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ALKALINE COMPOSITION

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Various fused alkaline salt compositions have heretofore found wide application in metal treating operations, including carburizing, normalizing, martempering, austempering, stress relieving, quenching, hardening, annealing, and metal cleaning. This invention is particularly directed to improvements in fused salt metal cleaning baths and contemplates metal cleaning baths as including not only descaling baths, which are used to condition and remove surface oxide coatings and other surface imperfections, but also de-investing baths employed to remove siliceous material and other types of mold-forming substances adhering to cast metal objects.

Investment casting, employing molds formed of siliceous or other heat-resistant substances, such as various zirconia compounds, is highly advantageous in the formation of intricately shaped parts to relatively close tolerances. Although a number of separating agents or mold washes have been proposed and are used both in precision casting and in other casting operations to facilitate separation of the cast article from the mold, such materials frequently do not satisfactorily remove or de-invest the casting.

It is, therefore, a principal object of the present invention to provide new and improved compositions of matter which are useful in metal-treating operations generally and are particularly advantageous in descaling and de-investing processes.

A further object of the invention is the provision of new and improved methods for descaling and de-investing metals and alloys.

These and other objects and advantages of the invention will appear more fully from the following description.

It has heretofore been proposed to employ alkaline salt baths in the removal of oxides from steel surfaces. Moreover, alkaline salt baths have been used in prior de-investing operations. Typical of such prior art alkaline salt baths has been a fused salt consisting essentially of an alkali metal hydroxide, which admittedly possesses certain advantageous properties as a metal cleaning agent. However, such prior art fused alkaline salt baths have not satisfactorily solved the problem of de-investing castings, particularly intricately shaped cast articles, and, in many instances, have not been adequate in metal cleaning and descaling applications.

The present invention avoids the difficulties heretofore encountered and obtains highly advantageous results in the treatment of metal surfaces generally by employing as a treating material a composite salt bath consisting essentially of, on a weight basis, a major proportion of at least one compound selected from the class consisting of alkali metal hydroxides and a minor proportion of a source of fluoride ion. Such baths are particularly effective in the removal of investment materials from metal. Typical of such investment materials are zirconia compounds, such as zirconia silicate; clays, aluminum oxide, magnesium oxide, and various siliceous materials, the expression "siliceous materials," as used herein, being intended to include various silica-containing substances commonly employed in the preparation of investment molds, such as sand, silica powder, silica flour, sodium silicate, and the like.

More particularly, a composite salt of this invention consists essentially of, on a weight basis, a preponderant amount of at least one alkali metal hydroxide, i.e., a hydroxide of sodium, potassium, cesium, rubidium, and lithium, sodium preferred, and a minor proportion of an alkali metal fluoride, such as sodium fluoride, potassium fluoride, and the like, and/or an alkaline earth metal fluoride, such as calcium fluoride, strontium fluoride, or barium fluoride. In many instances, superior results are obtained when the major proportion of the salt comprises a mixture of potassium hydroxide and sodium hydroxide, a preponderant amount of the latter being preferred.

The practice of this invention contemplates treating metal articles by immersion in, or otherwise contacting with, the above-described alkaline salts in a fused condition. It will be understood, of course, that the temperature to which the salt should be heated will be dictated by a number of factors, including the particular bath formulation, the material being treated, the equipment used, and whether it is desired to combine certain heat-treating operations with the metal cleaning process. Satisfactory results have been obtained, however, using such alkaline baths in the fused condition at temperatures within the range from approximately 600° to 1100° F. In descaling treatments, particularly descaling of stainless steels, temperatures within the range from about 900° to 950° F. are preferred. In de-investing cast carbon steel articles, temperatures of 1100° F. or higher are satisfactory, although many types of castings may be de-invested at lower temperatures, such as temperatures within the range from 900° to 950° F.

The time of immersion or contact with the fused salt will depend on the bath temperature and other factors. In general, the time may range from a few seconds, for example, 15 to 30 seconds, to a number of hours, such as 6 or 8, or higher, depending on the particular application.

