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METHOD OF DESCALING NICKEL ALLOYS

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This invention relates to the descaling of nickel base alloys and particularly to a preliminary descaling treatment for nickel base alloys that form tightly adhering acid resistant complex oxide scales upon heat treatment.

In the production of nickel base metals that contain alloying elements, such as chromium, designed to impart corrosion resistance and high temperature properties, numerous difficulties are encountered in cleaning and removing oxide scale formed during hot working and heat treatment. When heat treated in an oxidizing atmosphere these alloys develop complex oxide films or scales that are immune to conventional chemical descaling methods. Conventional methods of descaling involve immersing the metal in various acid and caustic solutions that have generally been heated to enhance the chemical reactions that effect dissolution of the oxide film. However, complex scales presented by the high temperature high nickel content and nickel base alloys are left unaltered by conventional acid pickling. Methods are known of treating such complex oxide scales which involve contacting such scaled alloys with molten caustic salt baths and/or heated caustic salt solutions and in this manner effect a conversion of the complex oxide scale to a scale that may be effectively removed by subsequent immersion in acid solutions. However, such practice involves working at undesirably high temperatures with chemicals that create undesirable toxic conditions in the vicinity where it is being employed. Also, such methods are not effective in removing the particularly complex acid resistant adherent scale found in the high nickel alloys such as type 908.

Heretofore mechanical means had to be resorted to in order to descale the high nickel content heat resistant alloys such as type 908 in that prior art chemical descaling methods were found to be entirely unsatisfactory. Mechanical cleaning of metals and alloys is far more expensive, time consuming and inconvenient than chemical pickling or descaling.

It has now been found that by employing the method of the present invention nickel base and particularly high nickel content alloys may be given a predescaling treatment wherein their complex, acid resistant oxide scales are easily and effectively converted to a scale that is susceptible to acid pickling. The predescaling operation of the present invention may be accomplished at room temperature and in short periods of time.

It is therefore an object of the present invention to provide a method of converting complex oxide films or scales found on nickel base alloy to an oxide scale that may be removed with a simple acid treatment.

Another object of the present invention is to provide a method whereby the complex and tightly adhering oxide scales of nickel base and high nickel content alloys that may not be removed by ordinary chemical descaling methods may be removed chemically within practical periods of time and at reasonable operating temperatures.

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Other objects and advantageous features will be obvious from the following description.

In general, the present invention relates to the pretreatment of nickel base and high nickel content alloys to remote complex oxide films and scales therefrom and involves immersing such scaled alloys in an aqueous solution that contains from about 5% to 30% of glacial acetic acid, from about 1% to 30% of 52% hydrofluoric acid and that contains from about .1% to saturation of dissolved titanium. In the preferred treatment the nickel base or high nickel content alloy is lime coated prior to heat treatment and then immersed in a bath that contains from 5% to 15% glacial acetic acid, 3% to 15% of 52% hydrofluoric acid and .1% to 2% by weight, titanium for a time of from about 30 seconds to 30 minutes at a temperature of from room temperature to about 150° F.

The method of the present invention is particularly advantageous when employed to remove complex oxide scales of the high nickel content heat resistant materials that contain 70% or greater nickel. During manufacture such alloys must be frequently hot worked and annealed. To date no known chemical treatment has been developed which satisfactorily removes the oxide scale. However, the method of the present invention provides such a method.

In accordance with the present invention high nickel containing alloys are effectively descaled by first immersing the scaled alloy in an aqueous bath containing acetic acid, hydrofluoric acid and some titanium metal, at substantially room temperature, and subsequently descaling in a nitric acid bath.

The strength of the acids in the aqueous solutions is given by volume in that such chemicals are conveniently purchased in liquid form and may be conveniently prepared by volumetric measurements. Acetic acid is commercially available as glacial acetic acid which is approximately 99% pure and possesses a specific gravity of about 1.05%. Thus, the effective weight of acetic acid in the bath may be said to be approximately from 5% to 30% as well as about 5% to 30% by volume of glacial acetic acid. The hydrofluoric acid is commercially available as 52%, by weight, acid. Actually, however, such acid varies from 48% to 52%; 50% hydrofluoric acid has a specific gravity of 1.155%. Thus, the weight of hydrofluoric acid employed may be said to be in the range of from about 1/2 of 1% to approximately 17%. Although aqueous solutions falling anywhere within the above-specified ranges may be effectively employed in altering the complex oxide scale that occurs on nickel base and high nickel content alloys, the extremes of the given ranges do not offer the preferred treatment from the standpoint of time and temperature needed to effect subsequent complete removal of scale from the high nickel content alloys (70% or greater nickel). It has been found that in treating the oxidation resistant nickel alloys and particularly the high nickel alloys significantly low temperatures may be effectively employed when the solutions employed contain from 5% to 15% of glacial acetic acid (about 5% to 15% by weight acetic acid), from 3% to 15% of 52% hydrofluoric acid (about 1.7 to 8.7 weight percent) and from 0.1% to 2%, by weight, of titanium. In treating the high nickel content alloys it has been found that baths containing less than 1% of 52% hydrofluoric acid or more than 30% of 52% hydrofluoric acid are not sufficiently active or are too active in converting the complex scale to be used effectively within a practical time and temperature range. If such a bath contains less than 5% acetic acid there is an adverse heat generation effect and a concentration in

