United States Patent

[11] 3,620,808

[72] Inventor James E. Monroe, Jr.
Timonium, Md.

[21] Appl. No. 697,281
[22] Filed Jan. 5, 1968
[45] Patented Nov. 16, 1971

[73] Assignee The United States of America as represented by the United States Atomic Energy Commission

[54] METHOD OF FORMING A THERMAL EMISSIVITY COATING ON A METALLIC SUBSTRATE
2 Claims, 2 Drawing Figs.

[52] U.S. Cl. ..... 117/69, 117/46 FS, 117/105.2

[51] Int. Cl. C23c 7/00

[50] Field of Search ..... 117/212, 217, 222, 230, 69, 46 FS, 105.2

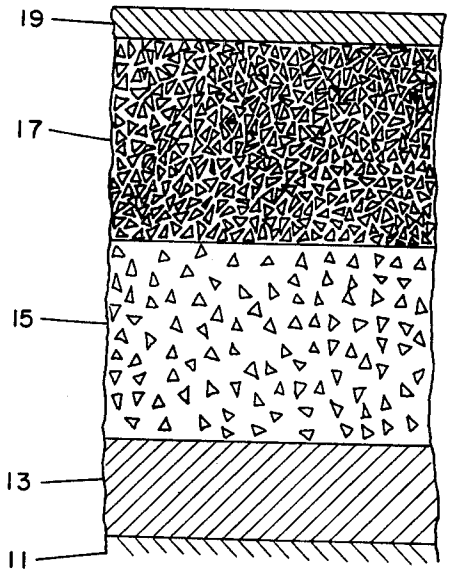
[56] References Cited

UNITED STATES PATENTS

2,966,430	12/1960	Schrewelius	117/212
3,326,648	6/1967	Provisor	117/230 X

Primary Examiner—Reuben Epstein
Attorney—Roland A. Anderson

ABSTRACT: A method for coating metallic substrates with high thermal emissivity coatings to prevent failure of the thermal emissivity coatings due to handling and thermal shock by applying an intermediate or base coat of nickel aluminide.



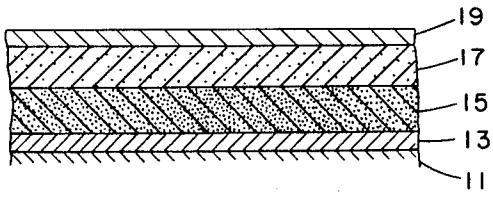


Fig. 1

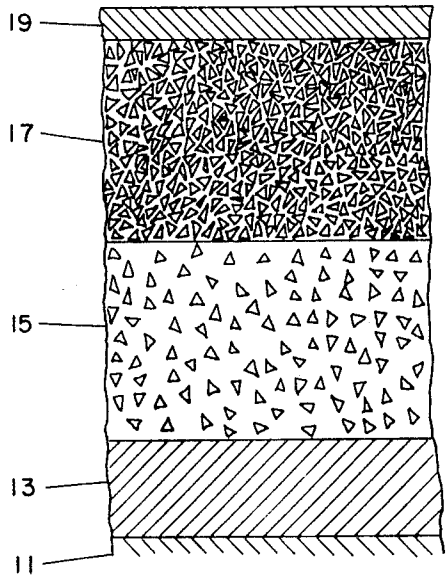


Fig. 2

INVENTOR.
JAMES E. MONROE, JR.
BY
Howard G. Goodman
Attorney

METHOD OF FORMING A THERMAL EMISSIVITY COATING ON A METALLIC SUBSTRATE

BACKGROUND OF THE INVENTION

Prior practices for systems for nuclear auxiliary power, referred to by the acronym SNAP, have employed thermal emissivity coatings, comprising a thin, oxidation resistant, thermal emissivity layer mechanically bonded to a substrate. To this end, a binder has been employed, which has been cured at a low temperature (less than about 750° F.) to bond the coating to the substrate, or the coating has been applied directly to form a mechanical bond on the substrate as described, for example, in U.S. Pat. No. 3,327,778. While these arrangements have been useful and have accomplished the desired mechanical bond, they have involved an interface connection of a coating layer on a substrate with abruptly different physical characteristics, including different coefficients of thermal expansion, that have limited the ability of the mechanical bond to absorb thermal or handling shock. It has thus been desirable to provide means that avoid these heretofore known limitations. It has additionally been advantageous to provide oxidation resistant high thermal emissivity coatings that can be patched and that can be constituted in such a manner as to tailor the thermal emissivity characteristics of the coating in a broad thermal emissivity spectrum.

SUMMARY OF THE INVENTION

This invention was made in the course of, or under a contract with the United States Atomic Energy Commission.