In order that those skilled in the art may more completely understand the present invention, the following specific examples of alkaline salt baths within the scope of this invention are offered wherein the quantities are expressed in parts by weight:

Example I

NaOH	80
KOH	15
NaF	5

Example II

NaOH	55
KOH	35
NaF	10

Example III

NaOH	90
NaF	10

Example IV

NaOH	80
NaF	20

Example V

KOH	90
NaF	10

Example VI

NaOH	80
KOH	10
NaF	10

Example VII

NaOH	77.5
KOH	13.5
NaF	9.0

Example VIII

NaOH	80
KOH	10
KF	10

Example IX

NaOH	70
KOH	20
CaF_2	10

Example X

NaOH	50
KOH	45
KF	5

Example XI

NaOH	80
KOH	10
BaF_2	10

Example XII

NaOH	75
KOH	10
NaF	15

In general, superior results are obtained using an alkaline salt bath containing, on a weight basis, from about 50% to 95% of sodium hydroxide, 15% to 50% of potassium hydroxide, and 4% to 15% of an alkali metal fluoride or an alkaline earth metal fluoride, the preferred fluoride at present being sodium fluoride. In certain cases, larger amounts of the alkali metal fluoride and/or alkaline earth metal fluoride may be used. Generally, however, the maximum practicable amount of fluoride varies and is dictated by its solubility in the fused salt at the operating temperatures employed. For example, in a salt bath consisting of NaOH and KOH in a 6:1 ratio, the solubility of NaF therein varies from 4.3% by weight at 650° F. to 16.5% at 1050° F.

The practice of this invention, while applicable to a wide variety of both ferrous and non-ferrous metals and alloys, including such metals as titanium, is particularly advantageous in the treatment of stainless steels, such as chromium-iron alloys, nickel-iron alloys, and other chromium-nickel-iron alloys which resist descaling and de-investing by prior art fused alkaline salts. As used herein, the term "metal" is intended to include both metals and alloys, as well as metallic mixtures.

In the practice of this invention, it is understood, of course, that the precise process details may be varied, depending upon the particular metal or alloy being treated, as well as the characteristics of the surface coating, if any, to be removed and/or conditioned. However, in most descaling operations, it is advantageous to employ a method which includes the successive steps of immersing the metal in a molten salt bath of the invention for a specified period of time; quenching the thus treated metal in water; immersing the quenched metal in a dilute inorganic acid, such as hydrochloric acid, sulfuric acid, phosphoric acid, nitric acid, or hydrofluoric acid, with or without corrosion inhibitor, while the acid is maintained at an elevated temperature, typically within the range from about 150° to 180° F.; rinsing the acid-treated metal in water; and finally immersing the rinsed metal in either dilute nitric acid or a dilute mixture of nitric acid and hydrofluoric acid, either of such acids or acid mixtures being maintained at an elevated temperature, typically within the range from 140° to 180° F. Such a nitric acid or nitric acid-containing solution treatment serves to brighten and passivate the metal surface and is particularly advantageous in the treatment of stainless steels. Following such passivation, the metal preferably is rinsed in hot water.

As in the case of descaling, the particular procedure to be followed in de-investing castings depends upon the type of metal to be de-invested and also the characteristics and composition of the investment material adhering to the casting. However, the following successive combination of steps constitutes the presently preferred method. The metal to be de-invested is immersed in a molten salt bath embodying the invention at a desired temperature and for a specified period of time. In many instances, only a water-quench in addition to the salt immersion step is necessary. Typical of such alloys which may be so treated are stainless steel and various cobalt-base alloys. In other cases, it is advantageous to use the same process in de-investing as is herein suggested for descaling operations.

As indicated by the foregoing paragraphs, it is frequently desirable, after the fused salt treatment, to contact the surface of the metal being treated with an inorganic acid at an elevated temperature. It will be understood, of course, that the conditions of acid treatment may be varied. In general, however, excellent results are obtained in providing a clean bright metal surface by using relatively dilute inorganic acids, i.e., about 5% to 20% by weight aqueous solution, preferably at elevated temperatures within the range from about 125° to 200° F., and for times ranging from a few seconds, i.e., 5 to 10 seconds, to a more extended period, in certain instances as high as 30 minutes or more.

