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1

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PROCESS FOR ANNEALING AND CLEANING OXIDIZED METAL IN A SALT BATH

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The present invention relates to the descaling of oxidized or scaled metals in fused salt baths and, more particularly, to a method for simultaneously annealing and descaling in a stable, fused salt bath of special composition oxidized metal articles made of heat- and/or corrosion-resistant alloys having relatively high recrystallization and annealing temperatures and to a salt bath suitable for use in said method.

It is well known that when heat- and/or corrosion-resisting alloys such as the alloys of nickel, iron and cobalt with each other and with chromium, copper, molybdenum, manganese, silicon, carbon, vanadium, tungsten, etc., and including stainless steels, nickel-chromium alloys, nickel-chromium-iron alloys, nickel-copper alloys, etc., are subjected to heating operations, including annealing, etc., in atmospheres oxidizing thereto during the production of mill products or articles or the fabrication of other articles from such alloys, an adherent oxide scale having a highly refractory nature is formed. It has been recognized that this adherent oxide scale usually must be removed from these alloys to produce an acceptable mill product such as sheet, strip, tubing, rods, bars, etc., or to produce other acceptable articles fabricated from such products. The production of these heat- and/or corrosion-resisting metals, including alloys, frequently requires that the metal or alloy be annealed and that it be descaled or pickled at various stages in the production scheme so that the required lowered hardness and/or a clean metal surface will be provided for subsequent manufacturing operations.

It has also been recognized in the art that the problem of pickling alloyed metallic articles which are resistant to heat and/or corrosion is a much more difficult and complex problem than that involved in pickling alloys such as mild steel and the like. An important factor which contributes to the greatly increased difficulty in pickling heat- and/or corrosion-resistant alloy articles is the fact that the oxides formed upon such alloys during heating, etc., are very tightly adherent to the parent or basis metal and are highly refractory in nature. The prior practice largely employed in pickling these alloys has been to immerse the oxidized articles in acid solutions of various types. This acid pickling process involved essentially the chemical dissolution of the refractory oxide scale in the acid and, accordingly, was slow and uncertain. This prior art practice has met only with indifferent success inasmuch as the acid pickling process has been found frequently to produce undesirable pitting, etching, etc., on the metal treated, to produce unduly high metal losses, etc.

The problem of removing scale at various stages in the production of the heat- and corrosion-resistant alloys has been a much more pressing problem than in the case of carbon steels, low-alloyed steels, etc. The tightly adherent oxide formed upon the heat- and corrosion-resistant alloys, if not removed, was worked into the surface of the metal during such mill operations as hot rolling, forging, etc., with the result that the surface quality of the resultant

2

products was poor and extensive overhauling as by grinding, chipping, milling etc., was required to provide good surface quality on subsequent working operations. After hot working operations, it is usually necessary to anneal and pickle the hot worked articles to reduce the hardness of the articles and to provide thereon a clean surface free of abrasive oxides which would produce excessive wear upon, and otherwise damage, rolls, dies, etc., used in subsequently cold working the metal. During cold working, anneals are frequently required to reduce the hardness of the cold worked metal and, if annealing is conducted in oxidizing atmospheres, the refractory oxides produced must again be removed.

It has been proposed to employ molten salt baths for the purpose of heating steels and the like as it was postulated that relatively high heating rates and comparative freedom from oxidation during the heating operation would be attained by this method. Salt bath heating processes for hardening steels, etc., are now well established. However, the salt bath compositions employed in heating carbon steels, tool steels, etc., prior to hardening are, in general, unsuitable for the purpose of removing oxides, scale, etc., from the surface of the metal treated and simultaneously annealing heat- or corrosion-resistant metals and alloys as these baths are either ineffective in removing scale or require a greatly excessive time at temperature to provide descaling with the result that excessive grain growth and other deleterious effects are encountered. Examples of these types of baths are those composed of mixtures of potassium chloride and sodium chloride, baths composed of sodium carbonate, etc. Other types of salt baths have been proposed for the specific purpose of descaling oxidized or scale-coated heat- and/or oxidation-resistant alloys in order to minimize or eliminate the acid pickling step in cleaning these alloys. However, these prior art baths specifically designed for the purpose of descaling oxidized metals cannot be operated at temperatures above about 800° F. to about 1100° F., and it is not commercially possible to anneal the heat- and/or corrosion-resistant alloys at these low temperatures. Examples of these latter types of baths are those composed of caustic soda to which an oxidizing agent such as sodium chlorate, sodium nitrate, etc., is added; baths composed of caustic soda to which hydrogen and metallic sodium are added; etc.

