

1

2,959,503

METHOD FOR TREATING TITANIUM METAL

John T. Lindson, Morgan, N.J., assignor to National Lead Company, New York, N.Y., a corporation of New Jersey

No Drawing. Filed May 23, 1958, Ser. No. 737,206

4 Claims. (Cl. 148—20)

This invention relates in general to a method for processing metals and more particularly, to a method for protecting the surface of titanium metal against oxidation during metal processing operations.

This application is a continuation-in-part of my application Ser. No. 704,307, filed December 23, 1957, now abandoned.

Titanium metal and titanium metal alloys, as produced, are usually forged into billets which are processed by hot rolling into sheets, plates or strips and the sheet metal is subjected to heat treatments in order to anneal, and to work or alter the internal structure of the titanium metal or titanium metal alloy. During hot rolling and the subsequent annealing or high temperature heat treatments, which operations are hereinafter referred to as metal processing operations, the surface of the titanium metal or titanium metal alloy is seriously oxidized, particularly during forging and hot rolling, such that relatively large amounts of metal are lost. Moreover, present methods for removing the oxidized surface from the cold rolled and annealed sheet metal not only consumes additional metal but add further to the cost and time required to produce sheet metal having oxide-free surfaces. For example, one commonly used method for removing an oxidized surface from sheet titanium metal is to treat the metal in a non-aqueous molten caustic soda bath at about 500° C. followed by a treatment in a sulfuric acid bath to remove the soluble salts from the metal surface. This molten caustic treatment, however, is harmful to the titanium metal in that it causes pitting and deterioration of the metal surface and consequently the sheet must then be ground to remove these surface defects.

An object, therefore, of the present invention is to provide an improved method for processing titanium metal or titanium metal alloys during metal processing operations so as to preclude large losses of metal as oxides.

Another object of the instant invention is to provide a method for preventing oxidation of the surface of titanium metal or titanium metal alloys during metal processing operations.

A further object is to provide a glass coating on the surface of titanium metal or titanium metal alloys which will prevent oxidation of the metal surface during metal processing operations.

2

A still further object is to provide a glass coating on titanium metal or titanium metal alloys which will prevent oxidation of the titanium metal surface during metal processing operations and which may be readily removed from the metal surface following said metal processing operations.

Still another object is to provide a simple and economical method for removing an oxide coating from titanium metal or titanium metal alloys without causing deterioration of the metal surface. These and other objects will become more apparent from the following more complete description of the instant invention.

Broadly, this invention contemplates a process for treating titanium metal or titanium metal alloys during metal processing operations to prevent oxidation of the surface of said titanium metal during the metal processing operations which treatment comprises applying a glass frit over the entire surface of said titanium metal, subjecting the glass frit-coated titanium metal to metal processing operations at temperatures in the range of from 700° C. to 1000° C. and during said metal processing operations fusing said frit to form a continuous fluid or viscous glass and maintaining said continuous glass coating over the entire surface of said metal at said metal processing temperatures, and then removing said glass coating from the surface of the titanium metal following the metal processing operations.

The glass frit use to coat the titanium metal prior to metal processing operations may be either in the form of a dry frit composition or in the form of a slip, the selection of one over the other being made on the basis of the particular processing operation to be used. For example, if the titanium metal is in the form of a red hot billet to be hot rolled into sheet stock, the glass frit composition would be applied preferably as a dry frit due to the high temperatures encountered, rather than as a slip; whereas in the case of annealing cold rolled sheet stock, a glass slip would be applied to the sheet metal. It will be understood, however, that selection of the particular form of frit will be dictated by the specific nature of any particular metal processing operation and is not limitative of the invention.

The specific glass frit composition referred to herein is an alkali metal-boro-silicate composition containing titanium dioxide.

As mentioned above, the metal processing operations to which the instant invention may be applied include annealing sheet titanium metal, or titanium metal, at temperatures in the range of from 700° C. to 800° C.; forging and hot rolling titanium metal ingots at temperatures in the range of from 800° C. to 1000° C.; and heat treatment of titanium metal alloy sheet material at temperatures in the range of from 800° C. to 1000° C. so as to change the internal structure of the alloy.

In all of the aforementioned metal processing operations recognized techniques are employed in working or heat treating the metal, that is to say, no significant changes in current methods of forging, hot rolling and annealing need be made to practice the instant invention.

