

UNITED STATES PATENT OFFICE

2,174,867

METHOD OF HEAT TREATMENT

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No Drawing. Application May 23, 1936

Serial No. 81,510

6 Claims. (Cl. 148—15)

This invention relates to methods of heat treatment; and it comprises a process wherein a metal is heat treated by immersing the same in a molten salt bath, said bath being internally heated and maintained in molten condition by passing an alternating electric current there-through, the said salt bath comprising a, relatively low-melting mixture of salts, at least one of said salts being unstable at the temperatures employed in said bath when said bath is heated externally by methods customary in the art; more specifically my invention provides a method of case hardening steel wherein the said molten salt bath comprises normally unstable nitrogen or carbon-containing salts which are soluble in said bath and are capable of transferring said nitrogen or carbon to steel articles during heat treatment of such articles in said bath; all as more fully set forth and as claimed.

In my prior Patents Nos. 1,792,674 of February 17, 1931, and 1,864,885 of June 28, 1932, I have disclosed a method of heating salt baths by electrical means, utilizing alternating current, and the present invention relates generally to the use of certain special fusion salt mixtures in conjunction with apparatus of the type set forth in my prior acknowledged patents, wherein alternating current is the specific means for generating heat and at least one normally unstable salt forms the bath electrolyte, the heat generated by the passage of said current through said electrolyte maintaining the bath in molten condition and at heat treating temperatures.

More specifically, the present invention comprehends the internal heating of salt baths containing normally unstable salts by alternating current, such salts comprising alkali and alkaline earth metal sulfates, such as sodium sulfate, potassium sulfate, ammonium sulfate and magnesium sulfate; magnesium chloride, caustic alkalis, such as sodium and potassium hydroxides, also carbon and nitrogen-containing salts such as boron nitride, alkaline metal cyanides and cyanamides, boron carbide, calcium carbide, magnesium carbide, non-volatile ammonium salts, etc. The salt baths containing these normally unstable salts have relatively low melting points and are capable of use over wide temperature ranges. By the term "normally unstable salts" as used in this specification and the accompanying claims, I mean salts which normally decompose in crucible heated salt baths but which are stable in baths heated internally by alternating current.

In the use of salt baths for the heat treatment of steel and the like, where crucible pots containing the salt mixture have been externally heated by a gas flame or external resistance coils, for example, it was necessary to use a relatively stable salt or mixture of salts; otherwise, if unstable salts were used, any overheating or local superheating (which was difficult to avoid) caused the unstable salts to break down and form oxides which would adhere to the crucible pot and act as heat insulators, with the detrimental effect of seriously burning the metal pot and producing progressive local overheating and further breaking down of additional salts, so that cleaning and replenishment were frequently required. The oxides resulting from the breaking down of unstable salts collect like sediment or sand in the bottom of the crucible.

In the prior art it was not possible to employ the additions of sulfates, and other normally unstable salts, such as those listed above, in crucible-heated furnaces. This was due to the rapid breaking down of these compounds at temperatures frequently employed in annealing baths, this breaking down resulting in the accumulation of high melting residues in the bottom of the baths and eventually in the burning out of the crucibles. On account of these difficulties the prior art was in general limited to the use of stable salt mixtures having high fusion points with all the attendant disadvantages of such mixtures.

I have now found that lower melting mixtures of unstable salts can be employed when the salt bath is heated internally by electric means, as disclosed in my acknowledged patents. For example, I have found it possible to employ sulfates in amounts ranging up to 40 per cent by weight, proportions which were impossible to utilize in indirectly heated salt baths. I have found that these sulfate baths are particularly advantageous for use in the bright annealing of steels, for example. An addition of about 10 per cent of sulfates is sufficient to produce an improvement in prior art salt baths.