Although many attempts have been made to provide a salt bath and process for simultaneously annealing and descaling oxidized heat- and/or corrosion-resistant alloys, none, as far as we are aware, was entirely successful when carried into practice commercially on an industrial scale.

It has now been discovered that heat- and/or corrosion-resistant alloys can be annealed and can be descaled in a single operation employing a fused salt bath of special composition.

It is an object of the present invention to provide a special process for simultaneously annealing and descaling oxidized heat- and/or corrosion-resistant alloys.

Another object of the invention is to provide a special salt bath composition adapted for the purpose of annealing and descaling heat- and/or corrosion-resistant alloys.

Another object of the invention is to provide a process for annealing and pickling heat- and/or corrosion-resistant alloys wherein substantially no loss of basis metal is encountered.

The invention also contemplates providing a process for descaling and pickling oxidized heat- and/or corrosion-resistant metal articles wherein substantially no pitting or etching of the metal articles is encountered.

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

Generally speaking, the present invention contemplates a process for simultaneously annealing and descaling oxidized metal articles made from heat- and corrosion-resistant alloys having the property of forming adherent refractory oxides and being resistant to alkalis which comprises immersing the articles in an alkaline fused salt bath containing about 20% to about 80% sodium fluoride with the balance substantially sodium carbonate, for time periods of at least about 2 minutes, e. g., about 3 to about 10 or 15 minutes, and at temperatures of about 1500° to about 2000° F., preferably about 1600° to about 1900° F., and thereafter bringing the descaled metals to atmospheric temperatures. The aforedescribed process removes the oxide scale adhering to the metal articles as a result of prior processing steps conducted at elevated temperatures and in atmospheres oxidizing to one or more constituents thereof, such as rolling, forging, extruding, hot pressing, etc. A feature of the invention resides in the fact that although this oxide scale is effectively removed, the parent or basis metal treated suffers no substantial attack. Another feature of the invention is that it can be employed to produce simultaneous annealing by carrying out the heating for the required annealing period, e. g., at least about 2 minutes and up to about 10 or 15 minutes at temperature. Of course, annealing and/or descaling can be carried out in the alkaline salt bath for longer periods of time (e. g., one-half hour or one hour or more) than about 10 or 15 minutes at temperature, but in most cases no good purpose is accomplished thereby and undesirable grain growth may be encountered in the metal treated. A particular bath which has been employed with excellent results in the treatment of many different types of heat- or corrosion-resistant alloys is one containing about 50% sodium fluoride and about 50% sodium carbonate by weight. This bath may effectively be employed to anneal and descale oxidized metal articles over a wide range of temperature without producing excessive fuming or undesirable attack on the basis metal. The operating temperature for this bath is preferably about 1750° F., at which temperature it has the further positive advantage that when the heated metal articles are removed from the salt bath after descaling and annealing, an adherent salt coating quickly forms therein and this salt coating prevents or decreases reoxidation of the annealed, descaled articles during cooling of the articles after their removal from the salt bath. Dragout losses from this bath at about 1750° F. are not excessive. A feature of the invention is that any salt remaining on the annealed, descaled articles treated in accordance with the invention is readily removable at non-oxidizing temperatures, e. g., approximately room temperature, by water washing or by immersing the salt-coated articles in a bath of a dilute mineral acid such as sulfuric acid or hydrochloric acid.

After oxidized metal articles are descaled and/or annealed in the special fused salt baths provided by the invention, the articles desirably may be quenched in water or other suitable quenching agents to provide rapid cooling. It is believed that a quench after the anneal further assists in removing any remaining adhering scale due to the resulting thermal shock. In addition, a quench insures that any age-hardening agents of precipitation-hardening alloys which have been placed in solid solution in the alloy during the annealing treatment in accordance with the invention will be retained in solid solution for subsequent age-hardening heat treatments at lower temperatures.

When desired, an acid pickling operation in a solution of the type conventionally used in practice may be employed subsequent to the salt bath annealing and descaling operation in order to brighten the surface of the annealed, descaled metal.

