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2,796,366

PROCESS AND BATH FOR DESCALING METALS

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This invention relates to a fused bath and to a process for descaling metals, ferrous metals in particular.

Gilbert, in U. S. Patent 2,377,876, shows a method for reducing oxide scale on metallic surfaces. In the patented method the metal to be descaled, usually iron or one of its alloys, is dipped into a molten bath of sodium hydride containing up to about 20% by weight of sodium hydride. For a decade or more this process has been widely used in the metal trades.

The utility of the Gilbert bath has largely been confined to the descaling of stainless steel. In particular it has been impracticable to descale low-grade carbon steels therein because the reduced scale adheres tightly to the surface of such metal. Removal of such reduced scale is too expensive for commercial acceptance.

An object of this invention is, consequently, to effect improvements in the process for descaling metals in hydride-containing fused baths.

A specific object is provision of a method for descaling carbon steels in hydride-containing fused baths.

Another object is provision of an improved fused bath for descaling metals.

A further object is provision of a fused bath for descaling carbon steels.

The above-mentioned and yet other objects are achieved in accordance with this invention by a process in which a metallic workpiece, generally formed of carbon steel, is first immersed in a molten bath of alkali metal hydroxide containing iron in addition to alkali metal hydride. This step reduces the scale to a form loosely held to the surface of the workpiece. The workpiece is then quenched in water while still hot and the loose scale removed therefrom.

The fused bath which serves as the basis of the invention is most conveniently prepared by forming a descaling bath of the type described by Gilbert, i. e. a molten alkali metal hydroxide containing up to 20% by weight of an alkali metal hydride, and then adding thereto a mixture of an iron oxide and an alkali metal oxide. The bath is subsequently maintained by analyses followed by addition of needed components.

The preferred alkali metal hydroxide for use in the invention is sodium hydroxide. Between about 50 and 95% by weight of this compound is normally utilized. The hydroxides of other alkali metals may be substituted in whole or in part for that of sodium but to no particular advantage. For economic reasons, up to about 50% by weight of the caustic may also be replaced by sodium carbonate, sodium chloride or mixtures thereof or by other inert alkali metal salts.

In like manner sodium hydride is the preferred hydride for addition to the bath. Between about 0.3 and 5% by weight of the bath should consist of this material. Larger percentages up to about 20% are usable but unnecessary. The hydride can be added preformed to the bath or generated in a separate compartment of the bath itself. Generation is easily accomplished by adding sodium metal to molten caustic and passing hydrogen or cracked ammonia therethrough. Potassium or other alkali metal hydrides can be substituted for sodium hydride if it is so desired.

To obtain reduced scale easily removable from the

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workpiece, the bath should contain about 0.2–10% by weight of dissolved iron, calculated as the metal. About 0.3–1% by weight is preferred. The best operation of the bath occurs when some particular weight of iron within the range is chosen and the weight is maintained constant. The iron is preferably supplied to the bath, not as the metal, but as an oxidic compound such as FeO , Fe_2O_3 , Fe_3O_4 , NaFeO_2 or the like. Iron oxide scale and ores can also be used.

Iron is soluble to a maximum extent of about 0.1% by weight in conventional hydride baths. Some method of increasing the solubility is therefore necessary. Addition of an alkali metal oxide, preferably sodium oxide, along with the iron will accomplish this result. The quantity of sodium oxide utilized can vary greatly from 0 to about 3 times the weight of iron oxide (Fe_2O_3). The preferred weight is 1–2 times that of Fe_2O_3 . A mixture of sodium ferrite (NaFeO_2) and Na_2O can readily supply these requirements. Expressed in terms of bath weight, sodium oxide may constitute between about 0.3 and 10% thereof, the larger quantities of course being employed with the larger amounts of iron oxide. Sodium oxide can also be supplied to the bath in other ways than by direct addition. Direct generation by the reaction between metallic sodium and caustic, for example, generally occurs when the bath is in operation.

