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PROCESS AND THE DESCALING OF METALS

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ABSTRACT OF THE DISCLOSURE

Metals having metal oxide scales are descaled with molten sodium metal. The descaling can be preceded and/or followed by treatment of the metal with molten alkali metal hydroxide. Preferably the sodium hydroxide treatment is carried out as a pretreatment in the austenitization range whereby the wires or bands after annealing are changed to a perlite structure.

This application is a continuation-in-part of application Ser. No. 706,108, filed Feb. 16, 1968.

BACKGROUND OF THE INVENTION

Field of the invention

The invention relates to the removal of metal oxide scales from metals.

Description of the prior art

It is known that hot or cold formed metal, such as rolled steel bands or drawn wire, must be annealed, in order to obtain a recrystallization of the structure of the metal. If the annealing is conducted in an atmosphere which contains oxygen, metal oxides form on the surface of the metal in the form of so-called "scales" or "forge scales" and they must be removed.

In addition to mechanical processes for removing the scales, a number of chemical processes have also been developed for this purpose, among which is one in which the metal oxide scales are removed by having the metal object pickled in acid.

The treatment of steel objects in an acid pickling process for the removal of scales therefrom, however, gives rise to a number of disadvantages. Not only does the waste water from the process create disposal and handling problems, as are common to all pickling installations, but, due to the fact that the through-put time for the steel in the acid pickling bath must be relatively long, when steel band or wire must be passed through the bath at a high rate of speed, then extraordinarily large pickling installations have to be provided in order to accommodate the needs of the process. Furthermore, and particularly in those cases where highly alloyed steel is being processed, the pickling acid not only attacks the scales but the base material as well, and thus leads to expensive losses of metal. In addition, the acid pickling process also leads to the absorption of hydrogen by the metal being treated which causes undesirable embrittlement of the metal.

Because of such disadvantages in the use of aqueous pickling baths, salt bath processes have been developed which are significantly short and have more limited process times than is required with the acid treatment processes. Such salt bath processes include those involving the use of molten alkaline salts, in which the scales are more or less given a preremoval treatment with the aid of direct electrical current in order to assure the quick removal of the scales in a subsequent heat treatment in

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the molten salt, as well as processes in which a reducing agent, for example, sodium hydride, is used in order to extensively remove the scales. For the same purpose, other processes have also been developed wherein a caustic soda melt which contains metallic sodium in suspended form is used as the reducing agent. In addition it has also been proposed that a reducing agent such as sodium hydride be sprayed or scattered on the surface of the steel band which is to be treated for the removal of scales therefrom.

All these prior art processes, however, including those which involve the use of reducing agents, have the disadvantage that they do not remove all the metal oxide scales from the surfaces of the treated metal bands without the use of a subsequent acid pickling treatment, and where a reducing agent is used, an acid pickling pretreatment is also required.

SUMMARY OF THE INVENTION

An object of the present invention is to provide a process whereby metal oxide scales can be readily removed from metal surfaces.

Another object of the present invention is to provide a process for the removal of metal oxide scales from metal surfaces which does not require the use of an extensive acid pickling treatment of the metal surface before or after the process of this invention.

A further object of the present invention is to provide an installation in which to conduct the novel process of this invention.

A further object of the present invention is to provide an installation in which to conduct the novel process of this invention.

The essence of the process of the present invention involves treating the metal to be descaled with molten sodium metal, which treatment is preferably both preceded and followed by treating the metal with molten alkali metal hydroxide.

BRIEF DESCRIPTION OF THE DRAWINGS

FIG. 1 is a side view of an installation in which the process of the present invention may be conducted.

FIG. 2 is an end view of the installation of FIG. 1.

DESCRIPTION OF THE PREFERRED EMBODIMENTS

It has now been unexpectedly shown, that by treatment thereof with molten sodium metal, and in particular at temperatures between about 230° and 700° C. and preferably at temperatures above 300° C., all types of steel, the unalloyed as well as the highly alloyed types, can be readily descaled. The reduction of the metal oxide scales is so complete with such treatment that subsequent acid pickling treatments are usually not necessary. The process of the present invention has important advantages, therefore, in that material losses due to overpickling are avoided, even if for some reason the metal object being treated must remain stationary in the molten sodium, and in that hydrogen absorption by the metal, which is associated with acid pickling treatments, does not occur. In addition, due to the direct descaling of the metal by means of the sodium metal, the reducing time is confined to only a few seconds, so that through-put speeds can be achieved for the descaling process which have not been possible to date. The molten sodium metal treatment is preferably conducted at 230° to 700° in about 60 to 5 seconds.