The aforedescribed stable alkaline salt baths may contain, in addition to the aforementioned amounts of the essential ingredients sodium fluoride and sodium carbonate, small amounts of other materials such as the chlorides

and hydroxides of the alkali metals without appreciably affecting the novel characteristics of the salt bath composition. These materials tend to fume off from the bath when it is held at operating temperatures, and the aforesaid chlorides tend to produce a dark finish on certain alloys, e. g., nickel-copper alloys containing about 67% nickel and about 30% copper (such as are sold under the trade-mark "Monel") descaled and annealed in accordance with the invention. However, small amounts of these materials up to about 5% of the composition may be present in the bath, although the presence of these materials is not desirable and they preferably are avoided. Certain other more stable salts, such as barium chloride, may be present in the bath in amounts up to about 2% of the total composition. Certain other salts such as fluorspar (CaF_2), cryolite (Na_3AlF_6), etc., have a deleterious influence in the bath and should be avoided, although small amounts not exceeding about 2% of the composition may be tolerated. In addition, the stable alkaline salt baths provided by the invention should be devoid of sulfate salts and other sulfur-containing compounds, as these compounds deleteriously affect many alloys, e. g., nickel and nickel-base alloys.

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

EXAMPLE 1

An oxidized metal sheet, about 0.125 inch thick, in the hot rolled condition and made of an alloy containing about 30% copper, about 1% manganese and about 1.4% iron, with the balance essentially nickel (such as is sold under the trade-mark "Monel"), was immersed in a molten alkaline salt bath containing about 50% sodium fluoride and about 50% sodium carbonate. The bath temperature was about 1700° F. Before treatment, the oxidized sheet was covered with a dark brown oxide coating. The sheet was removed from the bath after an immersion of about 10 minutes, quenched in water and then dipped in a dilute sulfuric acid solution to remove adhering salt. The salt bath immersion removed substantially all the oxide scale which had been adhering to the sheet as a result of the hot rolling operation and reduced the hardness of the sheet from about 90 to about 64 on the Rockwell "B" scale. The sheet was then dipped for about ten minutes in an acid pickling solution containing about 95 grams per liter of sulfuric acid, about 65 grams per liter of sodium nitrate, about 110 grams per liter of sodium chloride and about 30 grams per liter cupric chloride. The sheet then exhibited a bright, smooth and clean surface very suitable for further processing, etc. The annealed, descaled and pickled sheet had a fine grain size of about 0.0014 inch.

EXAMPLE 2

An oxidized metal sheet, about 0.125 inch thick, in the hot rolled condition and made of an alloy containing about 14% chromium, about 6.5% iron, with the balance essentially nickel (such as is sold under the trade-mark "Inconel"), was immersed in a molten alkaline salt bath having the composition given in Example 1. The bath temperature was about 1800° F. Before treatment, the oxidized sheet was covered with a tightly adherent oxide film. The sheet was removed from the bath after about ten minutes and was treated to remove adhering salt as in Example 1. It was then given a ten minute dip in the pickling solution set forth in Example 1. The foregoing treatment reduced the hardness of the sheet from 98 to 78 on the Rockwell "B" scale and produced a bright, smooth and clean surface. The final grain size of the annealed, descaled and pickled sheet was about 0.0010 inch.

EXAMPLE 3

An oxidized wrought nickel sheet containing about

99.4% nickel and having a thickness of about 0.114 inch was immersed for about 5 minutes at 1700° F. in an alkaline salt bath having the composition set forth in Example 1. The sheet was then removed from the bath and treated to remove adhering salt. After a short pickle in an acid pickling solution, the sheet had a bright appearance. The hardness of the sheet was reduced from about 84 to about 31 on the Rockwell "B" scale.

EXAMPLE 4

A heavily-oxidized type 304 stainless steel sheet having a thickness of about 0.031 inch was immersed in an alkaline salt bath having the composition set forth in Example 1 for about 5 minutes at about 1750° F. The thus-treated sheet was then dipped in a dilute sulfuric acid solution for about 2 minutes to remove adhering salt and immersed in a nitric acid-hydrofluoric acid pickling solution for about 3 minutes. The stainless steel sheet then had an excellent pickled surface.

