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DESCALING PROCESS FOR ALLOYS CONTAINING CHROMIUM

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No Drawing. Filed June 25, 1971, Ser. No. 157,005

Int. Cl. C23g 1/14, 1/28

U.S. Cl. 134—2

7 Claims

ABSTRACT OF THE DISCLOSURE

Process for descaling high chromium alloy members in which the scaled alloy members are first provided with a coating of sodium carbonate and then heated to obtain a reaction between the coating and the scale. The reaction product is readily removed from the members, as by rinsing in water, for example, and the remaining scale may then be removed by conventional means, i.e., an acid pickling bath.

This invention is directed to a process for descaling high chromium alloys.

Alloys subjected to high temperature processing, such as preheating, hot rolling and annealing, develop a surface scale composed of oxides of the component metals of the alloys which are formed at elevated temperatures in the presence of the oxygen of the air. Stainless steels which have been hot worked in air, for example, form quite tenacious coatings of oxides which may be removed by mechanical means, i.e., grinding or sand blasting, by acid pickling or by immersing in a bath of a molten salt such as sodium hydroxide. As the chromium content of alloys becomes greater, the difficulty in descaling is increased because the oxides of chromium formed at elevated temperatures are remarkably stable and closely adhere to the surface of the alloy.

The problems encountered in removing scale formed at elevated temperature on high chromium alloys have the effect of inhibiting and limiting the application of these alloys by industry, since the use of otherwise meritorious alloys may be rendered economically unfeasible by this processing difficulty. For example, in the processing of an alloy containing, by weight, about 26% chromium, about 6.5% nickel and the balance essentially iron, during soaking and hot rolling a scale forms that cannot be removed by the usual pickling treatments. Because of this, an expensive process such as grinding must be used to remove this scale. Accordingly, there is a real need for a process which is capable of descaling high chromium alloys in an economical fashion.

It is an object of the invention to provide a process for descaling high chromium alloys.

It is a further object of the invention to provide a treatment for the scale of high chromium alloys which produces a readily removable reaction product.

Other objects and advantages of the invention will become apparent from the following description.

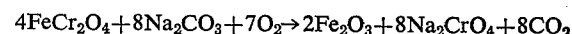
Generally speaking, the process of the invention comprises contacting a scaled chromium-containing alloy member with sodium carbonate (Na_2CO_3) at an elevated temperature and under oxidizing conditions to produce a reaction involving the Na_2CO_3 and the scale and thereafter removing the reaction products and the remaining scale. The reaction is carried out at a temperature in the range from about 1000° F. to about 1700° F.

In the process set forth in the preceding paragraph, it is convenient to contact the alloy member with Na_2CO_3 by forming a coating of Na_2CO_3 on the member. This may be accomplished by spraying a hot alloy member with a solution of Na_2CO_3 containing at least 50 grams of Na_2CO_3 per liter of water and ranging up to a satu-

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rated solution of Na_2CO_3 , e.g., 250 grams of Na_2CO_3 per liter of water. The coating may also be obtained by immersing the member in a slurry of Na_2CO_3 . Dusting Na_2CO_3 on the surface of the member in the form of dry powder is another way of contacting the alloy member with Na_2CO_3 . In any case, it is necessary that a relatively heavy and adherent coating of sodium carbonate be obtained on the alloy member, i.e., from about 3 g./m.² to about 100 g./m.² or, more advantageously, from about 10 g./m.² to about 24 g./m.². Spraying of a solution of the sodium carbonate has been found to be the most convenient and effective way of establishing the sodium carbonate coating on the hot alloy member. In this connection, the temperature of the alloy member during the application of the sodium carbonate solution is important and, accordingly, the member must be preheated to a temperature in the range from about 300° F. to about 1500° F., i.e., about 400° F. to about 600° F. In the spraying operation, the water is quickly flashed off as the spray touches the hot alloy member, i.e., strip, and a white, continuous and adherent dry coating remains. At preheating temperatures over 1000° F., it is more difficult to lay down a coating due to the increasingly rapid and violent transformation of the water to steam, and generally substantially thinner coatings are obtained even though large volumes of solution are employed.