Specifically, in a forging and hot rolling operation a glass frit is applied to the ingot at temperatures in the range of from 800° C. to 1000° C. at which temperatures the glass frit matures to form a continuous viscous or fluid coating on the ingot which coating is maintained on the surface of the metal during forging of the ingot into a billet and subsequent hot rolling of the billet into the form of sheet stock. In an annealing operation the sheet metal stock is first coated with a glass slip which matures at the annealing temperatures to coat the metal with a fluid or viscous continuous glass coating which is maintained on the sheet metal throughout the annealing period which may vary from 1 to 10 minutes at temperatures between 700° C. and 800° C. for the heat treatment of sheet metal alloys wherein the crystal structure of the metal is changed, higher heat treating temperatures are used usually in the range of from 800° C. to 1000° C. and the heating periods may range from 1 to 5 minutes. For example, with a titanium alloy containing aluminum and vanadium, the alpha phase of the alloy may be dissolved in the beta phase of heat treating and quickly quenching the alloy.

As stated above a glass frit may be applied in any suitable manner to the titanium metal or titanium metal alloy surface, as for example by dusting the sheet metal with a dry frit powder, or spraying the sheet metal with a slip, after which the metal is subjected to a metal processing operation at a temperature in the range of from 700° C. to 1000° C. during which time the glass frit fuses and forms a continuous glass coating on the metal surface which remains on the surface of the metal during the metal processing operations and thus protects the surface from oxidation.

In addition to its function as a protective coating against oxidation of the metal it has also been found that if the titanium metal to be processed already has an oxide coating that this oxide coating will be dissolved by the application of the glass coating and will be removed from the metal surface upon removal of the glass coating.

According to the instant invention, the glass frits employed to form the continuous glass coatings are alkali metal-boro-silicate compositions containing titanium dioxide and more particularly compositions in which the constituents are in various proportions such that different frit compositions will have different maturing temperatures. As a consequence, a particular frit composition may be selected having a maturing temperature at or below the temperature used in a particular metal processing operation so that the frit composition will form a continuous glass coating on the metal at the processing temperature employed.

The glass frits selected to form continuous glass coatings on metal being processed at temperatures in the range of from 700° C. to 1000° C. have compositions as follows:

15% to 25% by weight of alkali metal oxide
10% to 20% by weight of boron oxide
30% to 60% by weight of silicon dioxide
4% to 45% by weight of titanium dioxide

In these compositions either sodium or potassium or mixtures thereof may be used as the alkali metal. Lithium may be substituted for part of the alkali metal provided that it replaces only up to 1/2 of the total alkali metal. Alkaline earth metal oxides also may be substituted for part of the alkali metal oxide provided that they replace only up to 1/4 of the total alkali metal oxide.

Following any of the above described metal processing operations the glass coated metal is first cooled and then flexed, whereupon the glass coating will immediately shatter and drop off. In the higher heat treating process the metal is heated from 800° C. to 950° C. for 1 to 5 minutes and while still hot the metal is usually subjected to a quick quenching operation, for example, by em-

ploying a cold water spray, which shatters the coating and upon flexing the metal the glass coating will drop off. The metal surface uncovered will be clean and free from an oxide coating.

In both of these processes the metal may be subsequently leached if desired in a dilute acid solution to brighten the surface after the glass coating has been removed. The acid leaching solution should contain from 1% to 5% by weight of total acid. Both HF and HNO₃ should be employed and at least 0.5% by weight of each acid should be present in solution. A preferred composition should contain 1% to 2% HF and 1% to 2% HNO₃.

Although compositions containing from 4% to 45% TiO₂ may be employed as frit compositions in the instant invention, it is desirable to have at least 10% TiO₂ in the frit composition when the temperatures used in heat treating the metal or alloy are above 800° C. With 10% or larger quantities of TiO₂ present, the glass coating flexes off more easily after heat treatment. Where lower treatment temperatures may be employed i.e. between 700° C. and 800° C. lower quantities of TiO₂ may be employed.

In order to more fully illustrate the instant invention the following examples are presented.

EXAMPLE 1

The following method was used to prepare a frit composition:

94.5 parts of Na₂CO₃, 88.6 parts of H₃BO₃, 133.0 parts of SiO₂ and 62.2 parts of TiO₂ were thoroughly mixed and heated to 1250° C. for 30 minutes to melt the ingredients and to form a homogeneous molten glass. This molten glass was then poured into water and the quenched glass formed a frit composition having the following chemical composition:

Composition:	Percent by weight
Na ₂ O	18.4
B ₂ O ₃	16.6
SiO ₂	44.3
TiO ₂	20.7

This frit composition was then mixed with water and various mill additions to form the following mill batch:

Ingredient:	Parts by weight
Frit composition	100
Clay	2
NaNO ₂	0.3
K ₂ CO ₃	0.3
Water	50

This mill batch was then ground for 16 hours and the milled slurry or slip was then screened through a 100 mesh sieve. The ground slip was then sprayed onto the surface of a cold rolled titanium metal sheet in the amount of 30 grams per square foot dry weight.

