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PROTECTIVE COATED ARTICLE

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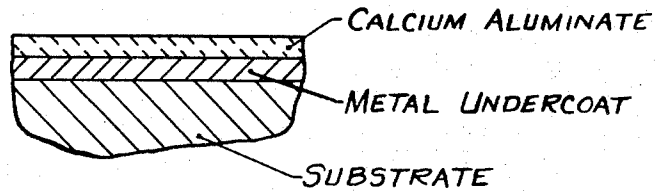


Fig. 1

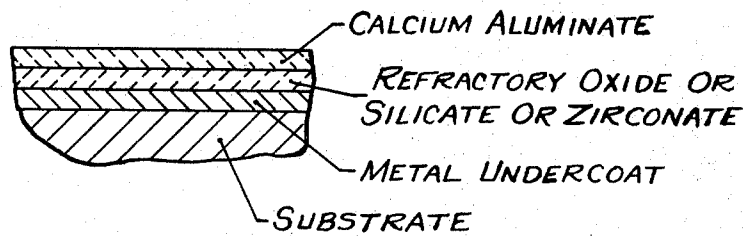


Fig. 2

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PROTECTIVE COATED ARTICLE

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ABSTRACT OF THE DISCLOSURE

A process for the protection of steel, ferrous metals and ferrous alloy substrates which are particularly subject to corrosion from molten aluminum and molten metal alloys melting at temperatures below 1200° C. by spraying the substrates with a metal melting above 700° C. and stable in air onto the substrate and thereafter spraying a resistant outer coating of calcium aluminate. The process also provides for a refractory coating intermediate the metal undercoat and outer coating of calcium aluminate.

The present invention relates to a process for the protection of steel, ferrous metals, ferrous alloys and other substrates which are particularly subject to corrosion from molten aluminum and molten metal alloys, by coating such substrates with a new and particular combination of metal and ceramic materials, whereby a resistant outer coating of calcium aluminate is provided and to the article thereby produced. More particularly, the present invention relates to a composite coating resistant to attack by molten alloys and metals, particularly aluminum and metal alloys melting below 1200° C., wherein the coating components are applied by a flame-spraying process.

In the manufacture of molten metals, such as in the aluminum industry, containment of the molten metal is a problem. For example, in handling molten aluminum, steel and ferrous metal containers are readily attacked by the molten metal, creating a severely rapid corrosion problem, and the attendant economic problem of high monetary outlay for replacement parts. There is thus a need in the aluminum industry for a protective coating material that will resist this attack and at the same time be practical and economical to apply.

It is, therefore, a principal object of this invention to provide an economical protective coating for devices and parts of steel and ferrous metals that are used to contain and process molten aluminum and aluminum alloys.

Another object of this invention is to provide a coating for protecting substrate materials which are to be used in contact with molten metals and alloys, particularly those molten materials, melting at temperatures below 1200° C.

Other and further objects and advantages of this invention will become more apparent as this description proceeds.

Broadly stated, the present invention is a unique combination of materials and includes processes of manufacture, therefore, which form coatings that insulate steel and ferrous alloys from contact with and the resulting damage produced by molten aluminum and metal alloys melting below 1200° C. The preferred practice of the invention results in the formation of a composite coating having excellent thermal shock resistance that is surprisingly resistant to the attack of the molten metals. In the case of molten aluminum, for example, the inventive coating is not only resistant to the molten aluminum, but aluminum peels off the coating surface readily even after it has solidified.

The coating of the present invention is a laminated

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structure comprising a combination of metal and ceramic coatings, the outer layer of the coating being a calcium aluminate composition. All coating layers are desirably applied by flame-spraying of wire and rods of the respective materials through an oxyacetylene torch. According to the invention, however, these coatings may also be applied by powder-spraying using plasma-jet or combustion flames, but oxyacetylene rod type flame-spraying is presently preferred for ease and simplicity.

