United States Patent [19]

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[11] 3,836,380

[45] Sept. 17, 1974

[54] **DUAL COATING FOR PROTECTING METAL SURFACE DURING HEAT TREATMENT**

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[22] Filed: **Sept. 21, 1972**

[21] Appl. No.: **290,806**

[52] **U.S. Cl.** ..... **117/6**, 117/70 B, 117/70 C, 148/13.1, 148/14

[51] **Int. Cl.** **C21d 1/68**, B44d 1/14

[58] **Field of Search** ..... 117/70 C, 70 B, 6; 148/22, 148/13.1, 14

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[57] **ABSTRACT**

A temporary vitreous protective coating composition for metal to protect the metal against oxidation and decarburization at temperatures in the range of 1100°F to 2350°F. The coating composition includes a glass frit ground coat which is applied to the metal base and has a sintering temperature in the range of 1600°F to 2000°F. A glass frit cover coat is applied over the ground coat and has a sintering temperature in the range of 1050°F to 1300°F. During heat treatment of the metal base, the cover coat will initially sinter to provide an impervious outer coating, and on continued heating, the inner ground coat will sinter to provide a complete impervious barrier to protect the metal against oxidation and decarburization at the heat treating temperature. On cooling, the coating composition will spall away from the metal so that it can be removed for subsequent processing of the metal base.

12 Claims, No Drawings

DUAL COATING FOR PROTECTING METAL SURFACE DURING HEAT TREATMENT

BACKGROUND OF THE INVENTION

Steel and other metals are often heat treated at elevated temperatures, either to facilitate subsequent fabrication of the metal by rolling or forging, or to develop certain desired metallographic properties. When subjected to elevated temperatures for extended periods of time, oxidation and decarburization can occur, and in many cases, the oxidation is so severe that substantial loss of metal results.

To prevent oxidation and decarburization, metal can be heat treated in non-oxidizing atmospheres. However, the use of non-oxidizing atmospheres requires expensive equipment and is not practical when heat treating articles of large size or large quantities of articles.

In the past, protective coatings have been used to prevent oxidation and decarburization of metals during heat treatment. Protective coatings used in preventing oxidation and decarburization are of a temporary nature and will protect the metal during heat treatment, and should be readily removable after the heat treatment.

Protective coatings of the temporary type should be capable of forming a continuous impervious coating which will prevent oxidation of the metal at elevated temperatures. The coating must adhere to the metal surface in order to provide the protective shield, yet it must not melt and fuse to the metal at the temperatures involved because the molten coating will attack and allow oxidation of the metal. In addition, the protective coating should be resistant to handling so that the metal article can be handled by mechanical handling equipment before and during heat treatment without danger of the coating being marred or damaged. As a further requirement, the coating must be of a nature that it will easily spall from the metal on cooling after heat treatment so that the coating is removed for subsequent processing of the metal articles.

The copending patent application, Ser. No. 267,240, filed June 28, 1972, relates to an improved vitreous coating for protecting metal against oxidation at temperatures in the range of 1600°F to 2350°F. In accordance with the invention of the above patent application, the protective coating is a potassium-alumina-magnesia silicate produced by smelting a mixture of refractory oxides and fluxing materials in proportions such that the resulting smelted frit has a sintering temperature in the range of 1600°F. to 2000°F. When applied to the metal to be protected in the form of a thin coating, the frit particles sinter during heat treatment to provide an impermeable protective layer which shields the metal against oxidation. On cooling, the coating readily spalls from the metal.

SUMMARY OF THE INVENTION

The present invention is directed to an improvement to the above-mentioned copending application Ser. No. 267,240, filed June 28, 1972, and provides a protective coating for the base metal at temperatures in the range of 1100°F to 2350°F. In accordance with the invention, the protective coating composition includes a glass frit ground coat which is applied to the base metal. The ground coat has a composition similar to that set forth in the above-mentioned copending application and has a sintering temperature in the range of 1600°F to 2000°F. A glass frit cover coat is applied over the ground coat and the cover coat frit has a sintering temperature in the range of 1050°F to 1300°F.

During heat treatment of the base metal, the cover coat will sinter as the temperature reaches the sintering temperature of the cover coat to provide an outer impervious layer to protect the metal from oxidation and decarburization. As the temperature is further increased the ground coat will sinter to thereby provide a complete impervious coating to protect the metal against oxidation and decarburization at temperatures up to 2350°F.

The ground coat is a refractory type of coating having a coefficient of thermal expansion substantially different from that of metal base, so that on cooling following the heat treatment the coating will easily spall or fall away from the metal.