EXAMPLE 5

A heavily-oxidized type 347 stainless steel sheet having a thickness of about 0.031 inch was treated as was the sheet in Example 4. This type 347 stainless steel sheet likewise had an excellent pickled surface after the annealing and descaling treatment.

EXAMPLE 6

A heavily-oxidized sheet of an alloy containing about 17% molybdenum, about 15% chromium, about 5% tungsten, with the balance substantially nickel, was immersed in an alkaline salt bath having the composition set forth in Example 1 for about 5 minutes at a temperature of about 1760° F. The sheet was then dipped in a dilute sulfuric acid solution for about 2 minutes to remove salt adhering thereto after the salt bath immersion and was immersed in a nitric acid-hydrofluoric acid pickling solution for about 3 minutes. The sheet then had an excellent pickled surface.

The present invention is particularly applicable to the treatment of high-nickel alloys, including commercial wrought nickel, nickel-chromium alloys, nickel-chromium-iron alloys, nickel-copper alloys, nickel-molybdenum alloys, nickel-iron alloys, etc., austenitic nickel-chromium stainless steels, etc. These alloys may also contain other elements such as cobalt, aluminum, titanium, silicon, columbium, zirconium, etc., which are commonly employed to influence the properties, including castability, soundness, malleability, heat or oxidation resistance, creep resistance, corrosion resistance, age hardenability, etc. The foregoing alloys are characterized by the formation of adherent refractory oxide coatings containing oxides from the group consisting of nickel oxide, cobalt oxide, chromium oxide and iron oxide upon heating to hot working or annealing temperatures in atmospheres oxidizing thereto, said oxides being removable only with difficulty when acid pickling methods are employed. Among the metals and alloys which may be treated in accordance with the invention are those containing up to about 22% chromium, up to about 17% or even about 32% molybdenum, up to about 70% copper, up to about 4% silicon, up to about 0.3% carbon, up to about 5% manganese, up to about 5.5% tungsten, up to about 2% vanadium, up to about 4.5% aluminum, up to about 3.5% titanium, with or without small amounts of elements such as columbium, zirconium, phosphorus, boron, calcium, magnesium, etc. The balance of the compositions is substantially metal from the iron group. Usually the alloy will contain at least 7% nickel. The foregoing alloys may also contain small amounts of impurities and deoxidizers. Illustrative compositions of alloys which may be annealed and descaled in accordance with the invention are set forth in Table 1.

Table 1

Alloy No.	Class	Percent Ni	Percent Cr	Percent Fe	Percent Cu	Percent Mo	Percent Others
1	Ni-Cr	80	20	------	------	------	------
2	Ni-Cr-Fe	79	14	6.5	------	------	------
3	Ni-Cr-Fe	60	15	25	------	------	------
4	Ni-Cu	67	------	1.4	30	------	------
5	Ni-Mo-Fe	58–60	15	------	------	17	3.5-5.5 W
6	Wrought Ni	99.4	------	------	------	------	------
7	Austenitic stainless steel.	8–12	17–20	Bal.	------	------	------

Other illustrative alloys which may be annealed and descaled in accordance with the invention include nickel-chromium-iron-aluminum and nickel-chromium-iron-titanium age-hardenable alloys; nickel-chromium-titanium and nickel-chromium-cobalt-titanium alloys such as are sold under the trade-mark "Nimonic"; nickel-aluminum-titanium-carbon alloys such as are sold under the trade-mark "Duranickel"; nickel-copper-aluminum-titanium alloys such as are sold under the trade-mark "K" Monel; nickel-copper-silicon alloys such as are sold under the trade-mark "S" Monel; etc. In general, the metals which are annealed and descaled in accordance with the invention will have practical annealing temperatures of at least about 1500° F., e. g., about 1600° F. to about 1900° F. or 1925° F., and the alkaline sodium carbonate-sodium fluoride bath provided by the invention is usually operated within this range.

The proportion of sodium fluoride in the bath can be varied somewhat depending upon the nature of the metal being treated. Thus, the amount of sodium fluoride in the bath desirably can be increased depending upon the operating temperature of the bath for descaling and annealing. Preferably, the bath provided by the invention has a melting point about 150° F. below the desired operating temperature to insure optimum operating conditions, including the formation of a protective salt coating about the work when it is removed from the bath and minimization of salt dragout. Accordingly, a bath containing about 30% sodium fluoride, balance sodium carbonate, preferably is operated at about 1550° F.; a bath containing about 50% sodium fluoride, balance sodium carbonate, preferably is operated at about 1750° F.; and a bath containing about 70% sodium fluoride, balance sodium carbonate, preferably is operated at about 1850° F.

