United States Patent Office

2,711,975

Patented June 28, 1955

2,711,975

VITREOUS COATED REFRACTORY METALS, METHOD FOR PRODUCING THE SAME, AND VITREOUS ENAMEL COMPOSITION

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No Drawing. Application July 1, 1949, Serial No. 102,708

6 Claims. (Cl. 117—129)

The present invention relates to the coating of refractory metals such as molybdenum and tungsten with vitreous material to provide corrosion resistant material having high hot strength properties and being suitable for use in gas turbine engines.

The manufacture of metals which have the ability to withstand the corrosive atmospheres present in gas turbines, while retaining their strength has always been a difficult problem in jet engine manufacture. While metals such as molybdenum have good hot strength properties, the native metals cannot be used because of their tendency to oxidize at temperatures below the normal operating temperature of the gas turbine engine, which may be as high as 1600 to 1800° F. For example, molybdenum forms an oxide at about 1463° F. which sublimes, giving rise to a characteristic "smoking" of the metal which ultimately results in its disintegration.

While it has been previously suggested to coat refractory metals such as molybdenum with other metals or metalloids, these coatings have not proven to be satisfactory in all respects. In any such coating process, conditions must be present such that a firm bond occurs between the coating metal and refractory base metal without too deep a penetration of the coating metal into the base metal. Further, the coating must have thermal-shock resistance and must be impervious to oxygen and oxidizing gases. In addition, the coefficient of thermal expansion of the coating metal must be equal to or slightly less than that of the refractory metal body. This latter condition is necessary so that the coating metal is always under a stress under operating conditions thus giving a much closer fit to the surface of the base metal. Probably the most important consideration in such a coating process is that the coating metal must be non-volatile at the operating temperature of the engine, and maintain a good bond to the base metal.

An object of the present invention is to provide a non-volatile coating for molybdenum articles capable of forming a firm bond with the refractory metal, rendering the same impervious to oxygen and oxidizing gases.

Another object of the present invention is to provide coatings for refractory metals which have coefficients of thermal expansion approximately equal to or slightly less than that of the refractory base metal.

Another object of the invention is to provide a coating having the ability to reflect infrared radiation and thereby assist in cooling the body metal.

A still further object of the invention is to provide a method for the production of a coated refractory metal having a high degree of hot strength and the ability to withstand corrosion at elevated temperatures.

The invention comprises providing a coating for molybdenum articles by means of coating the same with a prefused mixture of alkaline earth aluminum silicates, plus modifying agents, substantially free from alkali metal compounds. It has been found that conventional glass compositions are not suitable for this purpose since they almost invariably contain some alkali metal compounds,

i. e., compounds of sodium and potassium, which are volatile at the operating temperature of the turbine engine. The volatilization of the oxides of the alkali metal decreases the ability of the coating to withstand corrosion to a very substantial degree.

In particular, the refractory metal, according to the present invention, is provided with a coating consisting of a vitrified mixture containing about 10 to 30% calcium oxide, 10 to 30% aluminum oxide, 40 to 70% silicon dioxide, and 1 to 10% boric oxide. A preferred composition within the above range is one containing 10 to 20% calcium oxide, 15 to 25% aluminum oxide, 50 to 60% silicon dioxide, and 1 to 10% boric oxide. Where the coating is fired at high temperatures, boric oxide may be eliminated from the glass formula. Where the coating is applied at lower temperatures, boric oxide is included to bring the firing temperature down to the workable range. The firing temperature is an important consideration, and should be kept below 1900° F. to avoid impairing the physical properties of the molybdenum-base body.

Various other materials may be added to the composition to enhance the properties of the final coating, as will be hereinafter more fully described.

The method of the present invention is also applicable to alloys containing major proportions of molybdenum. For example, the coatings may be applied to a molybdenum tungsten alloy containing up to about 5% tungsten.

Prior to coating the molybdenum article with the vitreous coating, the body metal is worked to shape at appropriate forging temperatures.