This invention involves a method for providing an intermediate base coat of nickel aluminide and thermal emissivity coatings thereon of E=0.8 or higher. The method and construction involved in this invention utilize standard and well known techniques and apparatus and are highly flexible for a wide range of applications, thermal emissivities, materials and coefficients of expansion. To this end, this invention involves the use of a plurality of discrete coatings in which the number of coatings and compositions thereof can be varied over a wide range to achieve a transition from 0 percent to 100 percent thermal emissivity coatings. In one embodiment, this is accomplished with a plurality of coats of nickel aluminide and Al_2O_3 with decreasing nickel aluminide content to produce a thermal emissivity material transition of from 0 percent to 100 percent.

The above and further advantages of novel features of this invention will appear more fully from the following detailed description of an embodiment of this invention when the same is read in connection with the accompanying drawings, and the novel features will be particularly pointed out in connection with the appended claims. It is to be expressly understood, however, that the drawings are not intended as a definition of the invention but are for the purpose of illustration only.

BRIEF DESCRIPTION OF THE DRAWING

In the drawings where like elements are referenced alike:

FIG. 1 is a partial schematic cross section of one embodiment of this invention having a plurality of layers of varying thermal emissivity material on a metallic substrate;

FIG. 2 is a partial magnified view of the embodiment of FIG. 1.

DESCRIPTION OF THE PREFERRED EMBODIMENT

It is known that flame sprayed or plasma are sprayed metal or metal oxide powders can be applied as coats of varying thickness to a variety of metallic substrate materials. The flame spraying of these materials, comprises feeding the powder granules of standard predetermined particle size through an oxygen hydrocarbon flame of about 3,000° C., as provided, for example, by an oxyacetylene flame spray apparatus operating in accordance with standard metallurgical coating techniques followed in metallurgical and ceramic laboratories. U.S. Pat. Nos. 2,969,309; 3,270,098; 3,294,698 and 3,318,695 describe the use of flame spraying technique and apparatus in coating a substrate with various materials that are fed in powder form through an oxyacetylene flame. Plasma arc spraying is described on page 512 et seq. of Metals Handbook, 8th Ed., by Am. Soc. for Metals, 1964. This invention hereinafter described utilizes these high temperature spraying systems in which a particular spraying sequence is used in a manner described hereinafter in connection with particular compositions or powders.

In accordance with this invention suitable emissivity materials having emissivities E of at least 0.8 are coated on nickel containing substrates with an intermediate nickel-aluminide emissivity material layer or layers. Suitable emissivity materials are: Al_2O_3, $CaOTiO_2$, Cr_2O_3–Y_2O_3, Iridium, $FeOTiO_2$, NiO, $CaTiO_3$ or combinations thereof. The following table illustrates emissivities of various of these and other emissivity materials on various substrates:

TABLE I.—EXPERIMENTAL SCREENING EFFORT OF EMITTANCE COATINGS ON CANDIDATE SUBSTRATES

Emittance coating	Substrate	Environmental treatment	Emittance, e.g. Gier-Dunkle (2,000° F.)	Application
$CaTiO_3$	Inconel-600	None	0.84, 0.88	Flame sprayed.
NiO	do	Stably oxidized in air at 2,100° F. for 1 hr	0.80	Do.
$MoSi_2$	do	None	0.76	Do.
ZrO_2	do	do	0.54	Do.
ZnO	do	do	0.60	Do.
$CaTiO_3$	TD nickel	do	0.88	Do.
NiO	do	Stably oxidized in air at 2,100° F	0.81	Do.
Iridium black	Aluminum	None	0.90	Do.
ZnO	TD nickel	do	0.56	Do.
ZrO_2	do	do	0.45	Do.
$CaTiO_3$	Pt-20% Rh	do	0.85	Do.
$CaTiO_3$	Pt-20% Rh	do	0.80, 0.81	Do.
$CaTiO_3$	Pt-20% Rh	Heated for 24 hrs. at 2,400° F. with graphite	0.92	Do.
Hf-27% Ta	Pt-20% Rh	None	0.58	Do.
$CaOTiO_2$	(1)	do	<.8	Plasma sprayed in argon.
$FeOTiO_2$	(1)	do	<.8	Do.
Al_2O_3	(1)	do	.8	Flame sprayed at 3,000° F.

[1] Ni_3Al coated TD nickel or Al_2O_3 containing Ni_3Al coated TD nickel.

Referring to FIG. 1, which illustrates one embodiment of the coating system of this invention, the surface of a metal substrate **11** is rendered chemically clean and the surface is roughened by grit blasting. A base coat **13** of 100 w/o nickel aluminide (Ni_3Al) is then flame sprayed or plasma sprayed in an argon atmosphere onto the surface of the roughened substrate to form a coating **13** having a thickness of approximately <0.007 inches. In one example, the nickel aluminide is flame sprayed to a thickness of 0.004 inches on the metal substrate **11**, e.g. TD nickel.