Those skilled in the art will appreciate that the total time required to anneal a given metal article from a given high hardness level to a given low hardness level is much shorter when the article is heated in a fused salt medium than when it is heated in a gaseous medium, even when the two heating media are at the same temperature. Thus, the heating period in the alkaline fused salt bath provided by the invention will usually be comparatively short. The actual heating time and bath temperature employed for treating specific metal articles in the alkaline fused salt bath provided by the invention will depend upon a number of factors, including the composition of the metal being treated, the size of the article being treated, the initial hardness of the material treated, the final hardness desired, the final grain size desired, and other practical considerations which those skilled in the art will recognize. In general, the higher the recrystallization temperature for the particular metal, the higher is the bath temperature that should be employed Of course, as in other methods of annealing, prolonged exposure of metal articles to high temperature may not be desirable because excessive grain growth may be encountered. Although the time and temperature conditions required for carrying out the annealing operation will vary considerably depending upon the factors outlined hereinbefore, the alkaline fused salt bath provided by the invention effectively removes the scale from the oxidized alloys being annealed over these same ranges of time and temperature. This effective descaling action is provided without appreciable attack upon the underlying or basis metal. As indicated hereinbefore, the special fused salt bath composition provided by the invention is very stable and provides simultaneous annealing and descaling of oxidized metal articles over a wide range of temperature without producing appreciable amounts of fuming.

In normal operation, the molten alkaline salt bath compositions provided in accordance with the invention can be held in metal pots, e. g., nickel-chromium-iron alloy pots, etc., as no undue corrosion of such pots is produced by the alkaline fused salt bath compositions. In general, the process comprising the present invention can be carried out in conventional salt bath furnace equipment. For example, furnaces having either externally or internally heated salt containers can be used.

It has been found that the descaling nature of the bath tends after considerable use to result in a pick-up of metal in the bath due to the oxides dissolved from the work treated therein. This metal pick-up does not harmfully affect the operation of the bath and is compensated for in part by fresh salt additions made to the bath to make up dragout losses. Some sludging effects also may be encountered and this sludge desirably is removed from the bath as, for example, by conventional mechanical means.

The novel salt bath provided in accordance with the invention can be prepared by simply melting together the salts employed to produce the bath, while observing due precautions against moisture, etc., It is preferable to blend the dry materials comprising the descaling salt or compound before adding the materials to the descaling pot, both when making up fresh baths and when making additions to an operating bath.

The theoretical explanation of the new and improved results produced in annealing and descaling metals according to the process embodying the present invention is not fully understood. However, it is believed that the fused salt bath embodying the invention converts the oxides present on the metallic surface into compounds which are soluble in the bath and which are dissolved in the bath. Although the oxides are dissolved from the metal, the metal itself is not noticeably attacked, as has been pointed out hereinbefore.

The process embodying the present invention is applicable not only to wrought mill products which are oxidized and/or scaled by heating operations during the course of fabricating, etc., but may also be applied to castings or the like to remove from the surface thereof oxides, sand, etc., present on the surface of the castings after their removal from the molds in which they are made. Thus, many alloy compositions described hereinbefore but which are not commercially forgeable can be descaled in the cast condition by employing the process embodying the present invention.

It is to be emphasized that the properties of the fused salt baths employed in carrying out the present invention are unique and are dependent upon the particular essential ingredients required in formulating the baths, to wit, sodium fluoride and sodium carbonate. In particular, it has been found that other fluorides may not be substituted for sodium fluoride in the fused salt bath provided by the invention, as the results provided by the invention are not then obtained. For example, calcium fluoride, cryolite, etc., may not be employed as substitutes for sodium fluoride, as it has been found that these salts are inoperative for purposes of the present invention. Potassium fluoride is not an equivalent to sodium fluoride for purposes of the present invention, as it has been found that this salt fumes badly at operating temperatures and produces less desirable results than when sodium fluoride

is employed as contemplated by the invention. The aforementioned fuming encountered when potassium fluoride is employed constitutes a serious health hazard, requires increased amounts of make-up salt, and is expensive. Likewise, chlorides such as sodium chloride, calcium chloride, potassium chloride, etc., cannot be used in place of sodium fluoride to obtain the results obtained in carrying out the present invention, as baths made up employing such salts produce dark work which will not become bright in a subsequent acid dip as referred to hereinbefore, and are characterized by other defects and disadvantages.

