United States Patent [19]

Bhat et al.

[11] **3,850,647**

[45] **Nov. 26, 1974**

[54] **CERMET PROTECTIVE COATING**

[75] Inventors: **Vasanth Kumar Bhat**, Fort Thomas; **Alan Richard Shapter**, Cold Spring, both of Ky.

[73] Assignee: **The Ceramic Coating Company**, Newport, Ky.

[22] Filed: **Sept. 29, 1972**

[21] Appl. No.: **293,673**

[52] **U.S. Cl.** **106/1**, 106/14, 106/54, 117/129

[51] **Int. Cl.** **C09d 5/10**

[58] **Field of Search** 252/512; 117/129; 106/1, 106/14, 54

[56] **References Cited**

UNITED STATES PATENTS

2,996,419	8/1961	Schmick	106/54
3,151,982	10/1964	Corrsin	106/54
3,484,284	12/1969	Dates et al.	106/1
3,748,170	7/1973	Michael	106/1

Primary Examiner—Lorenzo B. Hayes
Attorney, Agent, or Firm—J. Warren Kinney, Jr.

[57] **ABSTRACT**

A cermet protective coating composition for alloys like mild steels and enameling iron is disclosed. The coating protects the base metal from corrosion in aqueous, saline, and alkaline environments and from thermal degradation. The coating of the invention also serves as a protective ground coat for enamel cover coat applications.

5 Claims, No Drawings

CERMET PROTECTIVE COATING

BACKGROUND OF THE INVENTION

1. Field of the Invention

This invention is directed to a coating for relatively noncritical, inexpensive alloys like mild steels and enameling iron. The coating serves a two-fold purpose in providing an engineering material with extended serviceability and prolonged life. First, it serves to protect the base metal from general corrosion and thermal degradation, making it suitable for use in corrosive environments and elevated temperature applications. Second, it serves as a protective ground coat for decorative enamel cover coat applications, such as in architectural panels.

The composition of the subject coating falls under the general category of cermet, which may be defined as a heterogeneous combination of one or more metallic and one or more ceramic phases.

Critical alloys especially tailored for use in corrosive environments and at elevated temperatures outlive ordinary steel but, as a general rule, are prohibitively expensive. The use of such expensive, critical alloys is unwarranted when an inexpensive protective coating can be made available to prolong the life of cheaper, noncritical alloy such as mild steel.

While organic coatings like paint and metallic coatings such as of aluminum, cadmium or zinc on steel provide protection against general corrosion, they are prone to thermal degradation. Ceramic coatings, such as vitreous porcelain enamels, are resistant to corrosion and moderate temperatures, but they are inherently brittle.

2. Description of the Prior Art

Applicants are aware of the following U.S. Patents which disclose various cermet coating compositions intended for use on various metallic surfaces in different service conditions, viz:

U.S. Pat. No. 2,775,531 discloses a flame spraying process for plating a metal surface, such as mild steel, with a cermet coating composition, which comprises ceramic constituents such as Al_2O_3, MgO, and ZrO_2; and metallic constituents such as Al, Fe, Ni, and Co. These coatings are said to withstand high temperatures (temperature range not clearly specified) and protect the coated metals at these temperatures.

U.S. Pat. No. 2,889,238 discloses a heat reacted composition comprising: 2–5 molar parts of boric anhydride, ½–1 molar part of at least one alkaline earth oxide selected from a group consisting of BaO, CaO, SrO_2, MgO, up to 1 molar part of a compound selected from a group consisting of SiO_2 and CaF_2; metallic constituents such as bronze, Ag, Cr-Ni-B, and Ni-Mn. This coating is reported to have been successfully used on a great range of ferrous and nonferrous alloys including the superalloys like N-155, Inconel and other high chromium-nickel based alloys. The coating is stated to adhere at elevated temperatures (1300°–2200°F) and to "pop off" at room temperature.

U.S. Pat. No. 2,898,236 discloses a cermet coating slip consisting of 60–70 parts Al, Al-alloys; 30–40 parts frit (2–3 parts by weight Li_2O and 70 parts by weight the mineral constituents of Gerstley borate). This coating is fired between 1230° and 1260°F on such alloys as Timken 1722A(S) and "Chromoloy", and said to provide protection from oxidation, corrosion, acid attack, and erosion damage in continuous service temperatures up to 1300°F for long periods of time, and in temperatures up to 1500°F for short intermittent periods.

U.S. Pat. No. 2,898,253 discloses a cermet coating composition in which 100 parts by weight of a porcelain enamel frit (unclaimed composition), 10–200 parts aluminum flakes, 1–100 parts bentonite and diluent (e.g. water) is used. This coating is applied on titanium and its alloys for protection from oxidative and corrosive deterioration at temperatures in the range 1100° to 1850°F.