The ground coat, if used alone as a protective coating, will not sinter until the temperature of 1600°F to 2000°F is reached, so that the coating will not provide an impervious barrier to oxygen until this stage of the heat treatment. Thus, the base metal would be subject to oxidation and decarburization at temperatures up to the sintering temperature of the ground coat. On the other hand, if the cover coat was used alone as a protective coating, it would melt at a temperature in the range of about 1600°F to 1800°F and attack the metal base so that it could not be readily removed after the heat treatment had been completed. Thus, the two coats cooperate to provide an impervious barrier against oxidation and decarburization throughout the complete temperature range of 1100°F to 2350°F, while also providing a coating which can be readily removed from the metal following the heat treatment.

DESCRIPTION OF THE PREFERRED EMBODIMENT

The base metal to be protected can be any metal which has a tendency to oxidize or decarburize during heat treatment in the temperature range of 1100°F to 2350°F. The metal to be protected can be carbon steel, stainless steel, alloy steels, tool steels, nickel alloys, titanium alloys, molybdenum, and the like.

The coating composition of the invention is a composite coating consisting of a finely divided vitreous frit ground coat and a finely divided vitreous frit cover coat.

The protective ground coat is a finely divided potassium-alumina-magnesia silicate similar to that disclosed in copending application Ser. No. 267,240, filed June 28, 1972, and has the following composition in weight per cent as expressed in the form of the individual oxides:

K_2O	2 - 10%
Al_2O_3	15 - 40%
MgO	5 - 30%
SiO_2	35 - 55%
$Na_2O + Li_2O$	0 - 5%

In the above formulation, the Al_2O_3, MgO and SiO_2 are high melting point refractory oxides and in some instances other refractory metal oxides, such as ZrO_2, TiO_2, Cr_2O_3, or mixtures thereof, can replace from 0.1% to 25% by weight of the MgO, Al_2O_3, or SiO_2. In addition, 0.1% to 10% by weight of the refractory metal oxides can be replaced with intermediate oxides, such

as ZnO, BaO, Fe_2O_3, Sb_2O_3, or other oxides of the rare earth metal, such as cerium and lanthanum.

In the above formulation, the refractory metal oxides serve to provide the protective ground coat with refractory properties so that the coating will not melt and react with the base metal during the heat treating process. The fluxing materials provide a lower smelting temperature, in the range of 2400°F to 2850°F, and a sintering temperature for the resulting frit in the range of 1600°F to 2000°F. The smelting temperature is the temperature required to melt the refractory metal oxides and the fluxing materials to provide a composite frit. The smelting temperature will normally be below the melting temperature of the individual refractory metal oxides utilized in making the frit. This is due to the fact that during the smelting operation, the fluxing materials, such as the K_2O, melt and attack the refractory oxides so that the smelting temperature is not as high as the melting temperature of the individual refractory oxides.

In general, the sintering temperature of the smelted frit is directly related to the smelting temperature in that the higher the smelting temperature, the higher the sintering temperature. While there is a general relationship between the two, the sintering temperature can be varied to some degree relative to a given smelting temperature by varying the ingredients in the smelt. Thus, the refractory oxides and the fluxing materials are utilized in a proportion which will provide a sintering temperature for the frit in the range of 1600°F to 2000°F. The metal is heated during the subsequent heat treatment to a temperature generally in the range of 1600°F to 2350°F with the upper temperature being below the melting temperature of the frit so that the sintered frit will not fuse and attack the base metal.

The potassium-alumina-magnesia silicate is preferably produced by blending and smelting raw materials which will produce the oxides in the melt.

After smelting, the mixture is cooled rapidly, as by water-quenching to provide a frit which is then dry ground or wet ground to the desired particle size.

The frit can be applied to the base metal in the form of a slip or slurry. To provide the slip, the frit is milled or mixed with a mill addition and a liquid vehicle such as water. The mill addition can be any conventional mill addition used in vitreous enamel processing and a typical slip formulation is as follows in parts by weight:

Frit	100
Clay	8–10
Bentonite	0.5–1.0
Water	35–45

The slip or slurry containing the potassium-alumina-magnesia silicate frit is applied to the metal by any desired manner, such as spraying, brushing, slushing, dipping, or the like. The coating is preferably dried by heating to an elevated temperature in the range of 200°F to 400°F to evaporate the water or other carrier and provide a dry bisque coating, although drying can be accomplished at room temperature over more extended periods.

The ground coat has a thickness in the range of 0.005 to 0.035 inch and preferably in the range of 0.020 to 0.030 inch.