The present invention may be employed for the purpose of descaling the aforedescribed oxidized heat- and corrosion-resistant metal articles at various stages in the production and/or fabrication thereof, and is applicable regardless of the thickness of the oxide scale or oxide coating on the articles at the time of treatment according to the invention. Thus, articles which have been subjected to operations such as hot rolling, etc., usually have a relatively thick oxide coating or scale which is usually of an adherent nature but which may have a tendency to crack or spall depending upon the thickness of the coating while articles which have been subjected only to operations such as annealing operations, etc., in an atmosphere oxidizing thereto usually have a relatively thin adherent oxide coating or scale.

As pointed out hereinbefore, the present invention is particularly applicable to the treatment of oxide-coated nickel and nickel-containing alloys to anneal these alloys and to remove therefrom adherent oxide scale which contains oxides from the group consisting of nickel oxide, cobalt oxide, chromium oxide and iron oxide. It can be said that the invention is applicable to alloys comprised predominantly of metal from the group nickel, iron and cobalt, particularly alloys which are relatively high in chromium content, e. g., those containing over about 8% chromium. Such high-chromium alloys include ferritic stainless irons, stainless steels, etc., which may or may not contain nickel. Even alloys comprised essentially of iron, such as low-alloyed or even un-alloyed steels, irons, etc., may also be treated in accordance with the invention. For purposes of the invention, cobalt is considered to be equivalent to nickel. Thus, the salt bath descaling and annealing process provided by the invention is applicable to many alkali-resistant metals and alloys having relatively high annealing and/or recrystallization temperatures, including cobalt-chromium-iron alloys, cobalt-chromium-molybdenum alloys, cobalt-chromium-nickel alloys, etc.

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.

We claim:

1. The process for annealing and cleaning an oxidized metal article made of a metal composition containing up to about 22% chromium, up to about 32% molybdenum, up to about 70% copper, up to about 75% iron, up to about 4% silicon, up to about 5% manganese, up to about 5.5% tungsten, up to about 2% vanadium, up to about 4.5% aluminum, up to about 3.5% titanium, and the balance essentially nickel, with the nickel content being at least about 7% of the metal composition, which comprises immersing the oxidized article in a salt bath comprising about 20% to 80% sodium fluoride with the balance essentially sodium carbonate for at least about 2 minutes at a temperature of about 1500 to 2000° F. to anneal the metal of said article and to dissolve the scale therefrom.

2. The process for annealing and cleaning an oxidized

wrought metal article made of a metal composition containing up to about 22% chromium, up to about 32% molybdenum, up to about 70% copper, up to about 75% iron, up to about 4% silicon, up to about 5% manganese, up to about 5.5% tungsten, up to about 2% vanadium, up to about 4.5% aluminum, up to about 3.5% titanium and the balance essentially nickel, with the nickel content being at least about 7% of the metal composition, which comprises immersing the oxidized article in a salt bath comprising about 50% sodium fluoride with the balance essentially sodium carbonate for at least about 2 minutes at a temperature of about 1750° F. to anneal the metal of said article and to dissolve the scale therefrom.

3. In the process for annealing and cleaning an oxidized metal article made of an alloy used for resistance to heat and to corrosion and characterized by a refractory oxide coating containing predominantly an oxide of a metal having an atomic number from 24 to 29, the improvement which comprises immersing the oxidized article in a salt bath comprising about 20% to 80% sodium fluoride, with the balance essentially sodium carbonate, for at least about two minutes at a temperature of about 1500° to 2000° F.

4. In the process for annealing and cleaning an oxidized metal article made of an alloy used for resistance to heat and to corrosion and characterized by a refractory oxide coating containing predominantly an oxide of a metal having an atomic number from 24 to 29, the improvement which comprises immersing the oxidized metal article in a salt bath comprising about 50% sodium fluoride, with the balance essentially sodium carbonate, for at least about two minutes at a temperature of about 1750° F.

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