The coated titanium metal sheet was heated to 730° C. for 10 minutes to anneal the sheet. During the heat treatment the frit composition matured to form a fluid continuous glass coating on the titanium metal surface within the first two minutes at 730° C. After the heat treatment the annealed sheet was air cooled to room temperature and the glass coating became rigidly fixed. After cooling the annealed sheet was then flexed mechanically and the glass coating immediately shattered and dropped off. The surface of the titanium metal sheet after the glass coating had been flexed off was clean and free of any oxide coating or scale.

EXAMPLES 2-6

Additional examples were run using cold rolled titanium metal sheet in the manner described in Example 1 above except that different frit compositions were used to coat the metal. The particular frit compositions used in these examples correspond to those numbered 2 through 6 in the table below.

5

In all instances the glass coated titanium metal sheet was air cooled to room temperature after which the sheet was flexed mechanically whereupon the glass coating immediately shattered and dropped off leaving the surface of the titanium metal clean and free of any oxide coating or scale.

EXAMPLES 7-8

The frit composition identified as 7 and 8 in the table below were used to coat sheet metal in the manner described in Example 1 above except that frit composition 7 was used to coat a titanium base alloy sheet containing 6% aluminum and 4% vanadium by weight; and the frit composition 8 was used to coat titanium metal sheet having an oxide coating on its surface. In both of these examples the removal of the glass coating from the annealed sheet metal by flexing the latter left the surface of the sheet metal clean and free of an oxide coating.

EXAMPLE 9

The frit composition described in Example 1 was used to coat a titanium metal alloy sheet containing 6% Al and 4% V by weight. This coating was prepared in the same manner as Example 1 except that the slip was sprayed onto the surface in amount of 15 grams per square foot dry weight.

This coated sheet was then heat treated at a temperature of 950° C. for 2 minutes after which it was immediately quenched with cold water which shattered the glass coating. The sheet was then flexed to remove any of the remaining adhering pieces of glass. This heat treatment not only produced a clean surface free from an oxide coating but some of the alpha phase converted to the beta phase thus producing a metal alloy possessing a clean surface and desirable working properties. The frit composition used is recorded in the table below.

EXAMPLE 10

An additional example was run using the same titanium metal alloy sheet described in Example 9 and the same mode of treatment except that the sheet titanium base alloy was coated with a frit having the composition identified as composition 10 in the table below. Again the glass coating was readily removed from the sheet metal simply by flexing the latter, the surface of the sheet metal being left clean and free of any oxide coating.

EXAMPLE 11

A frit similar to that described in Example 1 was applied as a dry powder to the surface of a titanium metal alloy containing 6% aluminum and 4% vanadium by weight in an amount of 15 grams per square foot dry weight. The coated metal was then heated to 850° C. and the frit formed a glass on the metal surface. The coated metal was passed through hot rolls which reduced the thickness of the metal by 100%. During passage of the glass coated metal through the hot rolls a thin viscous glass coating on the metal remained intact and continuous. Following cooling of the hot rolled metal the glass coating was removed by flexing. The surface of the rolled titanium metal sheet was oxide free. The frit composition used is recorded in the table below.

EXAMPLE 12

Using the procedure of Example 11 nonalloyed titanium metal was hot rolled. The frit composition used is disclosed in the following table. The hot rolled glass-coated metal after cooling and flexing possessed on oxide free surface.

