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PROCESS OF REMOVING SURFACE OXIDE FILMS ON METAL

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This invention relates to an improved process for the cleaning, descaling and deoxidizing of metal surfaces, more particularly of alloys of the ferrous group, and especially of those usually referred to as stainless steel. In present practice these operations are usually carried out by immersing the metal in an aqueous solution of strong acids, which operate principally by attacking the metal itself and so bringing about a detachment of the surface scale or oxide. This is a continuation-in-part of our co-pending application Serial No. 538,536, filed June 2, 1944, now Patent No. 2,538,702, dated January 16, 1951.

The object of this invention is to provide a treating bath acting directly and preferentially on the scale or oxide itself.

Another object of this invention is to provide means for preliminarily affecting the character of the scale to make it more amenable to this and other scale removing operations.

According to this invention the oxide coating on the metal is substantially converted, by immersion in a bath of fused salts containing appropriate ingredients to bring about this conversion, so as to be soluble in the bath itself or more readily removed by subsequent treatment in suitable acids. Oxide films on many alloy steels of widely varying composition may be removed by treatment in baths of fused alkali metal hydroxides containing a minor proportion of oxidizing agents or which has been made oxidizing in character.

These baths favor further oxidation of some or all of the components of the oxide film to higher, more acid forms which will more readily react with the fused alkalies of the bath, so that upon removal from the bath any residual oxide film exists in a form which, possibly due to the removal of some of its original component oxides, and partly due to the changed form of the remaining compounds, is removed much more readily with acids.

In certain cases it is advantageous to give the material to be descaled a preliminary treatment in a weak inorganic acid solution applied for a short period of 2 to 5 minutes before immersion in the fused salt. It is thought that certain oxide components amenable to solution during this preliminary acid treatment may be removed, resulting in a degree of porosity of the film and facilitating penetration of the fused salts.

Another method by which the character of the scale may be preliminarily affected in order to make it more amenable to removal by various methods, is that of treating the metal surface at

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scale forming temperatures in the presence of sodium chloride applied to already scaled surfaces. This would consist of heating in the presence of sodium chloride when fused or in the vapor state. However, this method of modifying the character of the scale may be used coincidentally with the necessary scale forming operations themselves. For instance, annealing may be carried out in a sodium chloride atmosphere or the material coated with crystalline sodium chloride prior to annealing, hot rolling or other scale forming operation. The coating may be applied by heating and immersion of the material in a saturated sodium chloride solution which forms a continuous coating of crystalline sodium chloride on the surface immediately on removal.

Such a treatment so preconditions the scale that it is more easily removed by any of the existing descaling methods, including acid, or by fused sodium hydroxide alone followed by acid, or, under properly controlled conditions is capable of producing a scale which is so loosely bonded to the surfaces that it separates upon quenching from high temperatures.

In addition to the two essential types of active components previously listed, these baths, which are both basic and oxidizing, may contain proportions of salts which contribute little or nothing to their action, but which are added to act as inert vehicles to satisfy other criteria such as cost, melting point, etc.

The reaction compounds usually formed, when they are not soluble in the bath itself, may show one or more of the following characteristics:

1. They are decomposed by water or are soluble in water.

2. They are much more readily reacted upon by acids than the original oxide or oxides.

The oxidizing conditions of the fused bath can be produced in various ways. For example:

1. Free oxygen, air or ozone may be introduced into the fused bath.

It should be noted that this method results in effecting a modification of the scale in spite of the fact that the surfaces in being heated need not be in contact with the gases being introduced in order to be further oxidized. This is thought to be due possibly to the formation of an iron-oxygen couple in which the added oxygen becomes the cathode and the surfaces being treated the anode, where an external circuit is completed, but due also to physical or chemical retention of the added oxygen by the bath as evidenced in the continuation of the effect for a

considerable period after cessation of the oxygen supply.

2. Substances such as the oxides of chromium, sulphur, manganese, phosphorus, chlorine and boron alone or as compounds in combination with an alkali or an alkaline earth metal may be introduced into the fused sodium hydroxide bath to combine with free oxygen also introduced into the bath to form unstable oxidizing agents which are continuously regenerated by the introduced oxygen, proportions of such higher, unstable compounds (such as $NaClO_3$, $Na_2Cr_2O_7$, $NaMnO_4$, etc.) being transiently available to catalytically give up oxygen to the scale.

3. The oxide coated article may be connected as an anode in an electrolytic fused salt bath to produce oxygen on the oxide coated surface.

4. Sodium peroxide may be continuously generated in the fused sodium hydroxide bath at suitably disposed electrodes so that anodic generated oxygen combines with cathodic generated sodium to form sodium peroxide. As the sodium peroxide is reduced or decomposes to a lower sodium oxide, a portion of the fused bath may be removed and treated by the introduction of water in the form of water, vapor, or steam for the purpose of reacting with and reconverting to the hydroxide the lower oxides of the metal of the bath formed by decomposition of the generated peroxide, which treated portion is returned to the main portion of the fused bath.

5. Sodium peroxide may be otherwise generated in the fused alkaline bath by reaction between physically introduced oxygen and sodium metal previously dissolved in the bath.

6. Oxidizing substances such as nitrates, chlorates, peroxides, perchlorates and persulphates as the salts of the alkali or alkaline earth metals may be added to the fused sodium hydroxide.

It will be noted that the physical introduction of oxygen, particularly in air, or continuous electrolytic generation of agents unstable at the temperatures used, constitute two ways in which oxidizing agents which are physically or chemically unstable may be economically regenerated.