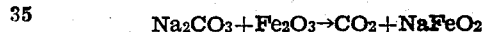
The addition of normally unstable salts to prior art salt baths, as accomplished in my present invention results in the production of baths with lower melting points and the invention thus has all the advantages attendant upon the use of low melting baths. These advantages are quicker heating of the baths to operating temperatures, a greater efficiency of heating and easier starting.

An illustration of a low-melting and easy-

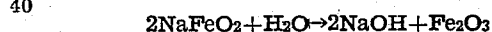
starting salt bath within the present invention is a bath containing sodium and potassium hydroxides. This bath can be operated at low temperatures and, since solid sodium and potassium hydroxides conduct electricity at temperatures as low as 200° F., it can be started at a remarkably low temperature. This bath can be employed advantageously in conjunction with a higher temperature bath containing sodium and potassium carbonates, for example in the heat treatment of rope wire and shovel blades.

I have found a convenient method for recovering the values from the quench bath solution which is employed in conjunction with the above hydroxide bath. By this method the drag over can be recovered either in the form of hydroxides or carbonates. In this method I usually employ a rotary evaporator consisting of a 6 or 8 inch standard iron pipe fired with a gun-type oil or gas burner. If it is desired to recover the values in the quench bath solution in the form of carbonates, the scale from the work is settled out of the solution and the carbon dioxide of the fuel flame converts any hydroxides into the corresponding carbonates.

On the other hand, if it is desired to recover the values in the quench bath solution in the form of hydroxides, the iron oxide scale, which accumulates in the quench bath from the work being processed, is added to the solution passed through the evaporator. This iron oxide reacts with the carbonates in the evaporator to form sodium and potassium ferrites, in accordance with the following equation:



The sodium ferrite thus formed can be readily converted into the hydroxide by treatment with hot water in accordance with the equation:



The iron oxide is regenerated in the last reaction and can be separated readily from the solution by settling and then reused.

It is thus seen that, when the hydroxide bath is used in conjunction with the carbonate bath, the values in the quench bath solutions can be recovered either in a form high in hydroxides or high in carbonates and then added to the corresponding low or high temperature salt bath, respectively. This constitutes an important advantage.

The combined use of hydroxide and carbonate salt baths is advantageous in carrying out interrupted preheating quenching operations. In the heat treatment of rope wire, for example, with hydroxide and carbonate baths, I have found it desirable to operate the carbonate baths, at a temperature of about 1550° F. and the hydroxide bath at a temperature ranging from about 350° to 650° F. The work is first treated in the high temperature bath and then quenched in the low temperature bath. This treatment results in a rope wire of greater ductility than is obtained by the usual process of heating to 1550°, quenching to room temperatures and then drawing back (tempering) at temperatures of 300° to 950° F. In connection with this particular heat treating process I have found that the recuperative and regenerative method, described in my Patent No. 1,916,407, can be employed advantageously. In this method the quenching heat is employed for preheating the work, thereby economizing heat. In the heat treating process described it is also possible to employ the method of my copending

application Ser. No. 9,645, wherein the heat treating baths are brought up to temperature by off-peak current and maintained at operating temperatures, if necessary, by small additional increments of current during the operation period. This results in a further economy in the present process.

The use of electrical heating by passing current through a molten salt would seem to imply that only those fused salts having relatively good stability would be useful; and that only those salts which are exceedingly stable under the conditions of external pot heating would be applicable. The discovery is highly surprising that internal heating by the electric current has less tendency to break down salt mixtures.

The advantages of electrical heating, as disclosed in my prior patents above referred to, include the direct application of the heat to the salt bath material itself, rather than a heat transfer through an intermediate medium such as a metal pot. Such advantages are also present in and are ancillary to the present invention. The application of electrolytic resistance heating to a salt material always involves considerations of stability against electrolysis and stability toward overheating at the electrodes. These considerations are solved in the present invention by the use of salts stable under conditions of electrolysis and having proper specific heats, specific resistances and heat conductivities to permit an alternating current of low voltage to pass therethrough without destroying their stability and with the production of temperatures useful in the heat treating of metals.