While the application of the coating and the reaction of the coating with the scale can be conducted simultaneously, in accordance with this invention, by selecting a relatively high temperature for applying the coating, i.e., 1000° F. or higher, it is advantageous to use a relatively lower temperature, say about 600° F., to facilitate the coating operation. At such lower temperature the reaction between the coating and the scale proceeds slowly, if at all. Once the coating is established, the alloy member is reheated in air to a temperature in the range 1000° F. to 1700° F., resulting in a chemical reaction between the coating and the scale which is believed to proceed substantially as follows:



Whatever the reaction, it is found that the chromium is oxidized from Cr^{+3} to Cr^{+6} , and in this higher oxidation state the chromium is soluble in water. It is advantageous in some cases to add an oxidizer such as sodium nitrate (NaNO_3) to the Na_2CO_3 coating to make the conditions more oxidizing. Thus, NaNO_3 may be added to the coating solution in the amount of from about 3 g./l. to about 75 g./l., or, more advantageously, from about 10 g./l. to about 40 g./l. It is found that the reaction temperatures for Na_2CO_3 coatings containing NaNO_3 fall in the range from 1000° F. to 1100° F. or 1200° F., whereas the reaction temperatures for Na_2CO_3 coatings without such an NaNO_3 addition are found to reside in the range from about 1400° F. to about 1600° F. Other oxidizing agents may also be used, for example, sodium peroxide or sodium persulfate are suitable for this purpose.

At the lower end of the reaction temperature range, the reaction may not go to completion, whereas at the higher end of the range additional oxidation of the base metal may occur, resulting in a difficult-to-pickle scale. For each alloy treated by this process there is an optimum temperature range which can be determined in each case by a few preliminary runs, but the temperatures will be found to fall in the indicated range for high chromium alloys. In the treatment of alloy strip the reaction temperature range, in some cases, coincides with the annealing temperature range and, when this occurs, the two processes can be carried out simultaneously.

Following completion of the above reaction, sodium chromate and a chromium depleted oxide scale remain on the surface of the alloy member. The sodium chromate

is soluble in water and it can therefore be washed off with water alone. In the treatment of alloy strip, this washing in water may be a distinct and separate stage in the process or it may conveniently take place during water quenching after the annealing treatment, when such a quench is employed. Of course, immersion in an acid pickling bath will also wash off the sodium chromate, but this may not be desirable because the sodium chromate tends to neutralize and possibly contaminate the acid bath.

After the sodium chromate has been removed as described above, the alloy member is subjected to an acid pickling treatment to remove any residual scale, which is composed of oxides of the constituents of the alloy member (with only small amounts of chromium oxides remaining). For example, with iron-base alloys the scale remaining after the sodium chromate has been removed consists primarily of Fe_2O_3 . It has been found that warm nitric acid-hydrofluoric acid pickling baths at temperatures from about 45° C. to about 60° C. and containing, by volume, at least about 6% or 8%, e.g., about 10%, and up to about 23% of nitric acid plus from at least about 1% or 2%, e.g., about 4%, and up to about 5% of hydrofluoric acid are satisfactory for removing residual scale from iron-base and nickel-base alloys after treatment in accordance with the invention. A two-step process, calling first for a warm pickling bath (45° C. to 80° C.) composed of, by volume, from about 8% to about 12% sulfuric acid, e.g., about 10% to loosen the residual scale, followed by a warm bath composed of the aforementioned nitric acid-hydrofluoric acid solution, may also be used.

The descaling process of the invention is capable of removing scale from alloys containing at least about 11% up to about 30% or 35% chromium, e.g., about 16% or 18% to about 30% chromium, and having a base of nickel, iron or cobalt or combinations of these base metals. The invention is applicable to stainless steels of the austenitic, ferritic or martensitic types. Molybdenum may be present in these alloys in amounts up to about 15% or higher, e.g., 9%. Molybdenum produces a most tenacious oxide on these chromium-containing alloy members which, nevertheless, are susceptible to descaling by the process of this invention. Other elements may be present in substantial amounts in these alloys without apparent adverse affect on the descaling process of the invention. Thus, expressed in weight percent, the age-hardening elements aluminum, titanium and columbium may be present in amounts up to 10% total. Copper may be present in an amount up to about 5%, manganese in an amount up to about 20%, silicon in an amount up to about 10% and carbon in an amount up to about 4%. Nickel may range up to about 85%, e.g., about 6.5%, iron up to about 89%, e.g., about 30% and cobalt up to about 50%. Small amounts of incidental impurities, e.g., sulfur in an amount not exceeding about 0.5%, by weight, may also be present. While the descaling process of the invention is effective in descaling alloy members within the above-indicated composition ranges, it should be understood that conventional descaling procedures such as acid pickling may be entirely adequate for treating certain of the alloys within the above ranges, particularly those at the lower end of the chromium range. The descaling process of the invention is particularly directed to the treatment of alloys containing relatively large amounts of chromium, e.g., about 20% or more chromium, which have been proven resistant to the conventional descaling treatments.