The cover coat which is applied over the ground coat is a finely divided, vitreous frit composition having a sintering temperature in the range of 1050°F to 1300°F. In general, the composition of the ground coat can be expressed in the form of individual oxides except for F_2) in weight percent as follows:

$Na_2O + K_2O + Li_2O$	20 - 35	P_2O_5	0 - 4
Al_2O_3	0 - 5	CdO	0 - 6
SiO_2	25 - 35	Sb_2O_3	0 - 5
TiO_2	15 - 25	B_2O_3	0 - 5
BaO	0 - 6	CaO	0 - 8
ZnO	0 - 3	F_2	0 - 5

The specific formulation of the cover coat is not particularly critical, but it is important that the cover coat have a sintering temperature in the range of 1050°F to 1300°F.

The sintering temperature can be defined as the cohesion temperature, or the temperature at which two polished flat discs of the same kind of glass placed in optical contact will coalesce (*The Properties of Glass*, Morey, 1938). Thus, in effect the sintering temperature is the temperature at which the outer periphery of the particles of frit will soften, but the interior will remain solid, as opposed to the softening temperature in which the entire particle is in the softened state. Both the sintering temperature and the softening temperature are below the melting temperature which is the temperature at which the softened particles become fluid and start to flow.

The melting temperature of the cover coat frit is not critical in that the sintered particles provide a sealed or impervious coating, and the subsequent melting of the frit during heat treatment will merely retain the impervious nature of the coating.

The cover coat frit can be applied to the dried ground as a slip or slurry. To prepare the slip, the finely divided frit is melted or mixed with a conventional mill addition, similar to that previously described with respect to the ground coat, and a liquid vehicle such as water. The slip can be applied to the metal base by spraying, brushing, dipping, or the like, and the coating is then dried, preferably by heating to a temperature of 200°F to 400°F. In some cases, the frit can be applied to the coated metal base as a dry dust coating.

The cover coat has a thickness in the range of 0.002 to 0.010 inch and has a substantially lesser thickness than the ground coat. In most cases the ground coat is from 3 to 10 times as thick as the cover coat. If the ground coat to cover coat thickness ratio is less than this range, the molten cover coat may penetrate through the ground coat and fuse to the base metal. Thus, it is important that the ground coat be considerably thicker than the cover coat.

When the coated base metal is heated to a temperature in the range of 1600°F to 2350°F for purposes of heat treatment, the particles of frit in the outer cover coat will initially sinter as the temperature reaches the sintering temperature of the cover coat frit to provide a seal and prevent the diffusion of oxygen through the coating. As the temperature of heat treatment increases, the frit particles of the ground coat will sinter to thereby provide a fully sintered and impervious coating to prevent the oxidation and decarburization of the base metal.

As previously noted, at the final temperature of heat treatment the cover coat may melt, but the molten nature of the cover coat will not detract from the impervious barrier. The ground coat provides a dual function

in that it not only sinters at an elevated temperature in the range of 1600°F to 2000°F, to provide a thicker impermeable barrier to prevent oxidation of the metal, but it also serves as a barrier to prevent the molten cover coat from contacting the base metal and chemically attacking and fusing to the base metal. If the ground coat did not provide this barrier, the molten cover coat would attack and fuse to the base metal with the result that the fused coating would be very difficult to remove from the metal after cooling from the heat treating temperature.

After heat treatment, the metal is cooled and on cooling the coating will tend to spall or break away from the metal. The ground coat is a refractory type of coating having a coefficient of thermal expansion considerable less than that of the base metal, thereby promoting breaking away of the coating from the metal on cooling to room temperature. The base metals generally have a coefficient of thermal expansion above 10 $\times 10^{-6}$/in/in/°C, while the ground coat has a coefficient of thermal expansion in the range of 5.5. to 9.4 $\times 10^{-6}$/in/in/°C.

During the heat treatment, the molten cover coat will tend to attack the ground coat to provide an intermediate, integrated coating at the interface, but the integrated intermediate coating will not interfere with the removal of the entire coating composition from the base metal after heat treatment.

If desired the coating composition can be removed from the heated base metal by high pressure water streams or mechanical scale breaking equipment before further processing of the metal. The coating of the invention has an unusual property in that it is not slippery so that the metal can be subjected to rolling without complete removal of the coating so the rolls can grip the coating. During rolling the remaining coating is broken away from the metal. The high frictional resistance of the coating differs from that of conventional coatings which are slippery and act as a lubricant during working.