preferred

excluded

excess of 30% acetic acid inhibits the action of the hydrofluoric acid. The presence of from 0.1% to 2%, by weight, of titanium is preferred in that a bath containing less than 0.1% titanium does not effect complete scale removal. The acetic-hydrofluoric solutions are substantially saturated with titanium when they contain approximately 2%.

It is to be understood that the concentration of chemicals in the bath employed in the method of the present invention may be supplied from a variety of chemical sources, the use of glacial acetic acid and 52% hydrofluoric acid being given only as an illustration of a convenient method of preparing such a solution. For example, the acetic acid need not be glacial acetic but may be of a cheaper grade of commercially available acid and the hydrofluoric acid need not be from a 52% source.

The necessary presence of titanium dissolved in the solution particularly where treating high nickel alloys is not fully understood. The titanium may be acting as a catalyst in the chemical reaction that converts the complex oxide scale to one which may be pickled, or the titanium may, in some manner, enter into the chemical reaction that effects such a conversion. At any rate, titanium may be present in a wide range of concentration of from a trace amount to saturation. It has been found that after a certain amount of titanium metal is dissolved in the bath there is a precipitation which appears to correlate with additions of more titanium. Where this precipitation takes place additions of more titanium are ineffective or serve no purpose and therefore this concentration is considered to be saturation for purposes of the present invention. Satisfactory results may be obtained by employing from about 1 gram per liter to a concentration of about 20 grams per liter when treating high nickel content alloys.

Titanium may be added to the bath in any form that will supply the titanium ion to the solution. In other words, titanium compounds that will dissolve in the bath will be satisfactory. A simple and satisfactory method of adding titanium to the solution is to introduce the desired quantity of titanium metal into the solution and permit it to be dissolved.

The temperature at which predescaling is carried out in the bath of the present invention is of particular significance in that it may advantageously be room temperature. When the optimum bath concentrations are employed, the hazardous operating conditions created by working at high temperatures with strong chemicals are eliminated. The temperature may be raised to facilitate conversion of the complex oxide films and reduce the time necessary to effect such conversion; however, it has not been found necessary to exceed about 150° F. in obtaining quick and efficient conversion of the high nickel content alloys. The chemical reaction which takes place in converting the complex oxide scale to a removable scale does not materially affect the temperature of the bath being employed. Thus, close temperature control of such a predescaling bath is not necessary.

The time required to effect scale conversion while immersing high nickel alloys in the bath of the present invention is not critical in that the bath temperature or strength of solution may be easily adjusted to alter conversion time whenever desired. However, practical considerations of production dictate that the time period be maintained below about 30 minutes, preferably within the range of from about ½ to 30 minutes.

In the treatment of metals and alloys that form complex oxide scales that must be altered before acid pickling it has been found advantageous in some instances to provide the metal with a coating prior to heat treatment. For example where nickel base and high nickel content alloys are predescaled in molten caustic baths it has been found to be highly advantageous to provide the metal with a lime coating prior to heat treatment. In fact, for the high nickel content alloys chemical descaling has been

comparatively unsuccessful when this practice was not employed. Sheets of such alloys are passed through an aqueous slurry of hydrated lime prior to heat treatment. The strength of the aqueous solution is not critical in that the sheets may be passed more slowly through the weaker solutions to acquire a heavier coating and vice versa. The most important factor involved is that a continuous lime coating be obtained. Such a coating so alters the resulting complex scale that it may be further treated for removal.

The treatment of the present invention is also enhanced in value by lime coatings prior to heat treatment, particularly where high nickel alloys, such as type 908, are being descaled. The lime employed need not be pure CaO or Ca(OH)₂ but may contain impurities; however, such material should be predominantly composed of CaO or Ca(OH)₂. The weight of application need be only such weight as will provide a continuous coat.

It is unlikely that such a coating could be applied at a weight of less than .005 ounce per square foot and obtain a continuous coating or that more than 1.5 ounces per square foot could be deposited from an aqueous solution.