For the purpose of giving those skilled in the art a better understanding of the invention and/or a better appreciation of the advantages of the invention, the following illustrative examples are given:

EXAMPLE I

A stainless steel (Alloy 1) ingot normally containing, by weight, about 26% chromium, about 6.5% nickel,

about 0.05% or 0.06% carbon (max.), about 0.5% silicon (max.), about 0.5% manganese (max.), about 0.025% phosphorus (max.), about 0.025% sulfur (max.), from about 0.2% to about 0.35% titanium and the balance essentially iron was soaked 1 hour at 2300° F., forged to a thickness of 1 inch, reheated to 2200° F. for one-half hour, hot rolled to 0.150 inch and then air cooled. The alloy member following this treatment had a dark-colored, smooth and tightly adherent scale coating on the surface thereof. The scaled alloy member was subjected to a two-step pickling process in which the member was first immersed in a 10% (by vol.) H_2SO_4 solution at 60° C. for 5 minutes, and then in a 10% (by vol.) HNO_3 plus 4% (by vol.) HF solution at 60° C. for 5 minutes, a treatment which is commonly employed to descale stainless steel. The scale was not removed by this pickling procedure.

A specimen of this same material with the as-hot-rolled scale was reheated to 1650° F. in air for one-half hour, removed from the furnace and a large part of one side promptly sprayed with a solution containing about 250 grams per liter (g./l.) of sodium carbonate and about 40 g./l. of sodium nitrate and then after a time lapse from sodium carbonate application of only a few seconds, the specimen was water quenched. Upon subsequent pickling in accordance with the two-step process outlined above, the sprayed portion of the scale cleaned up readily, while the scale on the unsprayed portion remained intact.

Descaling of the same alloy as that described in Example I was successfully accomplished at substantially lower reaction temperatures as set forth in the following Example II.

EXAMPLE II

Hot rolled strip samples of Alloy 1 having scale on the surface thereof as described in Example I were heated to a temperature of 600° F. and then were sprayed with a solution containing about 225 grams of Na_2CO_3 and 37.5 grams of $NaNO_3$ per liter of water at a pressure of 60 p.s.i. using a nozzle capable of delivering 0.12 gal./min. at that pressure while maintaining a relative movement between strip samples and spray of 60 feet per minute. The coating obtained was firmly adherent to the surface of the samples. The samples were reheated to about 1000° F. in air for a period of either 15 minutes or 30 minutes to obtain the reaction between the coating and the scale. Following the reaction the samples were pickled for either one minute or 5 minutes in a 10% (by volume) HNO_3 plus 4% by volume) HF bath. Very clean surfaces resulted from this treatment.

At both higher (1100° F.) and lower (900° F.) reheat temperature, but with the other conditions unchanged, results were not as satisfactory. Coating solutions containing 225 grams of Na_2CO_3 with 75 grams or 12.5 grams of $NaNO_3$ per liter of water were also tried with less uniformly satisfactory results, and in this case a pickling time of 5 minutes was required to produce clean surfaces.

EXAMPLE III

Alloy strip samples having a heavy scale thereon developed during hot-rolling and annealing had the following composition:

Cr	25.69
Ni	6.78
C	.059
Mn	0.44
P	0.016
S	0.013
O	0.45
Ti	0.38
Al	0.07
N	0.006
Fe	Bal.

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The scaled samples were heated to 600° F. (preheating) and then sprayed with a solution containing 250 grams of Na_2CO_3 and 40 grams of NaNO_3 per liter of water. An atomizing nozzle was employed in the spraying operation at its rated capacity of 0.12 gallon per minute at 60 p.s.i. The relative rate of travel between the nozzle and the strip sample was 60 feet per minute. The spraying operation was repeated. A relatively uniform and continuous coating of sodium carbonate having thereby been established on the surface of the strip, the strip samples were then reheated to either 1000° F. or 1100° F. for 15 minutes to obtain the reaction between the coating and the scale. The samples were then water quenched to remove the reaction product. Since some unreacted scale remained on the strip samples, the steps of preheating, applying the coating, reheating and quenching were repeated as described above. Thereafter, the samples were immersed in an acid pickling bath composed of 10% (by volume) HNO_3 and 4% (by volume) HF at from about 50° C. to about 60° C. for 5 minutes. The scale removal obtained was excellent.

