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# PROTECTIVE CERMET COATING METHOD AND MATERIALS

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The present invention relates generally to protective coatings, methods, and materials. More specifically, it is directed to low-cost low-firing ceramic-aluminum cermet coatings for protecting metals, metallic alloys and certain non-metallics, and to novel methods and frits and slips for producing these coatings.

This application is a continuation in part of our copending application Serial No. 512,315, filed May 31, 1955, for "Protective Coating Methods and Materials." It also relates to an improvement over the "Protective Coating Methods and Materials" disclosed in our copending application Serial No. 623,550, filed November 21, 1956.

In our copending application Serial No. 512,315, we disclose aluminum-ceramic cermet coatings including ceramic components, which contribute refractoriness, high temperature strength, and chemical and physical stability at high temperatures, and aluminum components which contribute ductility and high resistance to erosion and thermal and mechanical shock. We also disclose therein a method of providing an article with a ceramic-aluminum cermet coating by an inexpensive production process comprising the steps of applying and firing on the article to be coated a slip composed of a water vehicle, aluminum or aluminum alloy powder, a suspension agent and binder, and a ceramic frit which forms the ceramic phase of the end coating and also fluxes the aluminum powder and coated surface during the firing cycle.

The coatings disclosed in our copending application Serial No. 512,315 are fired at a minimum temperature of about 1350° F., and at temperatures up to 2200° F. These coatings are being used successfully in a large number of applications, on such metals as mild steels, stainless steels, and the super alloys like N–155, Inconel and other high chromium-nickel based alloys. However, when certain alloys and/or non-metallics are to be coated, it is desirable to provide a coating which fires at temperatures lower than the minimum 1350° F. involved in our copending application. For example, the chromium-molybdenum-vanadium alloys, including but not limited to Timken 1722 A(S) and General Electric "Chromoloy," are worked in the annealed state; and the finished part is normalized at about 1750° F., then tempered at 1250° F. for from two to six hours. If subsequent to the tempering operation, a coating were applied and fired at 1350° F. or higher, the work piece might be deleteriously affected.

Therefore, when alloys like Timken 1722 A(S) and "Chromoloy" are to be coated, it is necessary to provide a coating which fires at a temperature not above the tempering point, and preferably fires at about 1250° F. In our aforementioned application Serial No. 623,550, filed November 21, 1956, we disclose successful low firing cermet coating methods and materials developed for application to such alloys with a firing temperature of about 1250° F. The low firing aluminum-ceramic cermet coatings disclosed in that application are produced from coating slips including a frit comprising boron oxide, lithia, and beryllia as principal constituents. These coatings have proven successful, but the coating frit is quite expensive because the beryllia costs about $28 per pound, making the cost of the frit about $25 per pound. A substantial reduction in materials costs without loss in coating efficiency would not only yield savings, but would also increase the industrial applications of low firing aluminum-ceramic cermet coatings. Drastic cost reduction has been achieved by the present invention which utilizes a frit costing about 5 to 6 cents a pound because it is made principally from a natural ingredient readily available at about 4 cents a pound.

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It is the primary object of the present invention to provide novel ceramic-aluminum protective cermet coatings which fire in a range of from 1230° F. (the melting point of aluminum) to 1300° F., with a preferred firing range of from 1230° F. to 1260° F.

It is a principal object of the present invention to provide low-cost, low-firing ceramic-aluminum protective cermet coatings and methods, which utilize low cost materials.

It is another object of this invention to provide such low-cost cermet coating compositions and methods utilizing a fluxing ceramic frit based on an inexpensive readily available natural borate that can be successfully used in the "as is" state. It is a related object to provide low-firing cermet coating compositions and methods utilizing, "as is," natural "Gerstley borate," which is readily available in quantity at about 4 cents a pound.

It is also an object of this invention to attain the objectives and improved results in aluminum-ceramic cermet coating as set forth in our copending application Serial No. 512,315, of which this is a continuation in part.