There is no direct way of determining sodium oxide in hydride-caustic baths. The form in which it is present—or even its presence—is consequently unknown. Equilibrium considerations suggest, however, that appreciable quantities of Na_2O are dissolved as such in the bath, at least as long as the partial pressure of hydrogen is not too high. Iron may begin to precipitate if this partial pressure rises above about 0.5 atmosphere. The effect on the solubility of iron suggests that some may be tied up in compounds of the type $\text{Na}_2\text{O} \cdot x\text{FeO}$, where x is probably 1.

Iron, of course, does not exist in the bath as the metal. Its exact form, like that of the sodium oxide, is unknown although the presence of ferrites seems likely. Direct and conventional analyses for iron are, nevertheless, possible and the concentration can be reported in terms of any compound. While in this specification weights are reported in terms of metallic iron, it will be appreciated that an iron compound is actually dissolved.

A nonoxidizing atmosphere may be employed to protect the present baths from attack by air and oxygen. This can be provided by nitrogen, argon, neon or other inert gas. Most conveniently, however, the bath may be protected by the use of floating covers of a form of carbon such as graphite or charcoal. Floating pans or lids fastened to the container for the bath may also be used.

The mechanical operation of the descaling baths of this invention is quite simple and substantially that of the prior art. The workpiece to be descaled is given a preliminary brushing, if desired, and dipped for about $\frac{1}{2}$ –30 minutes in the molten bath. The exact time required will vary to some extent with the thickness of the scale. The temperature of the bath should be between about 325° and 550° C. Around 500° C. is satisfactory and preferred. After the immersion, the workpiece is removed and quenched while hot in water. Further treatments such as washing in a high-pressure water spray, scrubbing or rinsing in dilute acid may be carried out if desired. The quench, however, removes substantially all of the finely divided reduced scale from the metal.

Maintenance of the bath during prolonged operation involves principally the addition of sodium hydroxide, sodium and iron. Caustic may be added directly to the bath. Sodium hydride may also be added as such but is preferably generated in situ by the reaction of hydrogen gas on sodium, the method of generation conventionally

employed in hydride descaling operations. The ratio of hydrogen to sodium metal should, however, be carefully controlled during this generation to avoid precipitation of iron. Usually this ratio will vary between $\frac{1}{4}$ and 2 liters of hydrogen for each gram of sodium. If the ratio is less than that recommended, the bath is likely to become corrosive. An increase in the $H_2:Na$ ratio within the range given will decrease the solubility of iron while a decrease in the ratio will have the reverse effect.

Iron should be added along with sodium oxide as the need therefor is indicated by analysis. Great care should be exercised if sodium oxide is added alone since a bath containing the oxide and no iron will corrode the container or any other ferrous metal it contacts. This fact explains the desirability of keeping the weight of iron constant.

It will be understood that the iron-containing baths of this invention are useful for descaling bases other than carbon steel. In general, iron bases or alloys carrying oxide scale can be descaled therein. Various nonferrous metals such as copper and nickel and alloys such as nichrome can also be cleaned by these baths. In fact, almost any metal that can withstand the high alkalinity of the molten caustic can be treated in the iron-containing baths.

There follow some examples which illustrate the invention in more detail. In these examples all percentages are weight percentages. Total gas pressure in all cases was ambient.

Example 1

This example, which shows an attempt to descale carbon steel in a conventional hydride bath, is included only as a control.

Several 6" samples of carbon-steel rod (.225" gauge, hot rolled, 0.08% carbon) covered with oxide scale were dipped at 400° C. for fifteen minutes into molten sodium hydroxide containing 2% of sodium hydride and less than 0.1% iron. The rods were quenched in water while hot. Most of the reduced scale was found to adhere to the rods despite the quench. It could be removed only by acid pickling or by scrubbing or spraying thoroughly with high pressure water.

