:

1. A base member having a protective coating thereon, said coating being designed to provide high corrosion resistance for the base member and to withstand the effects of heat and/or high-velocity gases, said coating being made up of individually flame-sprayed layers of a metal each layer having a thickness not exceeding approximately .0025 inch, such metal being selected from a group consisting of boron, columbium, iridium, molybdenum, tantalum and tungsten alternating with individually flame-sprayed layers each layer not exceeding approximately .005 inch in thickness of a ceramic having high thermal shock resistance and selected from a group consisting of aluminum oxide, magnesium oxide, hafnium oxide, silicon carbide and titanium carbide, said protective coating possessing as an outer surface covering a material selected from a group consisting of zinc, tin, nickel and cobalt, each of the said flame-sprayed layers possessing a porosity which permits a high degree of coherence and adherence to adjacent layers without the necessity of baking the ceramic substance or of bonding the respective layers as by alloying, the said outer surface covering acting to sublimate in that upon heating it passes directly from a solid to a gaseous state without apparent liquification.

2. A base member having a protective coating thereon, said coating being designed to provide high corrosion resistance for the base member and to withstand the effects of heat and/or high-velocity gases, said coating being made up of individually flame-sprayed layers of a metal each layer having a thickness not exceeding approximately .0025 inch, such metal being selected from a group consisting of boron, columbium, iridium, molybdenum, tantalum and tungsten alternating with individually flame-sprayed layers each layer not exceeding approximately .005 inch in thickness of a ceramic selected from a group consisting of aluminum oxide, magnesium oxide, hafnium oxide, silicon carbide and titanium carbide, said protective coating possessing as an outer surface covering a high heat-reflective material selected from a group consisting of aluminum, gold, silver, platinum and rhodium, each of the said flame-sprayed layers possessing a porosity which permits a high degree of coherence and adherence to adjacent layers without the necessity of baking the ceramic substance or of bonding the respective layers as by alloying, the said outer surface covering acting to sublimate in that upon heating it passes directly from a solid to a gaseous state without apparent liquification.

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