6

Table

GLASS COATINGS ON TITANIUM METAL SHEET

Ingredients Used	Parts by Weight					
	Ex. 1	Ex. 2	Ex. 3	Ex. 4	Ex. 5	Ex. 6
Na ₂ CO ₃ -----	94.5	102.6	82.0	87.1	87.1	-----
H ₃ BO ₃ -----	88.6	106.5	106.5	106.5	106.5	88.6
SiO ₂ -----	133.0	166.8	166.8	166.8	166.8	133.0
TiO ₂ -----	62.2	13.2	13.2	13.2	13.2	62.2
Li ₂ CO ₃ -----	-----	-----	29.8	-----	-----	-----
BaCO ₃ -----	-----	-----	-----	11.6	-----	-----
CaCO ₃ -----	-----	-----	-----	-----	16.0	-----
K ₂ CO ₃ -----	-----	-----	-----	-----	-----	81.0

Frit Composition	Percent by Weight					
	Ex. 1	Ex. 2	Ex. 3	Ex. 4	Ex. 5	Ex. 6
Na ₂ O-----	18.4	20.0	16.0	17.0	17.0	-----
B ₂ O ₃ -----	16.6	20.0	20.0	20.0	20.0	16.6
SiO ₂ -----	44.3	55.6	55.6	55.6	55.6	44.3
TiO ₂ -----	20.7	4.4	4.4	4.4	4.4	20.7
Li ₂ O-----	-----	-----	4.0	-----	-----	-----
BaO-----	-----	-----	-----	3.0	-----	-----
CaO-----	-----	-----	-----	-----	3.0	-----
K ₂ O-----	-----	-----	-----	-----	-----	18.4

Table

GLASS COATINGS ON TITANIUM METAL SHEET

Ingredients Used	Parts by Weight					
	Ex. 7	Ex. 8	Ex. 9	Ex. 10	Ex. 11	Ex. 12
Na ₂ CO ₃ -----	105.3	84.6	94.5	84.6	94.5	84.6
H ₃ BO ₃ -----	90.0	66.1	88.6	66.1	88.6	66.1
SiO ₂ -----	148.5	91.2	133.0	91.2	133.0	91.2
TiO ₂ -----	39.0	122.1	62.2	122.1	62.2	122.1

Frit Composition	Percent by Weight					
	Ex. 7	Ex. 8	Ex. 9	Ex. 10	Ex. 11	Ex. 12
Na ₂ O-----	20.5	16.5	18.4	16.5	18.4	16.5
B ₂ O ₃ -----	17.0	12.4	16.6	12.4	16.6	12.4
SiO ₂ -----	49.0	30.4	44.3	30.4	44.3	30.4
TiO ₂ -----	13.0	40.7	20.7	40.7	20.7	40.7

From the above description and by the examples presented it has been clearly shown that titanium metal and titanium metal alloys may be subjected to metal processing operations such as hot rolling, cold rolling and annealing or high temperature heat treatment without oxidation of the surface of the metal provided, however, a continuous glass coating is formed and maintained on the metal surface during the metal processing operations. By using the process of the instant invention, a glass coating may be readily applied to the metal surface and following the metal processing operation may be readily removed by flexing. The final surface of the titanium metal or titanium metal alloy will be free from an oxide coating and will possess a smooth free appearance. Moreover, any oxidation existing on the surface of the metal before the application of the glass coating will also be removed by this process. The process of the instant invention is relatively simple and economical to employ and is carried out without significant loss of titanium metal.

While this invention has been described and illustrated by the examples shown, it is not intended to be strictly limited thereto and other modifications and variations may be employed within the scope of the following claims.

I claim:

1. A process for protecting the surface of titanium metal against oxidation during metal processing operations which comprises: applying a glass frit composition to the surface of said titanium metal to form a contin-

7

uous glass frit coating thereon, subjecting said coated titanium metal to a metal processing operation at a temperature in the range of from 700° C. to 1000° C. and during said metal processing operation maturing said glass frit to form a continuous glass coating on said metal surface and maintaining said continuous glass coating on the surface of said metal, and thereafter removing said glass coating from the metal surface upon completion of said metal processing operation, said glass frit composition consisting of from 15% to 25% by weight of alkali metal oxide, from 10% to 20% by weight of boron oxide, from 30% to 60% by weight of silicon dioxide and from 4% to 45% by weight of titanium dioxide.

2. Process according to claim 1 in which the glass coating on said titanium metal is removed by flexing said metal.

8

3. Process according to claim 1 in which the titanium metal is annealed at a temperature in the range of 700° C. to 800° C.

4. Process according to claim 1 in which the titanium metal is an alloy of aluminum and vanadium and is heat treated at a temperature in the range of 800° C. to 1000° C.

References Cited in the file of this patent

UNITED STATES PATENTS

2,009,165	Cross	July 23, 1935
2,337,186	Caugherty	Dec. 21, 1943
2,526,299	Tinsley	Oct. 17, 1950
2,596,487	Jaffee et al.	May 13, 1952
2,645,575	Herres et al.	July 14, 1953