An additional advantage of my new process is that it provides a highly advantageous method of case hardening steel. In this method salts are added to the heat treating bath which contain the elements carbon or nitrogen, or carbon and nitrogen, these salts being soluble in the bath and being capable of transferring these elements to steel immersed in the bath for heat treatment.

In the prior art, case hardening has been accomplished by heating steel out of contact with the air while packed in carbon-rich material, such as charcoal, etc. Steel has also been case hardened by heating it in contact with fused potassium cyanide, with potassium ferrocyanide, or with acetylene or other gases containing carbon or nitrogen. While the use of fused cyanide baths is practiced to some extent commercially one important disadvantage of this method is that the pots burn out quickly and the temperature range and depth of penetration is limited. As the temperature is raised the cyanides deteriorate so that frequent replacement of the bath is required. In order to prevent burning out of the pots the expedient has even been employed of using alloy steel pots but these are expensive and their replacement delays production.

In my new case hardening method a small amount of at least one case hardening salt is added to the ordinary fused salt bath and this bath is heated internally by the passage of an alternating electric current through the bath, in accordance with the methods described in my acknowledged patents. I have found, surprisingly that the added salts exhibit a substantial stability when used in this fashion and that the heat treating baths can be used over long periods of time without replacement. All non-volatile, carbon or nitrogen-containing salts which are soluble in as well as inert towards the fused salt baths and which are capable of transferring

these elements to steel immersed in the baths for heat treatment are suitable for use in this connection. Examples of these salts are boron carbide, calcium carbide, magnesium carbide, magnesium cyanamide, boron nitride, alkaline metal cyanides and non-volatile ammonium salts. These salts can be added in small proportions, ranging from about 1/2 to 5 per cent by weight, any of the usual fused salt baths with the production of baths suitable for use in the case hardening of steel.

One specific heat treating bath which I have found useful in my new method of case hardening is a bath containing magnesium and potassium chlorides in the proportions required to give a melting point of about 750° F. and to which there has been added about 1 per cent by weight of a mixture of magnesium carbide and boron nitride the said added mixture containing magnesium carbide and boron nitride in substantially equal proportions. This bath cannot be employed in the ordinary fuel furnace without excessive deterioration. In fact in such furnaces this bath loses its effectiveness in case hardening steel after a few minutes use. The magnesium carbide and boron nitride can be added in proportions varying from about 0.5 to 3 per cent by weight.

It is possible to make suitable case hardening baths by adding cyanides to an eutectic mixture of magnesium chloride and potassium chloride. Or carbides of boron and calcium can be added with or without ammonium salts.

The use of a case hardening salt bath containing magnesium salts can be combined advantageously with the use of quenching baths containing ammonium salts, such as those described in my Patent No. 1,970,268. In this patent baths are described containing ammonium formate, or ammonium carbonate and sodium formate, these baths being capable of producing a bright finish upon the articles quenched therein. Aside from the advantages gained by the production of a bright finish, it is also possible to readily recover the salt bath material from the quench bath; that is, the material which is carried over by the work which is heat treated. The ammonium salts present in the quench bath prevent the separation of basic salts when the quenching bath is evaporated. And the ammonium salts of the quench bath are effective as case hardening agents when the recovered salts are re-used. The ammonium formate quenching bath not only gives a bright finish to case hardened steel quenched therein but also a harder case.

The above described method of recovering salt bath material from the quenching bath results in a very economical process. Thus the salt bath material can be recovered by simple evaporation of the quenching bath at a cost of about one twenty-fifth that of fresh raw materials.

As stated previously, it is possible by means of my new method to employ sulfates in relatively high proportions in salt baths. The addition of sulfates to several of the prior art salt baths produces an important improvement in these baths. For example, the well-known salt bath containing 29 per cent sodium chloride and 71 per cent calcium chloride has the disadvantage of being hygroscopic. This disadvantage is entirely obviated by the addition of from about 5 to 10 per cent of sodium sulfate.