The following examples illustrate the preparation of the coating composition and the application of the coating to metal for protection during heat treatment:

EXAMPLE I

The following materials in parts by weight were blended and smelted at a temperature of 2725°F:

Spodumene	10.14
Kaolin	35.30
Silica	14.13
$MgCO_3$	38.32
K_2CO_3	2.11

The smelted mixture was quenched in water and the resulting frit had the following composition expressed as oxides in parts by weight:

Li_2O	1
K_2O	2
Al_2O_3	23
SiO_2	50
MgO	24

The frit was ground with a mill addition to provide a slip having the following composition in parts by weight:

Frit	100
Bentonite	0.5
Clay	9
Water	30

After grinding the particles had a size such that 95% of the particles passed through a 200 mesh screen and all of the particles passed through a 150 mesh screen.

The slip was applied by spraying to a series of 4" × 4" × 4" H-12 tool steel blocks having a carbon content of 0.32% to provide dry bisque ground coats having a thickness of 0.020 to 0.025 inch.

The following materials in parts by weight were blended and smelted at a temperature of 2250°F.:

Rasorite	4.14
Na_2CO_3	17.73
K_2CO_3	10.45
Li_2CO_3	7.86
Rutile	16.64
$NH_4H_2PO_4$	3.39
CdO	4.51
ZnO	1.25
Sb_2O_3	1.92
Al_2O_3	0.84
SiO_2	31.27

The smelted mixture was quenched in water and the resulting frit had the following composition expressed as oxides in parts by weight:

Na_2O	14.3
K_2O	8.5
Li_2O	3.8
CdO	5.4
ZnO	1.5
Sb_2O_3	2.5
B_2O_3	3.2
Al_2O_3	1.0
SiO_2	37.4
TiO_2	19.9
P_2O_5	2.5

The frit was ground with a mill addition to provide a slip having the following composition in parts by weight:

Frit	100
Bentonite	0.5
Clay	9
Water	30

The slip was applied over the dried ground coat to provide a dry bisque cover coat having a thickness of 0.005 to 0.008 inch.

The coated tool steel was heat treated in a direct fire gas furnace with the following cycle:

600°F	Preheat
600–1000°F	45 minutes
1000°F	120 minutes
1000–1400°F	60 minutes
1400°F	60 minutes
1400–1700°F	90 minutes
1700°F	180 minutes
1700–1880°F	150 minutes
1880°F	300 minutes

After heat treatment no loss of surface carbon was noted in the coated tool steel blocks, while similar uncoated control samples had a surface carbon content in the range of 0.02 to 0.06% after heat treatment, indi-

cating a substantial loss of surface carbon from the original value of 0.32%.

EXAMPLE II

A frit was prepared in the manner of Example I having the following formulation, expressed as oxides in parts by weight:

K_2O	8
Al_2O_3	18
SiO_2	55
MgO	19

The frit was ground with a mill addition as described in Example I and applied to a series of 6″ × 6″ × 6″ M-2 tool steel blocks having a carbon content of 0.80%. The dry bisque ground coat had a thickness of 0.020 to 0.030 inch.

A second frit was prepared in the manner of Example I and had the following formulation expressed as oxides in parts by weight:

K_2O	30.0
CaO	5.8
BaO	5.1
B_2O_3	25.8
Al_2O_3	4.5
SiO_2	23.6
TiO_2	1.9
F_2	3.9

The frit was ground with a mill addition as described in Example I and applied over the ground coat bisque to provide a dry cover coat bisque having a thickness of 0.003 to 0.007 inch.

The coated tool steel was heat treated in a direct fire gas furnace with the following cycle:

600°F	Preheat
600–1000°F	45 minutes
1000°F	120 minutes
1000–1400°F	60 minutes
1400°F	60 minutes
1400–1700°F	90 minutes
1700°F	180 minutes
1700–2175°F	150 minutes
2175°F	120 minutes

After heat treatment no loss of surface carbon was noted in the coated tool steel blocks, while similar uncoated control samples had a surface carbon content in the range of 0.010 to 0.200% after heat treatment, indicating a substantial loss of surface carbon from the original value of 0.80%

Various modes of carrying out the invention are contemplated as being within the scope of the following claims particularly pointing out and distinctly claiming the subject matter which is regarded as the invention.