EXAMPLE IV

Samples of hot-rolled sheet with a tenacious scale thereon had the following composition:

Cr	25.3
Ni	6.85
C	0.04
Mn	0.42
Ti	0.09
S	0.008
P	0.011
Fe	Bal.

The samples were preheated to 500° F. and then sprayed with a solution containing 250 grams of Na_2CO_3 per liter of water using the spray nozzle and relative rate of travel as described in Example III. The coated samples were reheated at 1600° F. for 15 minutes and then water quenched whereby the reaction products were substantially entirely removed. After quenching, the samples were immersed in an acid pickling bath containing 10% (by volume) HNO_3 and 4% (by volume) HF at a temperature from about 50° C. to about 60° C. for one minute. Good cleaning resulted from this treatment.

The descaling process of the invention has been applied to other high-chromium alloys which develop tenacious scales during processing and the nominal compositions of three such alloys are set forth in the following Table I in weight percent.

TABLE I

Element	Alloy		
	2	3	4
Nickel	52.5	42	61
Chromium	19	21.5	21.5
Iron	18.5	30	2.5
Molybdenum	3.05	3	9
Columbium (+ Ta)	5.13	*N.A.	3.65
Carbon	0.04	0.03	0.05
Copper	0.51	2.25	*N.A.
Aluminum	0.5	0.1	0.2
Silicon	0.18	0.25	0.25
Titanium	0.9	0.9	0.2
Manganese	0.18	0.5	0.25
Sulfur	0.008	0.015	0.008

*N.A. = Not added.

EXAMPLE V

Strip samples of Alloys 2 and 3 of Table I which had been hot-rolled and, in the case of Alloy 2, car-bottom annealed, had a heavy scale on their surfaces. The samples were heated to 600° F. and then sprayed under 60 p.s.i. pressure, using the atomizing nozzle described in Example III with a solution containing 250 grams of Na_2CO_3 per liter of water. The relative rate of travel between nozzle and strip in the coating procedure was 60 feet per minute. A coating of sodium carbonate having thus been established on the surface of the strip samples, the samples

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were then reheated to obtain the reaction between the coating and the scale; selected samples being heated for 15 minutes to 1000° F., 1200° F., 1300° F., and 1400° F. Following this treatment the samples were quenched in water and then pickled in a 10% (by volume) HNO_3 plus 4% (by volume) HF solution for 5 minutes at about 50° C. to about 60° C. Some slight cleaning effect was observed on the samples heated to the lower reheat temperatures for the reaction; i.e., 1000° F., but the cleaning effect improved at the higher reaction temperatures, e.g., excellent scale removal was realized at a reaction temperature of 1400° F. and the samples thus treated were scale-free after pickling.

EXAMPLE VI

Alloys 2 and 3 were obtained in the same condition as described in Example V, and Alloy 4 was in the hot-rolled and car-bottom annealed condition. All samples were well scaled. The scaled samples were preheated to 600° F. and were sprayed with a solution containing 250 grams of Na_2CO_3 and 40 grams of NaNO_3 per liter of water using the spray nozzle previously described in Example III. Reheating to 1000° F. or 1100° F. for 15 minutes was carried out to obtain the reaction between the coating and the scale. The pre-heating, spraying and reheating steps, as just described, were repeated. The samples were then immersed in an acid pickling bath containing 10% (by volume) HNO_3 and 4% (by volume) HF at about 50° C. to about 60° C. for 5 minutes. Excellent scale removal was observed. Control specimens, which were sprayed with water alone, were otherwise treated as described above. The scale on these samples was essentially intact after pickling.

It was found in carrying out the process in this example, that the sodium nitrate addition improved descaling at the relatively low reheat temperatures employed, i.e., 1000° F. and 1100° F. The addition of sodium nitrate is not helpful at higher reheat temperatures because it decomposes. It was also found that Alloy 4 did not descale at temperatures of 1000° F. or above without the nitrate addition, probably due to its higher molybdenum content, which is responsible for excessive scaling of this alloy during the reheating operation.

With respect to suitable acid pickling solutions, in addition to those already described, it has been found that a solution containing about 8% to about 12%, by volume, of sulfuric acid and from about 3% to about 10%, e.g., about 5%, by weight, of ferric sulfate is a satisfactory acid pickling solution.