The molten sodium treating process can be further improved if the metal to be treated is pretreated or dipped in molten alkali metal hydroxide for a short time before the molten metal treatment. The alkali metal hydroxide

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used is preferably sodium hydroxide. Molten mixtures of alkali metal hydroxides and alkali chlorides can also be used. The pretreatment with alkali metal hydroxide is preferably conducted at 230° to 700° C. for 5 to 60 seconds. The wetting and resulting descaling of the surface of the metal being treated is so free of objectionable features that the descaling process is completed within a very short time without any trouble.

The alkali metal hydroxide bath which is used in conjunction with the actual pickling process, which latter process is conducted in the molten sodium metal, can be used as means for sealing the sodium metal processing chamber from the atmosphere. The alkali metal hydroxide melt which is used for pretreating such object. An alkali metal hydroxide bath can also be used as a post-descaling treatment in order to act as a scavenger and remove the metal object being processed not only pieces of sodium metal that may adhere to the metal object as it leaves the sodium metal bath, but also sodium oxide reaction products that may form during the descaling step. The pieces of sodium metal and sodium oxide reaction products that are taken up by the alkali metal hydroxide bath can be readily converted into sodium hydroxide upon contact with moisture in the atmosphere.

The molten sodium metal bath is preferably blanketed with an inert gas which will not react with the sodium metal. The purpose of this inert gas is primarily to seal off the molten sodium metal bath from gases or other components of the atmosphere which would either react with the sodium metal or with the metal being processed under the prevailing process conditions. Examples of the undesired gases or other compounds are oxygen, hydrogen, water. Nitrogen is the preferred inert gas to be used as the blanketing medium.

A metal processing installation in which the process of the present invention can be carried out can be constructed in such a way that the molten sodium metal is allowed to float on top of the molten alkali metal hydroxide bath. The sodium metal bath can be isolated from the atmosphere by means of a tower type structure erected over the sodium metal bath. Elongated metal objects, such as, wire and bands, to be treated in the sodium metal bath can be fed continuously through the bath and the tower type structure surrounding the bath by means of feeder devices, such as guide rollers.

A particularly advantageous installation for carrying out the process of the present invention is one in which the alkali metal hydroxide bath is used in a trough like container and the molten sodium bath is changed into a funnel shaped container which latter container is inserted into the alkali metal hydroxide bath in such a fashion that the alkali metal hydroxide bath completely surrounds the sides of the funnel shaped container. The funnel shaped container has a wide open top and a narrow open bottom whereby an interface between molten sodium metal and molten alkali metal hydroxide sets in inside the narrow open end of the funnel shaped container.

An example of such an installation is shown in the drawings. FIG. 1 shows a side view of the installation and FIG. 2 shows an end view of the same installation. The installation consists essentially of a furnace which has a wall 1 and a heating chamber 1a, an open topped trough or vat 2 for the molten alkali metal hydroxide 2a, an open topped container 3 for the molten sodium metal bath 3a, and air tight housing 4 and feeder or guide rollers 5.

Walls 4a of housing 4 extend on all sides down into bath 2a and housing 4 provides in combination with the molten alkali metal hydroxide 2a, an air tight area 7. Area 7 is thus bounded on its top and sides by housing 4 and at its base by the top of bath 2a. Area 7 completely isolates bath 3a from contact with the atmosphere, and during the operation of the installation area 7 is charged with an inert gas. The portions of the top of bath 2a which are outside walls 4a of housing 4 are in contact with the atmosphere.

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An elongated metal object O which is to be treated using the process of the present invention is fed into and through the installation, in the direction of the arrows, by means of guide rollers 5. As shown by the drawings, the metal object passes first through the NaOH bath, then through the Na bath and again through the NaOH bath before it leaves the installation. The furnace maintains both the NaOH bath and the Na bath in a molten condition. The NaOH bath is heated directly through its container wall 2 by means of heat generated in heating chamber 1a. The sodium is in turn heated by the molten NaOH.

The sodium bath 3a is housed in funnel shaped container 3. Container 3 may be suspended from above in the NaOH bath or it may be supported by a base which is itself resting on the bottom of trough 2. The walls of the lower half of container 3 slope inwardly to provide a narrow, neck 6 which is open at the bottom thereof. Neck 6 extends into the NaOH bath 2a in such a way as to leave a distance, on all sides of it, between it and the walls and base of trough 2. As a result of this arrangement, there is no horizontal wall separating the molten sodium in the bottom of neck 6 from the molten NaOH in trough 2 so that the molten sodium ($\gamma=0.95$ kg./dm.³) floats on the molten sodium hydroxide ($\gamma=1.8$ kg./dm.³). Container 3 is thrust so far into the molten NaOH that the interface between the molten sodium and the molten NaOH is inside neck 6. Thus, since neck 6 has a definite length, care must be taken during the operation of the installation to provide that fluctuations in the amounts of sodium and sodium hydroxide in their respective containers do not cause the interface between the sodium and the sodium hydroxide to be located outside of neck 6.