U.S. Pat. No. 2,900,276 discloses a cermet coating composition comprising 30 parts by weight BaO:3-B_2O_3:½ AlF_3 frit, 65 parts Al powder, 5 parts clay, and 45–50 parts water. The coating is intended for use on different bases ranging from ceramics such as glass, through copper, mild steels, stainless steels, and the superalloys such as N–155, Inconel, and other high chromium-nickel based alloys; and is characterized by high thermal shock resistance (temperature differential of about 1525°F). The coating provides an excellent ground coat for subsequently applied porcelain enamel, other ceramic or metal top coats.

U.S. Pat. No. 2,974,051 indicates that serious disadvantages attend the flame spraying method of applying a protective material to a metal surface. This reference discloses a cermet coating consisting of 30 parts by weight frit (44% BaO, 37.5% SiO_2, 6.5% B_2O_3, 5.0% ZnO, 3.5% CaO, 2.5% ZrO_2, 1% Al_2O_3), 70 parts metal (65–75% Ni, 13–20% Cr, 3–5% B, <10% Fe+Si+C), 5 parts clay, and 40 parts water. The base metal or substrates coated with this composition include low carbon steel, molybdenum and numerous nickel-chromium alloys and nickel-chromium-iron alloys. The coating is fired at temperatures in the range 1850° to 2000°F and is said to provide protection against temperatures up to 1200°F.

U.S. Pat. No. 2,977,251 discloses a cermet coating composition comprising 20–50 parts by weight of frit (65–70 Parts B_2O_3, 10–20 parts BeO, 15–25 parts Li_2O by weight), 50–80 parts powdered Al or Al-alloy, 5–10 parts suspension agent (ball clay) and a liquid vehicle (water).

U.S. Pat. No. 2,991,191 which is a division of U.S. Pat. No. 2,775,531 discloses a coating in which 33⅓% MgO and 66⅔% Ni particles are used.

U.S. Pat. No. 3,184,324 discloses a cermet coating composition made up of 100 parts of mixed glass frits, two 100 parts of refractory oxide, one-half 10 parts of suspension agent, and 40–70 parts of water with 7–8 parts of annealed nickel powder, to provide protection for materials such as steel, iron, copper, certain exotic metals and graphite against oxidation and corrosion at temperatures on the order of 1700°F.

U.S. Pat. No. 3,203,815 discloses a cermet coating composition comprising 15–60 parts by weight of frit (45–55% B_2O_3, 3–7% PbO, 5–12% CaO, 0.5% SiO_2, 8–13% Na_2O, and 8–13% Al_2O_3) and 20–80 parts powdered Al. This coating provides protection for low-alloy steels, stainless steels, cast iron, cast steel, and titanium against oxidation, corrosion, and chemical attack at temperatures in the range 1450° to 1500°F.

U.S. Pat. No. 3,508,938 discloses a cermet coating composition comprising ceramic and metallic ingredients within the following ranges: 0–10 Al_2O_3, 45–55 B_2O_3, 0–10 Cr_2O_3, 35–45 SiO_2, 0–10 ZrO_2, 5–30 colloidal alumina, 25–150 water, 0–30 Ni and 0–30 Fe — all parts by weight. This coating is intended for use on refractory metal and has high strength (>2000 psi both in shear and tension) at temperature on the order of 2200°F.

U.S. Pat. No. 3,597,241 discloses a metallo-ceramic (i.e. cermet) coating composition containing 10–40% of a ceramic oxide having a melting point > 1900°C, 15–60% Cr and 10–50% Ni. This coating protects ferrous and non-ferrous metals against oxidation at temperatures of about 1470°F.

SUMMARY OF THE INVENTION

A primary object of the present invention is to provide a novel and improved cermet composition which is less expensive and more effective than the cermet compositions of the prior art, and wherein the new composition excells in its corrosion resistance and thermal behavior characteristic of ceramic coatings, and (2) the high ductility exhibited by metallic coatings.

Another object is to provide a new and improved composition of ceramic (glass) frit which forms an integral part of the cermet coating.

A further object is to provide a cermet coating that can also serve as a protective ground coat on steel for decorative enamel cover coat applications.

Still another object is to provide a low-cost and intrinsically noncritical engineering material with extended serviceability and prolonged life.

DESCRIPTION OF THE PREFERRED EMBODIMENTS

The objects of the present invention are accomplished by providing a cermet protective coating composition comprising 35 to 60 parts by weight of a glass frit and 40 to 65 parts by weight of metal powder mixture consisting of 85 to 95 parts by weight of aluminum, 5 to 10 parts by weight of zinc and 0 to 5 parts by weight of cadmium.