While the coating may be applied directly to the refractory metal, the properties of the article can be greatly enhanced by first pre-coating the worked refractory metal with a surface coating of metal or metalloid such as silicon, aluminum, or zirconium. Preferably this pre-coating is carried in the manner described in our copending application, Serial No. 98,272, filed June 10, 1949.

The preferred glass compositions, according to the present invention, have the following analyses, in percentages by weight:

Component	Glass			
	No. 1	No. 2	No. 3	No. 4
CaO	20	15	10	10
Al_2O_3	20	20	25	15
SiO_2	55	60	55	50
B_2O_3	5	5	5	5
ZrO_2			5	20

In the above compositions the boric oxide was included to promote melting and also to improve the thermal-shock resistance of the glass. Boric oxide also helps to complex the mixture so that a glass is actually formed. An amount of boric oxide up to about 10% has been found to be sufficient for this purpose.

To reduce the firing temperature of a glass having a large refractory mill addition, minor amounts of compounds such as calcium fluoride, barium oxide and lithium oxide may be added. Examples of glass formulae which contain such additives are given below:

Component	Glass			
	No. 5	No. 6	No. 7	No. 8
CaO	14.6	14.6	14.9	14.6
Al_2O_3	19.5	19.5	19.9	19.5
SiO_2	58.1	58.1	59.7	58.1
B_2O_3	4.9	4.9	5.0	4.9
BaO	2.9			1.45
CaF_2		2.9		1.45
Li_2O			0.5	

Zirconium oxide has the effect of increasing the viscosity of the glass. The oxide of zirconium will be included in the mill additions in an amount from about 5 to 30% by weight of the glass composition with 20 parts per 100 parts of glass being the preferred amount. The particle size of the zirconium oxide added is preferably less than 5 or 6 microns. Some zirconium goes into solution in the glass and serves to increase the toughness and hardness thereof. Zirconium oxide also increases the refractoriness and lowers the coefficient of expansion of the glass, thus providing an improved fit between the coating and the base.

The procedure in applying the coating consists first of weighing and mixing the ingredients of the glass composition, and melting the batch at a temperature from about 2500 to 2700° F. Next, the glass composition is fritted by pouring the molten mass into water. The glass is next ground while wet in ball mills or the like to a particle size of approximately 200 mesh, whereupon it is dried. Next, the mill additions are weighed and added. These mill additions include refractory oxides, preferably zirconium oxide as mentioned above, together with binders and setting up agents. Typical mill additions which may be used are the various clays such as enamelers clay, bentonite, montmorillonite, Florida kaolin and the like. In addition, various metallic compounds, such as chromium oxide, zinc oxide, cobalt oxide, nickel oxide, strontium oxide, iron oxide, manganese dioxide, calcium fluoride, and barium oxide may be added.

The preferred setting up agent is methyl cellulose, since this agent has been found to increase the green film strength and reduce the tearing of the coat during firing. Methyl cellulose will be normally added in amounts up to about 1% with 0.1 part methyl cellulose per 100 parts glass being preferred. The various additives in the form of mill additions may be added in amounts from less than 1 part per 100 parts of glass, up to about 25 parts per 100 parts of glass, exclusive of water. The amount of mill addition other than refractory oxides should be in the range from 0.01 and 4.0%.

An eminently suitable coating composition may be prepared from the following formula:

Glass:

CaO	per cent	15
Al_2O_3	do	20
SiO_2	do	60
B_2O_3	do	5

Mill formula:

Glass	parts	100
ZrO_2	do	20
Methyl cellulose	do	0.1
Water	do	60

After the addition of the mill additions, the mixture is wetted and ground in a ball mill. Next, the glass is applied to the refractory metal article as by means of a spray gun.

The article is then transferred to a furnace for the purpose of vitrifying the coating previously applied. In baking the glass onto the surface of refractory metal precoated with a metal or metalloid of the type described previously, a temperature in the range of about 1700 to 1900° F. is employed. The vitrifying step may be carried out in atmospheres ranging from slightly oxidizing, e. g., argon with a small amount of water vapor, through inert atmospheres, e. g., argon, helium, neon, krypton, to strongly reducing atmospheres, e. g., pure dry hydrogen.