In the drawings, FIGURE 1 shows a preferred form of the invention wherein the calcium aluminate coating is bonded to the substrate directly through a metal undercoat. FIGURE 2 shows a preferred form of the invention for use under more severe conditions than the simpler form of FIGURE 1. In this case, a layer of refractory oxide, silicate, or zirconate is interposed between the metal undercoat and the calcium aluminate top coating.

The device used for the present flame-spraying, plasma-jet or powder-spraying technique may be one of many such devices already known in the art. The preferred rod flame-spraying device is described in Letters Patent No. 2,707,691, dated May 3, 1955, which device is generally suitable for fusing, atomizing and spraying refractory oxide. A similar gun structure having a feed mechanism and spray tip designed for metal spraying can be used for fusing, atomizing and spraying metals so long as the metal is provided in the form of wire or a rod of the proper diameter for the gun. In other cases, there may be used an acetylene-oxygen gun for flame-spraying the metal and refractory oxide that is adapted for the spraying of these constituents in powder form.

According to this invention, a preferred coating combination presently comprises a steel substrate first metallized with a film of an alloy of 80% nickel-20% chrome followed by an intermediate flame-sprayed zirconia coating layer and a final coating layer of calcium aluminate. Both the nickel-chrome alloy and zirconia coatings may be applied according to practice of Letters Patent No. 3,006,782, dated October 31, 1961, while the calcium aluminate may be applied from a newly developed rod or as a powder spray. Also according to this invention, it has been found possible and, sometimes desirable to provide metal substrates with a base coating of nickel-chrome alloy followed by one or more overcoatings of calcium aluminate. Still further according to the invention, it has been found possible to provide a nickel-chrome alloy base coating with one or a plurality of graded calcium aluminate and nickel-chrome alloy containing overcoating mixtures followed by a top coating of calcium aluminate. In severe corrosion and shock cases, however, a zirconia intermediate bonding coating is preferred for use with the nickel-chrome alloy and calcium aluminate.

Although the 80-20 nickel to chrome alloy has been found to be quite serviceable, it is possible to use other metal undercoating layers. Those described in the aforementioned Wheildon Patent 3,006,782 which have a melting point above about 700° C., the temperature of a molten aluminum bath, will be found to be satisfactory. The nickel base alloys are most useful for this purpose and the 80-20 nickel chrome alloy is preferred.

According to the present invention, the calcium oxide and alumina constituents may be admixed in varying proportions, although a mixture of from about 30 to about 50% calcium oxide and from about 70 to about 50% alumina, respectively, is preferred. Generally speaking, the optimum CaO to Al₂O₃ ratio for the coating will be a function of the environment to which the particular coating will be subjected. As with the zirconia above described, the calcium aluminate herein is utilized in the form of sintered rods made by firing the desired com-

ponents together at a temperature high enough to crystallize and/or react the particles of CaO and Al_2O_3 together.

As an illustration, a preferred calcium aluminate rod may be made by preparing a pulverized mixture of 30% CaO, 70% Al_2O_3 and a temporary binder, followed by pressing into a slug under two and one-half tons pressure and firing at 1450° C. for five hours. The sintered slug is then crushed to 80F mesh sizing and again mixed with temporary binders and extruded to produce 1/4" diameter rods, followed by a 1440° C. firing.

As above indicated, the objects of the invention are satisfied by utilizing the metal in either wire or rod form, as a normally thin base coating, that is fused from the wire or rod form, and then atomized and sprayed by the known flame-spraying device and projected onto a metal substrate in the form of discrete molten particles which freeze in situ. Thereafter, a tenacious coating of calcium aluminate or intermediate coat can be formed on the metal coating, by feeding a solid and pure sintered rod of such material into a high temperature flame that will fuse and melt the material, the spraying apparatus having sufficient velocity to atomize and spray the molten material and deposit it on the coated substrate as a smooth and uniform overcoating.