By reason of the arrangement of the installation as shown in the drawings various advantages are obtained in conducting the process of the present invention in such installation. When using the disclosed installation products such as the Na₂O, reduced metals, and impurities which are produced or formed during the descaling step in the molten sodium metal eventually end up in the molten sodium hydroxide. This arises due to the fact that such materials are all heavier than the molten sodium. They sink or slide, therefore, to the bottom of container 3 and through the open bottom of neck 6 into the molten sodium hydroxide. Such materials either than further fall to the bottom of trough 2 or they are taken up by the molten sodium hydroxide. The sodium oxide materials will dissolve in the molten sodium hydroxide. The dissolved Na₂O will not be an impurity in the molten sodium hydroxide since the Na₂O will react with moisture in the air that is absorbed into the molten sodium hydroxide and will form sodium hydroxide, i.e.,



The moisture in the air can enter the sodium hydroxide where the molten sodium hydroxide is exposed to the atmosphere, i.e., that portion of the molten sodium hydroxide bath which is outside walls 4a. The usual impurities which are present or formed during the descaling step, notably reduced metal, and which eventually fall to the bottom of trough 2, can be removed mechanically from the trough.

The narrowing of the interface surface between the molten sodium and the molten sodium hydroxide by means of narrow neck 6 has the purpose of preventing losses of sodium by reason of the sodium dissolving in the sodium hydroxide. The relatively narrow interface provided by neck 6 has the effect of providing a relatively small reaction surface between the two materials and thereby prevents a large scale dissolution of the sodium in the alkali metal hydroxide.

Since the lower portion of container 3 is completely immersed in the molten sodium hydroxide, the molten sodium hydroxide can be used as an air tight sealing

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means, in combination with air tight housing 4, in order to keep moisture and other materials in the air from reaching and reacting with the molten sodium. Housing 4 is so constructed that continuous metal wire or bands can be processed therein under an inert atmosphere from the time the wire or band enters the molten sodium hydroxide for the first time until it leaves the molten sodium hydroxide at the end of the process. In this way slits are not needed in walls 4a in order to provide ingress and egress means for the wire and bands. Particles of sodium metal that may adhere to the band after the band leaves the molten sodium bath are readily taken up in the molten sodium hydroxide the second time the band passes through bath 2a, and thus before the band passes out into the outside atmosphere.

As can be seen from FIG. 2, housing 4 is constructed wide enough so that there is sufficient open space on the surface of bath 2a between walls 4a of housing 4 and walls 3b of container 3 as to allow for the removal of impurities in the form of sludge from under container 3 in bath 2a through such open surface space.

Instead of using a single common bath housed in a single through for treating the continuous metal objects in two separate molten alkali metal hydroxide bath treatments, two separate alkali metal hydroxide baths placed in separate troughs can also be used. In such instance the sodium melt could also be housed in a separate trough shaped container of its own and the three troughs could still all be housed under a single air tight housing.

Those elements of construction which are to be used in the building of the installation and which are to come in contact with molten sodium during the operation of the installation, such as the inside of container 3 or the guide rollers which are partly immersed in bath 3a, must be made of a material which will not be attacked by the molten sodium. Such elements of construction should, therefore, be constructed of a sodium resistant material such as nickel, or be plated with such sodium resistant materials.

The elements of construction which are to come in contact with the molten alkali metal hydroxide should be such as are capable of withstanding attack from such hydroxides.

The sealing of the guide roller shafts 8 which are to pass through housing 4 can be done with stuffing boxes in order to maintain the air tight integrity of housing 4. The heat generated in the heating area 1a of the furnace can be generated electrically, as by using resistance elements, or by burning gas or oil. Heat generating electrodes can also be inserted directly into the baths.

The following examples are merely illustrations of the process of the present invention and are not intended as a limitation upon the scope thereof.

EXAMPLE 1

A test piece of ST-high grade steel was heat rolled and annealed in the atmosphere and oxide scales appeared on the surface of the test piece. The surface of the test piece was then treated for 5 to 10 seconds at 400° C. in molten sodium hydroxide (100% pure) and then for 5 to 10 seconds at 450° C. in molten sodium metal (100% pure). The surface of the thus treated metal piece was clear of oxide scales.

When test pieces of the same type of heat rolled and annealed ST steel were descaled in the customary pickling bath process using a HCl or H₂SO₄ pickling bath heated to 40° to 80° C. the treatments required a pickling bath time of at least two minutes in order to achieve the same descaling results as were obtained with the process of the present invention. (0.4% C, 1% Mn in the steel.)