Example 2

Through molten sodium hydroxide containing about 1% of iron (dissolved as an oxide of iron) and about 3% of sodium was bubbled a mixture of nitrogen and hydrogen with a hydrogen partial pressure of 0.02 to 0.1 atmosphere. About 2% of sodium hydride was thus formed and maintained in the bath. The sodium oxide concentration was probably between $\frac{1}{2}$ % and 4% by weight based on consideration of equilibrium constants.

Carbon-steel coupons covered with oxide scale were dipped into the bath at 400° C. for about five minutes, were withdrawn and then quenched in water without cooling. In each case the reduced scale was completely or almost completely removed by the water quench.

Example 3

3500 g. of sodium hydroxide were melted at 400° C. and dried by the addition of a few grams of Na_2O . 50 g. of sodium was added, the mixture was stirred, and 30 liters of hydrogen was passed thereover at a rate of 1 liter/min. to generate sodium hydride in situ. The bath was protected from the atmosphere by a charcoal cover and a metal lid both during the generation of hydride and in subsequent operations. After about 1% of hydride had been generated, a mixture of 100 g. of Fe_2O_3 and 100 g. of Na_2O was added. The bath was maintained non-corrosive to the metallic container or the workpieces at temperatures of 400°, 450° and 500° C. by the continuous passage of about 10 ml. of H_2 /min. thereover.

This bath was operated over a period of five months without appreciable corrosion of the tank or of samples

at several different concentrations of hydride and iron. The hydride concentration was increased by adding sodium and stirring while passing over the bath 3 liters of H_2 for every 5 g. of sodium. To increase the iron concentration, mixtures of sodium oxide and iron oxide (Fe_2O_3) were added, usually in a weight ratio of 2:1. The iron concentration was decreased upon occasion by passing an excess of hydrogen over the bath either while hydride was being generated or while the bath was not in use.

A strip of steel was weighed daily during the changes in conditions. The constancy of weight of the strip indicated that corrosion was negligible when the variables were maintained within the ranges indicated above. Analyses for iron and hydride enables the bath to be controlled at whatever set of conditions was desired.

Numerous steel samples of wire and rod having both high and low carbon contents were descaled in the hydride-oxide bath during the testing period. Reduced scale was removed completely or almost completely from all samples by a simple water quench.

Having described my invention, I claim:

1. The process for removing oxide scale from the surface of an article formed from a metal substantially non-reactive with alkali metal hydroxides which comprises contacting said article at a temperature below the melting point thereof with a molten composition comprising a molten alkali metal hydroxide to which has been supplied about 0.3–10% by weight, based on weight of the total composition, of the oxide of an alkali metal, about 0.3–20% by weight of an alkali metal hydride, and about 0.2–10% by weight of iron dissolved as one of its oxidic compounds and subsequently removing the resulting reduced scale therefrom.

2. The process of claim 1 in which the alkali metal is sodium.

3. The process of claim 2 in which the temperature of the molten composition is about 325°–550° C.

4. The process of claim 2 in which the time of contact between the article and the composition is $\frac{1}{2}$ –30 minutes.

5. The process of claim 2 in which the article is made from a carbon steel.

6. The process of claim 2 in which the resulting reduced scale is removed by a water quench.

7. A fused bath for descaling ferrous articles carrying an oxide scale comprising an alkali metal hydroxide to which has been supplied about 0.3–10% by weight, based on the total bath weight, of the oxide of an alkali metal, about 0.3–20% by weight of an alkali metal hydride, and about 0.2–10% by weight of iron dissolved as one of its oxidic compounds.

8. The bath of claim 6 in which the alkali metal is sodium.

9. The method of forming a bath for descaling ferrous articles carrying an oxide scale which comprises dissolving about 0.2–10% by weight of iron in the form of one of its oxidic compounds in molten sodium hydroxide to which has been supplied about 0.3–10% by weight, based on the total bath weight, of the oxide of an alkali metal, containing about 0.3–5% by weight of sodium hydride.

10. The method of claim 9 in which the iron is in the form of an oxide and is dissolved in the sodium hydroxide along with sodium oxide.

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