Other oxides, silicates, and zirconates can be employed successfully in place of the zirconia coating where an article requires more resistance to deterioration than that provided by the simplest FIGURE 2 form of the present invention. Thus alumina, zircon (zirconium silicate), magnesium zirconate, and chromia (Cr_2O_3) have been successfully employed as flame-sprayed intermediate coatings in the structure shown in FIGURE 1. Steel test pieces so coated were all resistant to molten aluminum for several days, those with the alumina, magnesium zirconate, and zircon undercoatings being superior in this environment to the chromia undercoated article.

The present invention envisions the production of composite coating type laminate articles having coatings of virtually any desired degree of thickness. For most purposes, it is advantageous to have a composite coating thickness of at least 0.012 inch, although thinner coatings down to .003 may be made.

Surprisingly, it has been found that the present composite coating is needed to optimize the properties of the entire coating, it having been found that none of the components alone will satisfactorily withstand the chemical and thermal environment. It has been found that the present coatings and their substrates constitute integral laminated pieces, the adhesive strength between the coating of metal and the coating of refractory oxides being substantially equal to the cohesive strength of the refractory oxide coating. The individual particles of the coating of metal and the individual particles of the coating of refractory oxides are self-bonded together so that each coating constitutes a rigid integral structure independently of the base member. The metal coating is made up from discrete molten particles of metal frozen in situ on the base member, while the oxide coating is made up from discrete molten particles of oxide frozen in situ on the metal coating.

The adhesion between substrate metal and coating may often be mechanical in nature, and under these conditions, the degree of surface roughness of the substrate metal becomes an important factor toward good adhesion. Mechanical anchorage is aided by reentrant angles which are often present in subsurface cavity type pores, particularly when abrasive blasting is employed. However, under some circumstances, chemical adhesion may also be involved. Observations have been made on a specimen with a metal coating on stainless steel, which had been given an overcoating of zirconia. It was subjected to cyclic heating and cooling and withstood the treatment very well. Dark areas that were thought to be oxide were observed in a microscopic examination of a cross section,

and this metal oxide may have contributed to the superior performance by a chemical or physical mechanism.

The understanding of this invention will now be facilitated with reference to the following example which is given by way of illustration only, and is not to be considered in a limiting sense.

EXAMPLE I

One-quarter inch diameter zirconia and calcium aluminate rods were produced by extrusion under pressure of plastic compositions containing the respective zirconia and calcium oxide-alumina particles, and a suitable temporary organic binder, for example a cellulosic material. The extruded ZrO_2 rods were made as taught in Ault Patent 2,876,121 and the calcium aluminate rods were made and fired as described above.

Steel slugs of one inch diameter and two and one-half inches in length were used as substrates for this test. Specimen No. 1 was uncoated for control purposes. Specimen No. 2 was a steel slug flame-sprayed by the process of Letters Patent No. 2,707,691 with a coating of 30% CaO and 70% Al_2O_3 , to a thickness of 0.025 inch. Specimen No. 3 was first flame-sprayed with Nichrome V to a thickness of 0.002 to 0.004 inch, then with stabilized zirconia to a thickness of 0.005 inch and finally with calcium aluminate (30/70) to a thickness of 0.020 inch.

The three slugs were then immersed in molten aluminum maintained at 800° C. for five days. At the end of this time the slugs were removed from the melt liquid, cooled, and examined. The table below shows the results obtained in this test.

TABLE

Specimen No.	Original volume, cc.	Volume after test, cc.	Percent volume loss
1-----	31.7	25.9	18
2-----	35.0	24.3	31
3-----	37.1	37.7	1-2

¹ Gain.

Uncoated Specimen No. 1 lost 18% of its volume in the test and was coated with a tightly adherent coating of aluminum, which was firmly attached to the specimen and could not be peeled off. Specimen No. 2 suffered great volume loss and was covered with an aluminum coating that had cracked in several places where the aluminum attacked the steel underneath. Where the coating remained, the aluminum was attached to the calcium aluminate, but could be peeled away. Specimen No. 3 showed no evidence of attack. The slight increase in volume is attributed to aluminum on the surface which had not been peeled off.