It is another object of this invention to provide an aluminum-ceramic water vehicle coating slip, which is stabilized to prevent aluminum-water reaction by small quantities of the boron oxide-alkaline earth oxide frit disclosed in our earlier application Serial No. 512,315.

As in the case of the coatings of our earlier copending application Serial No. 512,315, our present coatings are similarly obtained by applying to the work piece a water vehicle slip that includes a mixture of aluminum powder with a ceramic fluxing frit and an aluminum-water reaction inhibitor, and firing the part in the desired temperature range, in a gas or electric furnace with an air atmosphere.

In preparing our slip, we first combine in parts by weight 100 parts of Gerstley borate ($NaCaB_5O_9 \cdot 8H_2O$), and 5 parts lithium carbonate ($Li_2CO_3$). A typical chemical composition of Gerstley borate ($NaCaB_5O_9 \cdot 8H_2O$) is:

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|---|---|
| Boron trioxide ($B_2O_3$) | 33.0 |
| Calcium oxide (CaO) | 15.9 |
| Sodium oxide ($Na_2O$) | 4.9 |
| Water and organic matter | 28.2 |
| Silica ($SiO_2$) | 9.5 |
| Magnesia (MgO) | 3.5 |
| Alumina ($Al_2O_3$) | 1.1 |
| Iron oxide ($Fe_2O_3$) | .3 |
| Carbon dioxide ($CO_2$) | 3.2 |
| Undetermined | 0.4 |

To develop the frit, this mixture of Gerstley borate and lithium carbonate is smelted at approximately 2300° F. for about 30 minutes until a clear bubble-free condition is obtained. During the smelting operation, the water and $CO_2$ of the Gerstley borate and the $CO_2$ of the lithium carbonate volatilize out. The Gerstley borate loses water and carbon dioxide by volatilization up to about 31 percent of original weight. The final smelt therefore, contains by weight about 70 parts of the abovelisted mineral constituents of the Gerstley borate and about 2 parts lithia ($Li_2O$).

This smelt is then fritted, as by pouring into cold water, and the frit is dry milled to the preferred fineness. The end result is a low melting borate frit, which costs about 8–10 cents a pound (compared to about $25 per pound for the low melting borate-beryllia frit of our application Serial No. 623,550, filed November 21, 1956).

In a preferred coating process, 30 parts of the smelted frit are combined with 1 to 3 parts of the frit of our cermet application Serial No. 512,315, 70 parts of aluminum powder, 5–10 parts of ball type clay (suspension agent), and 55 parts of water (or sufficient water to produce a slip of desired fluidity depending on the method of applying it). The frit from our application Serial No. 512,315 consists essentially of boron oxide and barium oxide which may be replaced with an equal amount of calcium oxide, and if desired aluminum fluoride, in a molar ratio of about $BaO:3B_2O_3:0–\frac{1}{2}\ AlF_3$. The two frits and the aluminum powder are preferably of −200 mesh and can be finer, with no deleterious results down to −400 mesh. The ingredients may be merely agitated or ball milled to secure thorough mixing.

While in general we prefer to utilize comparatively pure aluminum in our coatings, we can use alloys of aluminum and silicon, aluminum and copper, and others of the aluminum base alloys.

The small amount of said frit disclosed in our application Serial No. 512,315 is added to the present aqueous vehicle slip to act as an inhibitor against the reaction between the aluminum powder and water. Without this addition, the aluminum and water would react, deleteriously affecting the aluminum and generating hydrogen which might cause a dangerous explosion, so that the slip could not be stored and would have to be used within a short time after it is made.

The work piece should be reasonably free of grease and oil but need not be cleaned as by sandblast or acid pickle. The work piece is coated by spraying, painting, dipping, slushing, or other like means, and the coat dried to a bisque either at room temperature or in artificial temperature up to 300° F. Thickness of the coat is not critical, and it has been found that an applied layer of from one to seven mils thick will fire to a satisfactory protective coating of approximately the bisque thickness.