Another salt bath to which sodium sulfate may be added with advantageous results is that de-

scribed in my Patent No. 1,520,744. In this patent a non-hygroscopic salt bath is employed containing about 52 per cent potassium chloride and 48 per cent sodium carbonate. An addition of sodium sulfate serves to materially lower the melting point of this bath. It can be added in proportions up to 40 per cent by weight. This new salt bath can be employed up to temperatures approaching 2000° F. without appreciable volatilization or sludge formation.

Another example of my invention is the addition of magnesium chloride to the salt bath described in my Patent No. 1,724,551. This bath contains from about 79 to 97 per cent of potassium chloride and from 3 to 21 per cent of anhydrous sodium metaborate. It has a melting point of about 1330° F., which is too high for some heat treating operations. The addition of magnesium chloride to this bath in small proportions reduces its melting point markedly.

In a specific embodiment of my case hardening method I took an automobile gear to be case hardened and heated it in a fused salt bath maintained at a temperature of about 1400° F., said bath containing a eutectic mixture of magnesium chloride and potassium chloride, as well as 1 per cent of magnesium cyanamide, the latter being a case hardening salt. The heat treated gear was then quenched by immersing it in an aqueous solution formed by dissolving in 100 pounds of water 4.1 pounds of ammonium carbonate and 5.9 pounds of sodium formate. It was found to have an excellent case hardened surface with an unusually bright finish.

After using the above heat treating and quenching baths for a period of about 24 hours, I evaporated the quenching bath and added the recovered salts to the heat treating bath. I found that this process can be repeated with only occasional additions of salts to make up for unavoidable losses.

As observed above, the invention permits much wider application of the use of salts for salt baths heretofore considered of no value for this purpose, and it opens up new uses for unstable salts and their admixtures in the heat treating art.

Various modifications may be made in the methods heretofore described without departing from the scope of the present invention. Those skilled in the art will readily comprehend such modifications as fall within the scope of the following claims.

What I claim is:

1. In the case hardening of steel, the process which comprises case hardening a steel article by dipping it in a fused salt bath containing an eutectic mixture of potassium chloride and magnesium chloride and also containing from about 0.5 to 3 per cent of a mixture of boron nitride and magnesium carbide, the said bath being maintained in fused condition and at heat treating temperatures by passing an alternating current therethrough.

2. In the case hardening of steel, the process which comprises establishing and maintaining a fused bath of salts containing a magnesium salt and a small proportion of at least one case hardening salt, the said bath being maintained at heat treating temperatures by the passage of alternating current therethrough, dipping steel articles in said bath in order to case harden the same and quenching by dipping said articles in an aqueous bath containing ammonium salts, evaporating said quenching bath and adding the salts thereby recovered to said fused salt bath.

3. The process of claim 2 wherein the said quenching bath contains ammonium formate.

5 4. A stable case hardening bath containing an eutectic mixture of potassium chloride and magnesium chloride and also containing from about 0.5 to 3 per cent by weight of a mixture of magnesium cyanamide and boron nitride, said bath being maintained fused at heat treating temperatures by passage of an alternating electric current therethrough.

10 5. A stable heat treating bath consisting substantially of a eutectic mixture of magnesium chloride and potassium chloride and also containing about 1 per cent of magnesium cyanamide as a case hardening salt, said bath being

maintained in fused condition at heat treating temperatures by the passage of an alternating electric current therethrough.

6. A stable heat treating bath consisting substantially of a eutectic mixture of magnesium chloride and potassium chloride and also containing a small amount of at least one case hardening salt selected from a class consisting of boron nitride, magnesium carbide and magnesium carbide and magnesium cyanamide, said bath being maintained in fused condition at heat treating temperatures by the passage therethrough of an alternating electric current.

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