It should be understood that in the reaction upon which this invention is based, there are phenomena involved which work at cross purposes. Thus, in the desired reaction it is important to establish oxidizing conditions to oxidize the chromium to the Cr^{+6} form which is soluble. Of course, the oxidizing conditions also tend to produce additional scale on the alloy member. For each alloy, then, adjustment of the conditions (in particular, time and temperature) will be necessary in order to assure that those processes favoring scale removal predominate over the processes favoring additional scaling.

The descaling process of the invention can readily be incorporated in continuous lines for annealing strip or sheet in which, conveniently, the strip or sheet moves through a continuous annealing unit arranged in tandem with a descaling installation (e.g., an acid pickling bath). A quenching stage is often provided between the annealing unit and the descaling operation. In a continuous line of this type, introduction of the process of the invention requires only the insertion in the line of a preheat stage followed by a spray station for applying the coating to the strip positioned just before the annealing furnace. With this arrangement, the coating on the strip reacts with the scale as the strip is annealed and the reaction products are removed in the quenching operation which may follow. If no quenching stage is provided after annealing, it would be necessary to add a wash unit at this point. Another ad-

vantageous arrangement involves spraying the sodium carbonate solution on the metal strip as it emerges from the annealing furnace (at a temperature of up to 2000° F., or even higher for certain alloys), in which case, the sodium carbonate solution replaces the water ordinarily applied in the spray quenching of the annealed strip. It is evident that the sodium carbonate solution is largely thrown off at the higher temperatures by violent flash evaporation, but as the sheet cools, e.g., to 1700° F., a sodium carbonate coating forms on the strip and the desired reaction occurs. An oxidizer such as sodium nitrate may be added to the sodium carbonate solution to extend the reaction temperature range to lower temperatures. Following the reaction, the strip or sheet may be water rinsed, if desired, before acid pickling.

There has thus been described a process for removing scale from metal alloys which resist removal by conventional means. The raw materials used in the process are relatively inexpensive and the process lends itself to incorporation in the lines for treating alloy strip which are presently used in commercial operations.

Although the present invention has been described in conjunction with preferred embodiments, it is to be understood that modifications and variations may be resorted to without departing from the spirit and scope of the invention, as those skilled in the art will readily understand. Such modifications and variations are considered to be within the purview and scope of the invention and appended claims.

I claim:

1. A process for descaling high chromium alloy members containing at least 11% chromium, by weight, comprising contacting the scaled alloy members with an aqueous solution of sodium carbonate, evaporating water from said solution and maintaining the said members in contact with the residual sodium carbonate within the range of about 1000° F. to about 1400° F. in an oxidizing environment to obtain a reaction involving the sodium carbonate and the scale and thereafter removing the reaction products and the remaining scale from the alloy members.

2. The process of claim 1 wherein the alloy members contain at least about 20% chromium and the reaction is carried out in air.

3. The process of claim 1 wherein contact between the scaled alloy members and the sodium carbonate is achieved

by first applying an aqueous solution of sodium carbonate to the alloy members when the members are at a temperature in the range from 300° F. to 1500° F. thereby forming an essentially continuous and relatively adherent coating of residual sodium carbonate on the said alloy members.

4. The process of claim 1 wherein the reaction products are removed by washing in water and the residual scale is removed by pickling in an acid solution.

5. The process of descaling hot-worked high chromium metal strip containing about 11% to about 30% chromium, by weight, comprising preheating the metal strip to a temperature in the range from about 500° F. to about 700° F., spraying a solution of at least about 50 grams per liter of sodium carbonate on the hot metal strip to produce a coating of sodium carbonate, reheating the coated strip in air to a temperature in the range from about 1000° F. to about 1400° F. to produce a reaction between the sodium carbonate, the scale and the oxygen of the air, washing the strip surface with water to remove the water-soluble products of the reaction and thereafter acid pickling the strip to remove the scale residue.

6. The process of claim 5 wherein the solution of sodium carbonate contains from about 10 g./l. to about 40 g./l. of sodium nitrate to aid in establishing an oxidizing environment for the reaction and the reaction is carried out at a temperature from about 1000° F. to about 1200° F.

7. The process of claim 6 wherein the high chromium metal strip contains, by weight, about 26% chromium, about 6.5% nickel and the balance essentially iron.

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U.S. Cl. X.R.

134—3, 4, 15, 28, 29