Following the drying cycle, the part is fired at from 1260° F. to 1300° F. (By a change in the lithia content, as discussed below, the firing temperature may be reduced to about 1230° F.) The part may be fired in an air atmosphere. Firing need continue only long enough to bring the part to at least 1260° F. (or 1230° F.) and hold it at temperature for about five minutes. However, a longer firing time will not deleteriously affect the coating, and, for this reason, the part may be tempered and coated during the same cycle. In many cases, the tempering will be carried out prior to final machining where close tolerances must be met, and machining may be carried out subsequent to coating. In some cases, it is preferable to coat the entire work piece, then machine following tempering; while in other cases, the areas to be machined may be masked, and the rest of the work piece coated. Both methods are satisfactory.

During firing, the aluminum melts and some of it coalesces into "fields," while some of the aluminum grains remain as independent bits. Although the end coating is extremely tenacious and bonding is excellent, there appears to be very little diffusion of the aluminum into the surface of the work piece. While this would seem to indicate a ceramic or glass matrix full of aluminum, the resulting cermet coating is an aluminum coat full of ceramic or glass because of the 70–30 ratio of aluminum and frit.

It appears from the evidence available that the boron oxide of the Gerstley borate fluxes both the aluminum powder and the surface of the work piece during the firing cycle, and that the lithia lowers the melting point and helps stabilize the boron oxide in the frit. The ceramic phase of the resulting cermet coating acts to plug up the porosity inherent in prior aluminum and aluminum alloy coatings.

In the above-discussed Gertsley borate frit example, the smelt is composed of 100 parts Gerstley borate and 5 parts lithium carbonate yielding a frit containing about 2 parts lithia. It has been found that an increase to 7½ parts of lithium carbonate will result in a frit containing 3 parts of lithium oxide with an even lower melting point such such that the bisque will melt at about 1230° F., the melting point of aluminum.

In the present process, it is important that the glass phase be held to not more than 40 parts frit to 60 parts of aluminum. However, it has been found that where it is desired that the end result be a coating with a decreased aluminum content, a filler of zircon, silica or alumina may replace up to 20 parts of aluminum with the coating still containing an aluminum-glass ratio of 60–40. The "filler" is practically unaffected by the firing cycle, and remains as an "inert" constituent of the final coating.

We have provided by the foregoing compositions and methods a highly protective ceramic-aluminum coating specially suitable for alloys of the type discussed. In the resulting cermet coating, the ceramic phase cooperates with the metallic phase 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. The resulting coatings provide protection combining the high temperature strength, refractoriness, and chemical and physical stability of ceramic with the ductility and good resistance to erosion and thermal and mechanical shock of metals.

Although our presently disclosed coatings will find wide use in protecting alloys like those specifically discussed above, this use by no means is the limit of the coatings. For example, these coatings provide highly satisfactory protective layers for graphite, glass, and other nonmetallics, and are particularly useful where it is desirable that the piece to be coated not be subjected to high temperatures during processing.

One of the useful applications of our described coating inventions presently in great demand is the sealing of ceramic insulation materials such as woven glass fibers or similar materials, to eliminate porosity and possible oil absorption. The above-disclosed slip is sprayed, dipped, or otherwise applied to the insulating material, and fired in the indicated temperature range. The result is a structure characterized by little or no porosity, good insulating capabilities, and excellent resistance to corrosive and erosive influences.

It will be appreciated that because our present coatings fire at comparatively low temperatures, the process is less expensive than other similar processes, the work piece is subject to less stress, and simpler, cheaper equipment can be used.

The invention may be embodied in other specific forms without departing from the spirit or essential characteristics thereof. The present embodiments are therefore to be considered in all forms as illustrative and not restrictive, the scope of the invention being indicated by the appended claims rather than by the foregoing description, and all changes which come within the meaning and range of equivalency of the claims are therefore intended to be embraced therein.

What is claimed and desired to be secured by United States Letters Patent is:

1. The method of providing the surface of an article selected from the class consisting of metal, glass and ceramic with a cermet coating having both ceramic and metallic phases, which includes the steps of: applying to the surface to be coated a slip comprising a liquid vehicle, a cermet composition including from about 60

to 70 parts by weight of a metal selected from the group consisting of aluminum and aluminum base alloys, in particle form, and from about 30 to 40 parts by weight of the smelted and fritted product of a composition consisting essentially of Gerstley borate and lithia, and a suspension agent; and firing the surface at a temperature of at least about 1230° F. to form a cermet coating.