When descaling high nickel content alloys while employing the method of the present invention the second acid dip, wherein the converted oxide scale is removed, is preferably an aqueous nitric acid solution. It has been found that the presence of hydrofluoric acid in this solution is detrimental to the scale removal. The strength of nitric acid is not in itself critical and the scale may be effectively removed by employing concentrations from about 1% to concentrated nitric acid (about 70% by weight). However, practical considerations dictate generally that from about 10% to 40%, by volume, of 70%, by weight, nitric acid should be employed. Thus the effective weight percent of nitric acid employed is approximately 9% to 34%.

The following specific examples are given to illustrate the method of the present invention and in no way limit the invention to the exact procedures set forth.

Samples of type 908 alloy sheet were tested that exhibited complex oxide scale resulting from a 1700° F. anneal. Some of the samples had been lime coated prior to heat treatment by being passed through an aqueous suspension of from about 30% to 35% hydrated calcium lime. Samples of similarly scaled Inconel (a product of the International Nickel Company of New York, New York) that had not been lime coated prior to heat treatment were also tested. These alloys possess the following approximate analyses:

Type 908 alloy:	Percent	Inconel	Percent
Ni -----	75 to 77	Ni -----	78
Cr -----	1.25 to 1.50	Cr -----	15
Cu -----	4.00 to 5.00	Fe -----	6
Mn -----	.75 to .100	Impurities -----	1
S -----	.025 max.		
Ph -----	.025 max.		
C -----	.05 max.		
Si -----	.5 max.		
Fe -----	Balance		

Samples of the type 908 that had not been lime coated prior to heat treatment were predescaled by immersion in baths of 10% glacial acetic acid, 5% of 52% hydrofluoric acid and the balance water. The titanium content was varied from 1 gram per liter to 15 grams per liter. The temperature was varied from room temperature to 150° F. Time of immersion varied from 30 minutes to several hours. The samples were subsequently pickled in aqueous nitric acid (30% of 70% nitric acid) solution. Descaling was approximately 90% complete.

Samples of the type 908 that had been lime coated prior to heat treatment and Inconel that had not been lime coated were descaled by immersion in various

strength aqueous acetic-hydrofluoric acid and titanium solutions plus nitric acid pickle. Results were as follows:

Descaling performance of various acetic acid-hydrofluoric acid baths on hot rolled annealed 908 and Inconel

Bath Concentration ¹		Percent Ti needed for Scale Conversion ²	Temp., °F.	908 and Inconel Imm. Time, min.	Scale Conversion for Removal ³	
Acetic Acid, percent	Hydrofluoric Acid, percent				Lime Coated 908	Inconel
10.....	15	.8-2 max.	85	30	Poor.....	Fair.
10.....	10	.6-2 max.	85	30	do.....	Do.
10.....	10	.6-2 max.	150	30	Fair.....	Good.
10.....	5	.6-2 max.	85	30	Fair to good.....	Do.
10.....	5	.6-2 max.	125	15	Good.....	Do.
10.....	5	.6-2 max.	150	15	do.....	Do.
30.....	30	.2.....	85	15	Fair.....	

¹ Percent by volume of glacial acetic acid and 52% by weight hydrofluoric acid.

² Baths having no dissolved titanium exhibited, no scale conversion properties.

³ To remove oxide scale converted in acetic-hydrofluoric, all samples were immersed for 5 to 7 minutes in 30% nitric acid at 130° F to 140° F.

Samples of Inconel were also satisfactorily descaled in 10% glacial acetic acid, 5% of 52% hydrofluoric acid in water with titanium contents as low as .1% at room temperature in times of 15 and 30 minutes.

We claim:

1. The method of treating a scaled metal article formed from a nickel base alloy which comprises, contacting the surface of said article with an aqueous bath that contains from about 5% to about 30%, by weight, acetic acid, about .5% to 17%, by weight, hydrofluoric acid and about 0.1% to 2% titanium.

2. The method of descaling a metal article formed from a nickel base alloy which comprises immersing said article in an aqueous bath that contains about 5% to about 30%, by weight, acetic acid, about .5% to 17%, by weight, hydrofluoric acid and from about 0.1% to saturation of titanium for a period of not more than 30 minutes while maintaining the temperature of said bath at from room temperature to 150° F. withdrawing said article from said bath and immersing said article in a second aqueous bath that contains from about 1% to about 70%, by weight, nitric acid to remove the scale therefrom.

3. The method of descaling a metal article formed from a nickel base alloy which comprises immersing said article in an aqueous bath that contains about 5% to about 30%, by weight, acetic acid, about .5% to 17%, by weight, hydrofluoric acid and from about 1 to 20 grams per liter of titanium for a period of from about 30 seconds to 30 minutes while maintaining the temperature of said bath at from room temperature to 150° F., withdrawing said article from said bath and immersing said article in a second aqueous bath that contains from about 1% to about 70%, by weight, nitric acid to remove the scale therefrom.