EXAMPLE 2

Test pieces of a highly alloy chromesteel identified as workpiece numbers 4006 to 4021 were heat rolled and annealed in the atmosphere whereupon oxide scales ap-

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peared on the surface of the test pieces. The surface of some of the test pieces were then treated for 5 to 10 seconds at 500° C. in molten sodium hydroxide (100% pure) and then for 5 to 10 seconds at 400° to 500° C. in molten sodium metal (100% pure). The surface of the thus treated metal pieces were clear of oxide scales.

When some other of the test pieces were descaled in a pickling treatment using a mixture of HNO₃ and HF as the pickling bath at 40° to 60° C. the treatment required a pickling bath time of more than five minutes in order to provide the same descaling effect as was provided by the process of the present invention. (18% Cr, 82% Fe steel.)

EXAMPLE 3

A test piece of highly alloyed chrome-nickel steel identified as workpiece number 4300 was hot rolled and annealed in the atmosphere whereupon oxide scales appeared on the surface of the test piece. The surface of the test piece was then treated for 5 to 10 seconds at 400° C. in molten sodium hydroxide (100% pure) and then for 5 to 10 seconds at 500° C. in molten sodium metal (100% pure). The layer of oxide scales was thus removed from the surface of the test piece.

When a test piece of the same type of steel as workpiece 4300 which had been hot rolled and annealed as the piece used above was descaled in a pickling treatment using a mixture of HNO₃ and HF as the pickling bath at 40° to 60° C. the treatment required a pickling bath time of five minutes in order to provide the same descaling effect as was provided by the process of the present invention. (18% Cr, 8% Ni in the steel.)

The molten sodium bath should contain sodium which is at least 100% pure. The alkali metal hydroxide bath should contain alkali metal hydroxide which is at least 100% pure. While sodium hydroxide is the preferred alkali metal hydroxide, there can be used potassium hydroxide.

The metals which may be descaled in accordance with the present invention include alloyed and non-alloyed iron and steel as well as copper, alloys of zirconium and titanium, iron-free alloys basing on Ni, Co and Cr.

The metals being processed in the process of the present invention may have any shape or configuration. The process is particularly suitable to the treatment of objects which may be fed into the molten sodium metal bath in a continuous fashion, such as wire, cable, strips, bands, sheets, and similar elongated objects.

A particularly preferred form of the invention is to utilize the sodium hydroxide pretreatment in a manner to produce the patentization effect and eliminate the customary lead bath thereby. Thus, the steel wires or bands are lead through the sodium hydroxide bath at 450° to 550° C., preferably 500° C., which is in the Austenitization range. As a result after the annealing the structure of the steel is changed to a perlite structure with its specific mechanical properties, e.g. improved wetting properties. This preferred procedure involving perlitization is of concern only with steels. Example 2 illustrates this preferred procedure. The steel should be held in the sodium hydroxide bath long enough to accomplish the desired structural change.

What is claimed is:

1. A process for removing metal oxide scales from the surface of a metal object which comprises treating the surface of a metal object having metal oxide scales thereon with a molten bath consisting essentially of molten sodium metal.

2. A process as in claim 1 in which said metal object is one made of iron or steel.

3. A process as in claim 1 in which the temperature is over 300° C.

4. A process as in claim 1 in which said surface is pretreated with molten alkali metal hydroxide prior to the treating with said molten sodium metal.

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5. A process as in claim 4 in which the temperature of said molten alkali metal hydroxide is maintained between about 230° and 700° C. during the pretreating.

6. A process as in claim 5 in which the alkali metal hydroxide is sodium hydroxide.

7. A process as in claim 1 in which said treating is conducted in the substantial absence of oxygen, carbon dioxide and hydrogen.

8. A process as in claim 1 in which said treating is conducted in 1 to 60 seconds.

9. A process as in claim 4 in which the pretreating is conducted in 1 to 60 seconds.

10. A process as in claim 1 in which the treating is conducted on a continuous object which is passed through said molten sodium metal.

11. A process according to claim 1 wherein the metal is iron or steel and the surface is pretreated with molten alkali metal hydroxide at a temperature of 450° to 550° C. to convert the material structure to a perlite structure and the molten sodium metal is maintained between 230 and 700° C. during said treating.

12. A process according to claim 11 wherein the alkali metal hydroxide is sodium hydroxide.

13. A process according to claim 12 wherein the temperature of the molten sodium hydroxide bath is about 500° C.

14. A process according to claim 13 wherein the temperature of the molten sodium metal is maintained at 400-500° C.

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