2. The method defined in claim 1, wherein the ceramic constituent comprises approximately 2–3 parts by weight lithia and about 70 parts by weight the mineral constituents of Gerstley borate.

3. The method defined in claim 1 wherein said coated article surface is fired at a temperature between 1230° F. and 1300° F.

4. The method defined in claim 3 wherein said coated article surface is fired at a temperature between 1260° F. and 1300° F.

5. A method as defined in claim 3 wherein said article is fired in an air atmosphere.

6. A heat reacted frit composition consisting essentially of lithia and the mineral constituents of Gerstley borate.

7. A cermet coating slip comprising: from about 60 to 70 parts by weight of a metal selected from the group consisting of aluminum and aluminum base alloys, in particle form; from about 30 to 40 parts by weight of the smelted and fritted product of a composition consisting essentially of Gerstley borate and lithia; 5–10 parts suspension agent; and a liquid vehicle in sufficient quantity to produce a slip of desired fluidity for coating articles.

8. A slip as defined in claim 7, wherein said liquid vehicle is water, and said slip contains 1 to 3 parts of a frit consisting essentially of boron oxide, and at least one alkaline earth oxide selected from the group consisting of barium oxide and calcium oxide in molar ratio of $3B_2O_3$:BaO.

9. A slip as defined in claim 7, wherein the ratio of frit content to aluminum metal content does not exceed 40:60.

10. A slip as defined in claim 7, wherein up to 20 parts by weight of the aluminum metal powder is replaced by an inert filler material.

11. A slip as defined in claim 10, wherein said inert filler consists of at least one material selected from the group consisting of zircon, silica or alumina.

12. A slip as defined in claim 7, wherein said suspension agent is a ball type clay.

13. A slip as defined in claim 8, consisting of about 70 parts metal powder, approximately 30 parts of said Gerstley borate-lithia frit, 5 to 10 parts ball type clay, and 1 to 3 parts of said last-mentioned frit.



14. A frit comprising a heat reacted smelted and fritted product of a mixture consisting essentially of about 100 parts Gerstley borate and 5 to 7½ parts lithium carbonate.

15. A heat reacted and fritted mixture consisting essentially of about 70 parts the mineral constituents of Gerstley borate and 2–3 parts lithia.

16. The method of preparing a ceramic frit which comprises the steps of admixing together about 100 parts by weight of Gerstley borate and between about 5 to 7½ parts by weight lithium carbonate, and smelting said mixture until a clear bubble-free melt is obtained, and fritting the smelted product.

17. The method of claim 16 wherein said mixture is smelted at about 2300° F. until clear.

18. The method of providing the surface of an article selected from the class consisting of metal, glass and ceramic with a cermet coating having both ceramic and metallic phases, which includes the steps of: applying to the surface to be coated a slip comprising an aqueous vehicle, a cermet composition from about 60 to 70 parts by weight of a metal selected from the group consisting of aluminum and aluminum base alloys, in particle form, and from about 30 to 40 parts by weight of the smelted and fritted product of a composition consisting essentially of Gerstley borate and lithia, a suspension agent, and an inhibitor for preventing reaction between the aluminum powder and the water vehicle; and firing the coated surface at a temperature of at least about 1230° F. to form a cermet coating.

19. A method of providing the surface of an article with a cermet coating as defined in claim 18, wherein said inhibitor is a frit consisting essentially of boron oxide, and at least one alkaline earth oxide selected from a group consisting of barium oxide and calcium oxide in molar ratio of $3B_2O_3$:BaO.

20. A slip as defined in claim 7 wherein said last-mentioned frit further includes aluminum fluoride in molar ratio of up to ½$AlF_3$.

21. A method as defined in claim 19 wherein said last-mentioned frit further includes aluminum fluoride in a molar ratio of up to ½$AlF_3$.

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