4. The method of descaling a nickel base alloy which comprises immersing said alloy in an aqueous bath that contains about 5% to 30%, by weight, acetic acid, about .5% to 17%, by weight, hydrofluoric acid and from about 1 to 20 grams per liter of titanium for a period of not more than 30 minutes while maintaining the temperature of said bath at from room temperature to 150° F., withdrawing said alloy from said bath and immersing said article in a second aqueous bath that contains from about 1% to 70%, by weight, nitric acid to remove the scale from the surface of said alloy, withdrawing said alloy from said second bath and rinsing with water.

5. The method of treating a nickel base alloy which comprises immersing said alloy in an aqueous bath that contains about 10% glacial acetic acid, 5% of 52% hydrofluoric acid and 5 grams per liter of titanium for a period of about 15 minutes.

6. The method of descaling a nickel base alloy which comprises immersing said alloy in an aqueous bath that contains from about 5% to 30%, by weight, acetic acid, .5% to 17%, by weight, hydrofluoric acid and from 1 to 20 grams per liter of titanium for a period of from 30 seconds to 30 minutes at room temperature, withdrawing said alloy and immersing said alloy in a second aqueous bath that contains from about 10% to 40%, by volume, of concentrated nitric acid to remove the scale therefrom, withdrawing said alloy from said second bath and rinsing.

7. The method of treating nickel base alloys that form acid resistant complex oxide scale upon heat treatment to remove said scale which comprises, coating said alloys with lime prior to said heat treatment and subsequent to said heat treatment immersing said alloys in an aqueous bath that contains from about 5% to 30%, by weight, acetic acid, about ½% to 17%, by weight, hydrofluoric acid and about 0.1% to saturation of titanium, withdrawing said alloys from said bath and immersing said alloys in an aqueous nitric acid solution to remove said scale.

8. The method of treating nickel base alloys that form acid resistant complex oxide scale upon heat treatment to remove said scale which comprises, coating said alloys with lime prior to said heat treatment and subsequent to said heat treatment immersing said alloys in an aqueous bath that contains from about 5% to 15%, by weight, acetic acid, about 1.7% to 8.7%, by weight, hydrofluoric acid and .1% to 2%, by weight, titanium, withdrawing said alloys from said bath and immersing said alloys in an aqueous nitric acid solution to remove said scale.

9. The method of treating nickel base alloys that form acid resistant complex oxide scale upon heat treatment to remove said scale which comprises, immersing said alloys in an aqueous slurry of hydrated lime and withdrawing said alloys so as to leave an even coating of said lime on said alloy prior to said heat treatment and subsequent to said heat treatment immersing said alloy in an aqueous bath that contains from about 5% to 30%, by weight, acetic acid, about ½% to 17%, by weight, hydrofluoric acid and about 0.1% to saturation of titanium, withdrawing said alloys from said bath and immersing said alloys in an aqueous nitric acid solution to remove said scale.

10. The method of treating nickel base alloys that form acid resistant complex oxide scale upon heat treatment to remove said scale which comprises, immersing said alloys in an aqueous slurry of hydrated lime and withdrawing said alloys so as to leave an even coating of said lime on said alloy prior to said heat treatment and subsequent to said heat treatment immersing said alloy in an aqueous bath that contains from about 5% to 15%, by weight, acetic acid, about 1.7% to 8.7% hydrofluoric acid and .1% to 2%, by weight, titanium, withdrawing said alloys from said bath and immersing said alloys in an aqueous nitric acid solution to remove said scale.

11. The method of treating a nickel base alloy that forms an acid resistant complex oxide scale upon heat treatment which comprises, immersing said alloy in an aqueous slurry of hydrated lime and withdrawing said alloy so as to leave a substantially uniform coating of said lime on said alloy prior to said heat treatment and subsequent to said heat treatment immersing said alloy in an aqueous bath that contains from about 5% to 15%, by weight, acetic acid, about 1.7% to 8.7%, by weight, hydrofluoric acid and about .1% to 2%, by weight, titanium, the temperature of said bath being from about room temperature to 150° F., after a time of from about 30 seconds to 30 minutes withdrawing said alloy and immersing said alloy in an aqueous nitric acid solution to remove said scale.

12. The method of treating a high nickel content

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alloy that forms an acid resistant complex oxide scale upon heat treatment which comprises, immersing said alloy in an aqueous slurry of hydrated lime and withdrawing said alloy so as to leave a substantially uniform coating of said lime on said alloy prior to said heat treatment and subsequent to said heat treatment immersing said alloy in an aqueous bath that contains from about 5% to 15%, by weight, acetic acid, about 1.7% to 8.7%, by weight, hydrofluoric acid and about .1% to 2% titanium, the temperature of said bath being from 10

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about room temperature to 150° F., after a time of from about 30 seconds to 30 minutes withdrawing said alloy from said bath and immersing said alloy in an aqueous nitric acid solution to remove said scale.

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