The baking is continued until a smooth vitrified coating is obtained. The thickness of the vitreous coating will normally be from about 0.002 inch to 0.005 inch.

The above range for firing temperatures is employed where the article is to be used at high temperatures and under high stress, as for example, is the case in a turbine bucket. Where the article is to be used at high temperatures at relatively low stresses, this range may be exceeded.

Turbine buckets produced according to the the above disclosed process show remarkable ability to withstand corrosion. A turbine bucket pre-coated with silicon and coated with a vitrified coating of type disclosed above can withstand 1000 hours of operation at 1600 to 1800° F. in air with no indication of failure.

Articles coated according to the process of the present invention exhibit a high degree of thermal-shock resistance. Thus, the articles may be heated to red heat and water quenched without destroying the coating.

The coatings are also extremely resistant ot oxygen and prevent passage of oxidizing gas into the base metal. The thermal expansion coefficient of the coating is somewhat less than that of the refractory metal base, so that a compression fit between the coating and the metallic base is effected under operating conditions. The coating also improves the damping capacity of the article.

In addition, the vitrified coating has the ability to reflect infra red radiations, as opposed to transmission. This reflection away from the body gives a substantial cooling effect to the article.

In addition, the non-volatile glass-like coatings form a smooth, firm bond to the surface of the molybdenum, or any pre-coat which has been applied thereto.

It will, of course, be understood that various details of the process may be varied through a wide range without departing from the principles of this invention and it is, therefore, not the purpose to limit the patent granted hereon otherwise than necessitated by the scope of the appended claims.

We claim as our invention:

1. A coated metal article comprising a base composed principally of molybdenum, and a corrosion resistant coating about said base consisting essentially of a vitrified mixture containing 10 to 30% calcium oxide, 10 to 30% aluminum oxide, 40 to 70% silicon dioxide, 1 to 10% boric oxide, and 5 to 30% zirconium oxide, the thickness of said coating being on the order of .002 to .005 inch.

2. The method of providing a corrosion resistant surface to molybdenum articles which comprises providing a shaped body composed principally of molybdenum, coating surfaces of the same with a glass composition consisting essentially of 10 to 30% calcium oxide, 10 to 30% aluminum oxide, 40 to 70% silicon dioxide, and 1 to 10% boric oxide, together with mill additions comprising zirconium oxide, said glass composition being substantially free of alkali metal compounds, and firing the coated article at a temperature sufficient to vitrify such coating.

3. The method of providing a corrosion resistant surface to a molybdenum-base article which comprises providing a shaped body of molybdenum, coating surfaces of said body with a glass composition consisting essentially of 10 to 30% calcium oxide, 10 to 30% aluminum oxide, 40 to 70% silicon dioxide, and 1 to 10% boric oxide, together with mill additions comprising zirconium oxide, said glass composition being substantially free from alkali metal compounds, and firing the coated article in an atmosphere of inert gas at a temperature sufficient to vitrify said coating.

4. The method of providing a corrosion resistant surface to a molybdenum-base article which comprises providing a shaped body of molybdenum, coating said shape with a surface layer of silicon, and coating surfaces of the thus coated shape with a glass composition consisting essentially of 10 to 30% calcium oxide, 10 to 30% aluminum oxide, 40 to 70% silicon dioxide, and 1 to 10% boric oxide, together with mill additions comprising zirconium oxide, said glass composition being substantially free from alkali metal compounds, and firing the resulting coated article to a temperature sufficient to vitrify said coating.

5. A ceramic composition for coating refractory metals consisting of a glass composition consisting essentially of 10 to 30% calcium oxide, 10 to 30% aluminum oxide, 40 to 70% silicon dioxide and 1 to 10% boric oxide combined with mill additions containing zirconium oxide, said composition being capable of being fired into said refractory metal at a temperature in the range from 1700° to 1900° F.

6. A coated metal article comprising a base of molybdenum, and a corrosion resistant ceramic coating over said base consisting essentially of a vitrified mixture of alkaline earth aluminum silicates together with mill additions comprising zirconium oxide.

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