The oxygen in the fused bath has proven very effective and the resulting compounds are either directly soluble in the bath or are more easily removable by after-treatment than the oxides in their original form.

The after-treatment of this invention may comprise immersion in any suitable acid bath. Immersion in a hydrochloric acid bath followed by a nitric acid treatment has been found to be of particular advantage in removing the oxidized scale.

The numerous advantages of the process as herein described are of great economic importance when considered in comparison with standard commercial day practices of descaling, pickling and metal oxide film removal in general. Some of the more outstanding advantages are now briefly pointed out:

1. The great reduction in time necessary for the cleaning operation by our process over the acid pickling process. The cycle of operations in our process can be completed in substantially less time than required by standard acid methods. For example, an illustrative cycle for the descaling of many types of hot rolled or annealed nickel-chromium "stainless" steels according to our invention is in general:

(*a*) 10 to 20 minutes in a bath of fused sodium hydroxide at 900 to 1000° F. to which oxygen has been introduced.

(*b*) Water quench, then

(*c*) Treatment in 10% hydrochloric acid in water at 160 to 180° F. for 1 to 3 minutes, followed in some cases by a 30 second treatment in 15% nitric acid in water at 150 to 180° F.

In the normal acid pickling process, or combination acid processes, as applied to comparable steels, the treatment time may, for example, run into hours in 17½% sulphuric acid solution at 180° F. It should be understood, however, that the subsequent short acid treatment usually required after treatment by our bath may vary within fairly wide limits of time, temperature, acid type, etc., between different alloys and degrees of scaling. Our invention merely comprises a means of greatly facilitating complete cleaning by acid should the bath itself fail to do so.

2. The normal acid pickling process leads to a great loss of metal by the acid attack on the base metal itself, this loss sometimes amounting to 60 lbs. of metal per short ton, whereas tests made on comparative metal loss caused by our process indicates actual metal sacrifice to fall substantially below 10 lbs. per short ton.

3. The great problem of spent pickling acid disposal is practically eliminated by the use of our process, the actual acid requirements and consumption for the subsequent acid treatment in this process being very small.

4. The fused bath utilized is very reactive with carbon, oxidizing it to removable products. Carbon is present in most annealed metal oxide films and is extremely difficult to remove by acid pickling. In these it is only thus completely removed by solution of the metal surrounding and beneath it.

5. The short subsequent acid treatment required as an adjunct to the process diminishes the etching of the metal surface which is produced by the sustained action of acids over a long period as is normally required in acid pickling.

6. The low cost of the chemicals required.

7. The low cost of operation of the process.

8. Simplicity of operation and of ingredients.

The metal alloys which are of general commercial application, and to which the invention can be beneficially applied, such as those of iron, chromium, nickel, manganese, cobalt, molybdenum, vanadium or tungsten, etc., in various combinations, are oxidized on the surface during certain stages of their fabrication into the customary forms required for industrial needs, such as billets, castings, sheet, rod, wire, etc. For example, heavy oxidation takes place during the annealing process, and this oxidized surface layer has in most cases to be removed before further fabrication or processing can be carried out.

The present process accomplishes this quickly and efficiently and is thus of wide scope and great practical utility.

We claim:

1. A process for the treatment of surface oxide films on a metal article for the purpose of removing surface oxides therefrom comprising providing a molten bath of the group consisting of the alkali metal hydroxides and alkali metal chlorides, immersing said article in said bath without connection of said article or bath as an electrode of an electric source, introducing oxygen in gaseous form from an outside source into said molten bath, subjecting the said surface ox-

ides of said immersed article to the oxidizing action of said molten bath into which said oxygen in gaseous form has been introduced and continuing said oxidizing treatment to the modification of said oxides to a form easily removable in acids.

2. A process for the treatment of surface oxide films on a metal article as set forth in claim 1 in which the oxygen in gaseous form is introduced as air.

3. A process for the treatment of surface oxide films on a metal article as set forth in claim 1 in which the molten bath includes substances adapted to form higher oxides intrinsically unstable in said molten bath and continuously reformed by said introduced oxygen.

4. In the removal of dense firmly adherent oxide from the surface of metals, including the step of subjecting the oxide to the action of a fused bath of caustic alkali containing an oxidizing agent stable therewith under the conditions of the process and susceptible of regeneration by oxidation from a lower to a higher state of oxidation, the method of accelerating the regeneration of the oxidizing agent, which comprises introducing oxygen in gaseous form into the bath.

5. The process for the treatment of surface

oxide films on a metal article as set forth in claim 1 in which the metal compound is an alkali metal hydroxide.

References Cited in the file of this patent

UNITED STATES PATENTS

Number	Name	Date
221,138	Wuth	Oct. 28, 1879
1,136,110	Eberhart	Apr. 20, 1915
1,247,086	Crowe	Nov. 20, 1917
1,714,879	Lang	May 28, 1929
1,729,765	Dinley	Oct. 1, 1929
2,244,526	MacKay	June 3, 1941
2,311,099	Tainton	Feb. 16, 1943
2,347,742	Keene	May 2, 1944
2,377,876	Gilbert	June 12, 1945
2,380,284	Young	July 10, 1945
2,389,488	Dailey	Nov. 20, 1945
2,395,694	Spence	Feb. 26, 1946

OTHER REFERENCES

Mellor: "Comprehensive Treatise on Inorganic and Theoretical Chemistry," vol. 2, page 489. Longmans, Green & Co., New York, 1922.

Mellor: "Modern Inorganic Chemistry," pages 318 and 550. Longmans, Green & Co., New York, 1939 (revised edition). Copy in Div. 27.