The batch compositions of two of the frits hereinafter referred to as A and B used in the cermet coating of the present invention are:

Ceramic Raw Materials	Weight Percent A	Weight Percent B
Borax	40.72	33.48
Boric Acid	6.14	12.96
Calcined Alumina	1.66	1.61
Calcium Carbonate	19.88	19.27
Silica	28.77	31.82
Zinc Oxide	2.83	0.86
Total	100.00	100.00

The aforesaid raw materials are pulverized to pass through at least an 80 mesh sieve and then thoroughly mixed and smelted at about 2100°F (1150°C). The resultant molten glass is tapped and fritted in the conventional manner.

The melted compositions of the frits are calculated and depicted thus:

Constituents	Weight Percent A	Weight Percent B
Na_2O	14.16	12.00
CaO	12.57	12.57
ZnO	3.20	1.00
Al_2O_3	1.87	1.87
B_2O_3	35.69	35.50
SiO_2	32.51	37.06
Total	100.00	100.00

Frit B is about 50 percent more refractory than frit A because it contains lower Na_2O and ZnO, and higher SiO_2. Frit B is used when refractoriness is desired in the coating.

Uniformly satisfactory results have been obtained in those instances where the composition of the glass frit consists essentially of 25–35 weight percentage of RO, wherein $RO=Na_2O+CaO+ZnO$; 30–40 weight percentage of R_2O_3, wherein $R_2O_3=Al_2O_3+B_2O_3$; and 30–40 weight percentage RO_2, wherein $RO_2=SiO_2$.

The frit is wet milled along with the conventional mill additions to form a uniformly distributed water suspension slip of desired fineness.

With proper amount of Al-Zn-Cd powder (100–200 mesh) mixture and, if necessary, some more water added to the slip, it is then thoroughly blended by mechanical means. The specific gravity of the slip is maintained at about 1.65 g/cc.

The procedure followed in the application of the resultant slip to the metal article (mild steel or enameling iron) is similar to that practiced in conventional porcelain enameling. The surface of the metal article to be coated is thoroughly cleaned by sand-blasting or pickling and subsequently coated with the slip to a uniform thickness in the range 3 to 7 mils by the conventional spraying, brushing or dipping techniques. The coated article is dried at 300°–400°F (150°–200°C) to drive off water and then fired [at 1500°–1700°F (815°–925°C) depending on the frit used] until maturity.

The coating thus obtained has a matte finish and gray appearance. It also comprises at least two distinct layers hereinafter referred to as outer or surface layer and inner or interfacial layer. The surface layer is made up chiefly of ceramic phase and porosity, while the interfacial layer consists essentially of rust-inhibitive diffusion-bonded complex Al-Zn-Cd-Fe alloys.

The cermet coating described herein is also so ductile that a sheet metal article coated with it can be bent over a very small radius without damaging the coating. Maximum ductility is obtained when the coating thickness is 5 mils. Repeated bending and straightening of the coated article causes the surface layer of the coating to flake off on the compression side, but it merely puts a few hairline cracks on the tension side of the coating. The interfacial layer of the coating remains intact on both sides.

The cermet coating of the present invention, when applied on mild steel or enameling iron, is found to protect the base metal from aqueous, saline, and to a lesser extent alkaline corrosion, as well as from oxidation at elevated temperatures. The cermet coated samples are found to be rust-free even when the surface layer of the coating is removed and the interfacial layer is exposed to aqueous and saline environments.

A proper choice of the amount of ceramic and metallic constituents will yield a coating that is adherent, ductile, corrosion-resistant, dense, smooth, and hence most suitable for use as a protective ground coat or interfacial layer for enamel cover coats or surface layers.

Examples

1. Corrosion Resistance Test

A preferred cermet composition for demonstration of corrosion resistance of the coating is 46 parts by weight of frit A and 54 parts by weight of metal powder mixture consisting of 89 parts by weight of aluminum, 6.5 parts by weight of zinc and 4.5 parts by weight of cadmium.

The corrosion test samples were partially immersed in both water and in 20 percent NaCl solution, with and without the surface layer of the coating flaked off. 500-Hour tests both in aqueous and saline environments did not show any sign of rust formation on the samples. Less pronounced resistance to corrosion was observed in alkaline environment, such as, in 5 percent NaOH solution.

2. Thermal Endurance Test

A preferred cermet composition for demonstration of thermal endurance at 1600°F is 60 parts by weight of frit B and 40 parts by weight of metal powder mixture consisting of 95 parts by weight of aluminum and 5 parts by weight of zinc.

150–200-Hour tests at temperatures up to 1600°F shows that the coating withstands the heat and protects the base metal from oxidation.