As already indicated, the present composite coating may consist in its simplest form of a layer of metal coating with a layer of calcium aluminate on top of it. It may also contain several layers between or a gradated layer between. An example of a multilayer coating is Specimen No. 3 of Example I. An example of gradated coating would be a coating of 80-20 nickel chrome as the substrate, with this undercoat plus calcium aluminate in intermediate layers increasing in calcium aluminate content to a substantially pure calcium aluminate coating at the outer surface. It should be understood that the exact coating will vary, depending on the optimum system for the material to be protected, the size of the pieces, the metal being melted, and the temperature of the molten metal, as well as the environment to which the coating is subjected.

EXAMPLE II

To illustrate the acceptability of varying the calcium oxide-alumina ratio, the procedure of Example I was repeated step-for-step, except that a sintered rod containing 50% calcium and 50% alumina was employed to cover the 30/70 calcium aluminate coating.

As with Example I, the 80-20 nickel-chrome alloy-zirconia-calcium aluminate specimen illustrated clear superiority.

It can thus be seen that the present invention offers an improved composite coating, which when applied to steel and ferrous substrates, provides a laminate structure that is surprisingly resistant to the attack of aluminum and metal alloys melting below 1200° C. Therefore, it is to be understood that while various preferred embodiments of this invention have been described, the present invention is not limited to the precise conditions set out. For example, the present invention can include a plurality of 80-20 nickel-chrome coatings, a plurality of zirconia coatings and a plurality of calcium aluminate coatings, each oxide or metal component being used in either the pure form, or in admixtures with varying amounts of either or both of the other oxide and/or metal. It is only necessary that the base coating be metal undercoat having proper melting characteristics and that the top coating be essentially pure calcium aluminate.

Accordingly, this invention is only to be limited to the extent shown by the following claims wherein we claim:

1. A process for protecting a ferrous metal substrate from attack by molten aluminum and metal alloys melting below 1200° C. comprising spraying a metal melting above 700° C. and stable in air onto the metal substrate to form a metal coating thereon, thereafter spraying molten calcium aluminate onto the surface of said metal coating to form a calcium aluminate coating upon said metal coating and provide thereby a coherent laminated structure.

2. The process of claim 1 wherein the metal coating is an alloy of about 80% nickel and about 20% chromium.

3. The process of claim 1 including the step of spraying molten zirconia to form an adherent coating on said metal coating prior to spraying the molten calcium aluminate.

4. The process of claim 1 including the steps of spraying a molten mixture of calcium aluminate and nickel containing metal to form an adherent coating on said metal

coating prior to spraying the molten calcium aluminate.
5. A process of producing a laminated article that is resistant to corrosion from molten aluminum and metal alloys melting below about 1200° C. comprising spraying a molten nickel and chromium alloy onto a ferrous metal substrate, to form a metal coating thereon, then spraying molten zirconia to form a zirconia coating on said metal coating, thereafter spraying molten calcium aluminate onto the surface of said zirconia coating to form a coating thereon and provide thereby a coherent laminated material.

6. As an article of manufacture, a coherent laminate having resistance to corrosive attack by molten aluminum and metal alloys melting below 1200° C., comprising a ferrous metal substrate, a first overcoating on said ferrous metal substrate of a nickel and chromium alloy, and an outermost coating of calcium aluminate.

7. The article of claim 6 wherein the nickel and chromium alloy contains up to about 80% nickel and up to about 20% chromium.

8. The article of claim 6 including an intermediate coating of zirconia between said nickel and chromium alloy and said outermost coating.

9. The article of claim 6 including as an intermediate coating a mixture of calcium aluminate and a nickel and chromium alloy between said nickel and chromium alloy and said outermost coating.

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