A second layer **15** of a composition having a major content, e.g. 65 w/o, of nickel aluminide and a minority content, e.g. 35 w/o, of emissivity material is then flame or plasma sprayed on top of the first coat **13**. The thickness of this second coat **15** varies from about 0.002 to 0.0015 inches, and in the above described example is 0.002 inches thick. In this example, the coat **15** is a flame sprayed composition having a nickel aluminide content of 65 w/o and 35 w/o Al_2O_3.

Tests to 1,200° F. or above on these and other materials showed they were stable against thermal and handling shock. Other coats **13** and **15** were, for example, 0.007 inch 100 percent Ni_3A1 and plasma arc argon atmosphere sprayed 0.005 in. 65 percent Ni_3A1+35 percent $FeOTiO_2$, which remained intact against thermal shock from 1,200° F. to room temperature. Likewise a plasma arc argon atmosphere sprayed $CaOTiO_2$ coating **13** remained intact under like thermal shock conditions.

A third layer **17** of a composition having a minority content, e.g. 35 w/o, of nickel aluminide and a majority content, e.g. 65 w/o, of the same thermal emissivity material is then flame or plasma sprayed to a thickness of between 0.002 and 0.015 inches on the surface of the second coat **15**, the above mentioned example being flame sprayed to a thickness of 0.002 inches. In this example, the nickel aluminide content of coat **17** is 35 w/o nickel aluminide and 65 w/o $A1_2O_3$.

A final top coat **19** of 100 percent of the emissivity coating material is then flame or plasma sprayed to a thickness of up to ~ 0.003 inches or less on the third coat **17**. In the above cited example, flame sprayed 100 percent $A1_2O_3$ is employed having a thickness of 0.002 inches.

The described coats are bonded to substrates **11** of stainless steel, TD nickel, nickel alloys, such as Inconel 600, or Hastelloy, or Haynes 25, by a combination of an actual diffusion bond of the nickel, e.g. in the first coating and the substrate, plus a mechanical interlocking transition of the nonmetallic thermal emissivity material and nickel aluminide particles in the subsequent coatings from the base coating to the top coating. This is illustrated in FIG. **2**. Moreover, the thermal emissivity material (e.g. $A1_2O_3$ or Y_2O_3 + 1 (to 50) w/o Cr_2O_3) can be merely physically blended to tailor the emissivity characteristics of the coating. Thus the weight percent (w/o) transition can be achieved in smaller or larger increments than the described example and combination of the various emissivity compounds can be used to achieve a wide emissivity spectrum.

In actual practice, the above-described four layer coating technique has successfully produced oxidation resistant high thermal emissivity coatings using nickel aluminide and $A1_2O_3$ as the emissivity material, while providing high thermal shock and handling shock resistance up to 2,000° F. and down to room temperature. For example, thermal emissivities E of up to 0.8 were measured using Martin Company test apparatus (Gier Dunkel) at room temperature with correction for operating temperature up to about 2,000° F. and a total hemispherical emissivity measuring device up to 2,000° F. experimentally. Moreover, any of the various respective layers can be patched with its corresponding coating layer composition if removal of the coating or chipping thereof occurs either advertently or adventitiously. Additionally, more layers than four can be employed wherein the transition from an 0 percent to 100 percent emissivity material is as gradual as desired. This invention thus insures shock resistance even with the use of substrate and emissivity materials of drastically different thermal expansions.

This invention has the advantage of providing a simple, effective and economic method of preparing emissivity coats on metallic substrates for SNAP and other systems. This method, moreover, provides high thermal and handling shock resistance, provides an easily patched emissivity coating, and provides a wide emissivity spectrum.

What is claimed is:

1. The method of forming a rugged coating on a metallic substrate for dumping heat into space from a radioisotope heat source, comprising the steps of preparing the surface of said substrate by cleaning and roughening said surface, coating the prepared surface of said substrate with a first coat of nickel aluminide, and coating said first coat with additional coats forming a compositional gradient from respectively decreasing amounts of nickel aluminide and correspondingly increasing amounts of a material selected from the group consisting of $A1_2O_3$, $CaOTiO_2$, Iridium, $FeOTiO_2$, NiO, and $CaTiO_3$.

2. The invention of claim 1 including the steps of flame spraying a first coat of 100 percent nickel aluminide 0.004 inches thick on said substrate, flame spraying a second coat on said first coat of 65 w/o nickel aluminide and 35 w/o $A1_2O_3$ having a thickness of 0.002 inches, flame spraying a third coat on said second coat of 35 w/o nickel aluminide and 65 w/o $A1_2O_3$ having a thickness of 0.002 inches, and flame spraying a top coat on said third coat of 100 w/o $A1_2O_3$ having a thickness of 0.002 inches.

* * * * *