3. Thermal Shock Test

A preferred cermet composition for demonstration of resistance to thermal shock is 60 parts by weight of frit A and 40 parts by weight of metal powder mixture consisting of 90 parts by weight of aluminum and 10 parts by weight of zinc.

Test samples were heated to 1400°F and quenched in water at room temperature. A total of 10 thermal cycles did not cause the coating to flake off, exhibiting excellent resistance to severe and rapid thermal change.

4. Ductility and Impact Resistance

A preferred cermet composition for demonstration of ductility and resistance to impact is 46 parts by weight of frit A and 54 parts by weight of metal powder mixture consisting of 89 parts by weight of aluminum, 6.5 parts by weight of zinc and 4.5 parts by weight of cadmium.

Test samples bent 180° over a conical mandrel of minimum radius of one inch showed resistance to fracture. Repeated bending and straightening of the samples causes the surface layer of the coating to flake off on the tension side, but the interfacial layer remains undamaged.

Test samples subjected to impact loading exhibit a resistance to impact shock far greater for the cermet coating than an enamel coating of equivalent thickness.

5. Protective Ground Coat

A preferred cermet composition yielding a coated surface suitable for enamel cover coat application is 50 parts by weight of frit A and 50 parts by weight of metal powder mixture consisting of 90 parts by weight of aluminum, 9.9 parts by weight of zinc and 0.1 parts by weight of cadmium.

Ground coats normally used for enamel cover coat applications are glassy, inherently brittle and do not adequately cover edges. Consequently, the base metal would become unprotected when the enamel coating fails. This is particularly critical in enameled architectural panels which are subjected to weather. The cermet coating disclosed in this invention is unique in that it is adherent, ductile, corrosion-resistant, dense, smooth, and covers edges. These properties make it highly suitable for use as ground coat for enamel cover coat applications. Should the enamel cover coat be abused to failure, the cermet coating under it will protect the base metal from weathering.

The above examples should not be construed as limitations but rather as illustrations of the characteristics and usefulness of the cermet coating disclosed in this invention.

What is claimed is:

1. A cermet protective coating composition consisting essentially of 35–60 parts by weight of glass frit consisting of 25–35 weight percentage Na_2O, CaO and ZnO, 30–40 weight percentage $Al_2O_3$and B_2O_3, and 30–40 weight percentage SiO_2, and 40–65 parts by weight of metal powder consisting of 85–95 parts by weight of aluminum, 5–10 parts by weight of zinc, and 0–5 parts by weight of cadmium.

2. The cermet coating of claim **1**, consisting essentially of 46 parts by weight of glass frit and 54 parts by weight of metal powder, and wherein the frit comprises essentially 14.16 weight percentage Na_2O, 12.57 weight percentage CaO, 3.20 weight percentage ZnO, 1.87 weight percentage Al_2O_3, 35.69 weight percentage B_2O_3, and 32.51 weight percentage SiO_2, and wherein the metal powder mixture comprises 89 parts by weight of aluminum, 6.5 parts by weight zinc, and 4.5 parts by weight cadmium.

3. The cermet coating of claim **1**, consisting essentially of 60 parts by weight of glass frit and 40 parts by weight of metal powder, and wherein the frit comprises essentially 12.00 weight percentage Na_2O, 12.57 weight percentage CaO, 1.00 weight percentage ZnO, 1.87 weight percentage Al_2O_3, 35.50 weight percentage B_2O_3, and 37.06 weight percentage SiO_2, and wherein the metal powder mixture comprises 95 parts by weight of aluminum, and 5 parts by weight zinc.

4. The cermet coating of claim **1**, consisting essentially of 60 parts by weight of glass frit and 40 parts by weight of metal powder, and wherein the frit comprises essentially 14.16 weight percentage Na_2O, 12.57 weight percentage CaO, 3.20 weight percentage ZnO, 1.87 weight percentage Al_2O_3, 35.69 weight percentage B_2O_3, and 32.51 weight percentage SiO_2, and wherein the metal powder mixture comprises 90 parts by weight of aluminum, 10 parts by weight of zinc.

5. The cermet coating of claim **1**, consisting essentially of 50 parts by weight of glass frit and 50 parts by weight of metal powder, and wherein the frit comprises essentially 14.16 weight percentage Na_2O, 12.57 weight percentage CaO, 3.20 weight percentage ZnO, 1.87 weight percentage Al_2O_3, 35.69 weight percentage B_2O_3, and 32.51 weight percentage SiO_2, and wherein the metal powder mixture comprises 90 parts by weight of aluminum, 9.9 parts by weight of zinc, and 0.1 parts by weight of cadmium.

* * * * *