I claim:

1. A composite structure, comprising a base metal subject to oxidation during heat treatment at elevated temperatures, and a protective coating composition disposed on the surface of the base metal, said coating composition comprising a finely divided vitreous frit ground coat disposed on the base metal and having a sintering temperature in the range of 1600°F to 2000°F, said ground coat being a finely divided potassium-alumina-magnesia silicate frit consisting essentially of the following composition in weight percent expressed in the form of oxides:

K_2O	2 – 10
Al_2O_3	15 – 40
MgO	5 – 30
SiO_2	35 – 55
$Na_2O + Li_2O$	0 – 5,

said coating composition also including a finely divided vitreous frit cover coat disposed on the ground coat, said cover coat having a sintering temperature in the range of 1050°F to 1300°F, said cover coat having the following composition in weight percent:

$Na_2O + K_2O + Li_2O$	20 – 35	P_2O_5	0 – 4
SiO_2	25 – 55	CdO	0 – 6
TiO_2	15 – 25	Sb_2O_3	0 – 5
BaO	0 – 6	B_2O_3	0 – 5
Al_2O_3	0 – 5	CaO	0 – 8
ZnO	0 – 3	F_2	0 – 5,

said ground coat having a greater thickness than said cover coat, said cover coat sintering to provide an impervious outer layer when the metal base reaches the second-named sintering temperature during heat treatment, said ground coat sintering to provide a fully impervious coating when said ground coat reaches the first named sintering temperature during said heat treatment, said ground coat and cover coat cooperating to provide protection for the base metal against oxidation and decarburization through the temperature range of 1100°F to 2350°F.

2. The structure of claim 1, wherein said ground coat has a thickness in the range of 0.02 to 0.03 inch and said cover coat has a thickness in the range of 0.002 to 0.010 inch.

3. The structure of claim 2, wherein said ground coat has a thickness of approximately 3 to 10 times the thickness of the cover coat.

4. The structure of claim 1, wherein the ground coat has a substantially different coefficient of thermal expansion than said base metal, whereby the ground coat will tend to spall from the base metal on cooling from the heat treating temperature.

5. The composite structure of claim 1, wherein the Al_2O_3, MgO and SiO_2 constitute refractory oxides, and from 0.1% to 25% by weight of at least one of said refractory oxides is replaced by an oxide selected from the group consisting of ZrO_2, TiO_2, Cr_2O_3, and mixtures thereof.

6. The composite structure of claim 1, wherein the Al_2O_3, MgO and SiO_2 constitute refractory oxides, and from 0.1% to 10% by weight of at least one of said refractory oxides is replaced by an oxide selected from the group consisting of zinc oxide, barium oxide, iron oxide, antimony oxide, cerium oxide and lanthanum oxide.

7. A method of protecting a base metal against oxidation and decarburization during heat treatment at temperatures in the range of 1100°F to 2350°F, comprising the steps of applying a finely divided vitreous frit ground coat to the metal base, said frit having a sintering temperature in the range of 1600°F to 2000°F, applying a finely divided vitreous frit cover coat to the ground coat frit, said cover coat frit having a sintering temperature in the range of 1050°F to 1300°F, heating the coated base metal to a heat treating temperature above the sintering temperature of the ground coat and below the melting temperature of the ground coat frit, said cover coat frit sintering as said coated base metal

is heated to said second named sintering temperature during heat treatment to thereby provide an impervious cover coat and said ground coat frit sintering when said coated base metal is heated during heat treatment to provide an impervious ground coat, said cover coat frit and said ground coat frit cooperating to protect the base metal against oxidation and decarburization throughout the temperature range of 1100°F to 2350°F, cooling the coated base metal after heat treatment, and removing the ground coat and the cover coat from the base metal.

8. The method of claim **7,** wherein the cover coat is applied with a substantially lesser thickness than the ground coat.

9. The method of claim **7,** wherein the ground coat is applied with a thickness 3 to 10 times the thickness of the cover coat.

10. The method of claim **7,** wherein the ground coat is a finely divided potassium-alumina-magnesia silicate frit consisting essentially of the following composition in weight percent expressed in the form of oxides:

K_2O	2 – 10
Al_2O_3	15 – 40
MgO	5 – 30
SiO_2	35 – 55
$Na_2O + Li_2O$	0 – 5.

11. The method of claim **10,** wherein the cover coat has the following composition in weight percent:

$Na_2O + K_2O + Li_2O$	20 – 35
SiO_2	25 – 55
TiO_2	15 – 25
BaO	0 – 6
Al_2O_3	0 – 5
ZnO	0 – 3
P_2O_5	0 – 4
CdO	0 – 6
Sb_2O_3	0 – 5
B_2O_3	0 – 5
CaO	0 – 8
F_2	0 – 5.

12. The method of claim **7,** wherein the ground coat frit is applied to the base metal in the form of a suspension in an evaporable carrier, and said method includes the step of evaporating the carrier prior to applying said cover coat.

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