Example XIII

To illustrate the effectiveness of salt compositions of the invention as de-investing agents, a precision cast turbine blade of Stellite 21, i.e., a cobalt base alloy having the following composition: 0.25% C, 27.0% Cr, 2.0% Fe, 5.5% Mo, 2.5% Ni, and the balance Co, is immersed in an alkaline salt bath comprising 80% by weight sodium hydroxide, 15% by weight potassium hydroxide, and 5% by weight sodium fluoride at 950° F. for 5 minutes. Upon removal from the bath and after a water rinse, the investment material is completely removed from the casting, including the investment material originally present in a blind hole in the turbine blade.

Example XIV

To demonstrate the effectiveness of compositions embodying this invention in dissolving siliceous material, a 3" diameter circular steel disk ⅜" thick with a tapped center hole, coated over a substantial proportion of its surface with a siliceous carburizing "stop-off" material (No-Carb), is immersed in a fused alkaline salt bath comprising 85% by weight sodium hydroxide, 15% by weight potassium hydroxide, and 5% by weight sodium fluoride for 5 minutes at 900° F. Upon removal from the fused bath, the siliceous stop-off material is completely removed from the steel disk.

Example XV

A fused bath is prepared by heating together 77.5 parts by weight of sodium hydroxide, 13.5 parts by weight of potassium hydroxide, and 9 parts by weight of sodium fluoride. Into this bath, maintained at a temperature of 1100° F., are introduced 6 steel alloy castings which have been formed in investment molds and bear upon their surfaces a substantial quantity of zirconia-silicate investment material. After 30 minutes immersion, the castings are removed from the bath and are completely de-invested.

Example XVI

To illustrate effectiveness in descaling operations of compositions embodying the invention, samples of stainless steel (S.A.E. 51410) bearing a substantial quantity of surface oxide scale are immersed in a fused alkaline salt bath comprising 80% by weight sodium hydroxide, 10% by weight potassium hydroxide, and 10% by weight sodium fluoride for 5 minutes at a temperature of 925° F.

The thus treated samples are then quenched in water and immersed in a 10% by weight sulfuric acid solution at 170° F. for 2 minutes. The samples are then rinsed in water and brightened by immersion in a 10% by weight nitric acid solution at 160° F. for 1 minute with a final water pressure spray rinse. It is noted that all scale is removed from the samples.

Example XVII

Samples of stainless steel (S.A.E. 30310) bearing a surface oxide coating are immersed in a fused alkaline salt bath comprising 80% by weight sodium hydroxide, 15% by weight potassium hydroxide, and 5% by weight potassium fluoride for 5 minutes at 925° F. The thus treated samples are then quenched in water and contacted with a 10% solution of sulfuric acid at 170° F. for 2 minutes. The samples are then rinsed in water and brightened by immersion in an aqueous solution comprising 10% by weight nitric acid and 2% by weight hydrofluoric acid at 140° F. for 2 minutes. The samples are then water-rinsed. It is noted that the scale is completely removed and the resultant surface is clean and bright.

The foregoing description of the present invention has been given for illustrative purposes and no undue limitations should be deduced therefrom. Accordingly, it is to be understood that variations and modifications capable of being accomplished by the mere exercise of skill of the art are to be embraced within the scope of the appended claims.

What is claimed is:

1. A composite alkaline composition consisting essentially of, on a weight basis, 50–95% sodium hydroxide, 15–50% potassium hydroxide, and 4–15% of an alkali metal fluoride.

2. The composition of claim 1 wherein the alkali metal fluoride is sodium fluoride.

3. A composition consisting essentially of, on a weight basis, 80% sodium hydroxide, 15% potassium hydroxide, and 5% sodium fluoride.

4. A composition consisting essentially of, on a weight basis, 77.5% sodium hydroxide, 13.5% potassium hydroxide, and 9.0% sodium fluoride.

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