SALT BATH FOR HEAT TREATING STEEL

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This invention relates to the heat treatment of steels and alloy steels and to improved salt baths and compositions therefor.

It is known that fused salt baths of widely different composition may be employed for the heat treatment of steels and that steel articles immersed in such salt baths will emerge after treatment carburised by the action of the mixture of fused salts, the depth of carbon penetration depending always on the precise conditions under which the treatment is carried out. It is common practice to employ for this purpose a fused mixture of cyanides and carbonates of the alkali metals or else such cyanide/carbonate mixtures in association with one or more of the halides of the alkali metals and in some cases the molten contents of the bath are composed of a mixture of cyanide and halides of the alkali metals and alkaline earth chlorides and carbonates. In most cases when such molten baths are used for heat treatment purposes it is usual to control the molten salt mixture with a layer of graphitic carbon.

The particular bath composition desirable for heat treatment of steel articles depends to a large extent upon the degree and depth of carburisation that is required in the treated product. If it is required that the carburised casing on the steel articles should be relatively small, for instance up to .020 to .025 inch then it is usual to employ fused salt mixtures of the cyanides and carbonates of the alkali metals or mixtures of these cyanides and carbonates with a halide or mixtures of halides of the alkali metals.

When greater depths of the carburised layer, or a better degree of saturation in the carburised case is required, it is usual to employ a salt composition consisting of a major proportion of the chlorides of the alkaline earth metals barium and strontium together with 10%—20% of alkali metal cyanide. There may also be present a minor proportion of an alkali metal halide.

While it is useful in cases where a relatively small degree of carburisation of the steel articles is required to use bath compositions containing mixtures of cyanides and carbonates of the alkali metals or mixtures of these with alkali metal halides the carburising potential of such baths is limited and where a thick casing is required on treated steel articles baths of other compositions must be used. The alkali halide/cyanide/carbonate baths are satisfactory, however, for many purposes and they have the advantage that the salt mixtures concerned are soluble in water and the salts therefore easily may be removed from the steel articles treated in the bath.

Although greater case depths can be attained by treating steel articles in molten salt baths containing barium chloride or strontium chloride with 10% to 20% of alkali metal cyanide such baths suffer from the defect that they leave a deposit on the articles treated which is insoluble in water or at the best only very sparingly soluble. The articles therefore require to be specially cleaned after treatment in the bath and if salt deposit is not entirely removed rusting is likely to occur.

We have now found an improved salt bath and compositions therefor which contain for the most part an alkali metal halide or a mixture of alkali metal halides and a lesser quantity of alkali metal cyanide together with 0.25% to 5.0% by weight of silicon.

According to the present invention therefore a fused salt bath and compositions therefor for the heat treatment of steels or alloy steels contain for the most part an alkali metal halide or mixture of alkali metal halides and a lesser quantity of alkali metal cyanide together with 0.25% to 5% by weight of silicon.

We prefer to include in the alkali metal halides a quantity of sodium fluoride suitably less than 10% by weight of the bath contents and this we have found maintains the carburising activity of the bath over a longer period.

The cyanide content of the bath must be less than that of the alkali metal halides and advantageously we use up to 15% by weight of alkali metal cyanide and preferably from 1% to 10% by weight.

The bath may be operated at any temperature above the fusion point of the salt mixture and as the temperature is increased above this point the rate of carburisation becomes greater but we prefer to operate at a temperature between 800° C. and 950° C.

One suitable method of operating the bath of our invention is to first make a melt of the alkali metal halides for example, sodium chloride and potassium chloride or a mixture of sodium chloride, potassium chloride and sodium fluoride and maintain the melt at a temperature of 750° to 950° C. Approximately 1% of silicon is then added, preferably in the form of powder and suitably 1%—10% by weight of sodium cyanide. Advantageously the bath is dredged at regular intervals, preferably each day and the sludge formed in the process of case hardening of the steel article is removed. At such intervals the bath is made up to the working level of its contents by further additions of the sodium/potassium chloride mixture or chloride/flouride mixture, as the case may be, and by addition of sufficient sodium cyanide to replenish losses. A fresh quantity of silicon power is then added, the amount of silicon added being dependent upon the particular working conditions of the bath. If for example, considerable aeration of the bath components takes place it may be necessary to increase the addition of silicon in order to remove the oxygen-containing products from the bath. After the silicon is added it may also be a convenient time to add powdered graphite to the bath so as to form a layer on the surface and it must be understood therefore that this invention envisages the presence of a powdered graphite layer in the bath whenever desirable.

The bath compositions of the present invention offer a number of advantages over salt baths which have been employed hitherto for heat treatment purposes. They possess all the desirable qualities of cyanide/carbonate baths; in particular the facilitates which adhering salt may be recovered from the treated articles by washing with water and also the wide range of temperature at which the bath can be operated satisfactorily. In addition, the salt bath compositions of our invention can be used either to confer on the articles treated cases equal in quality to the cyanide/carbonate baths and cases approaching in quality those of baths activated by cyanide and alkaline earth metal halide mixtures, without the attendant disadvantage of the salt composition being insoluble in water.

Certain of the highly alloyed case hardening steels after being the articles treated in a cyanide bath or in a cyanide/alkaline earth metal halide bath and subsequently quenched in oil often exhibit a soft surface layer. This is due to austenite remaining in the surface layers of the case
because of the relatively high proportion of nitrogen which is present in the surface layers. It is often necessary in these circumstances to submit the steel to sub-zero treatment in order to increase the hardness of the surface layers. When alloy steels are treated in baths of the present invention, however, a better hardness is achieved by the standard quenching procedures and no sub-zero treatment is necessary.

The following examples illustrate but do not limit our invention:

**Example 1**

A fused salt bath of the following composition was prepared and steel articles immersed therein:

- 23 lbs. sodium chloride
- 23 lbs. potassium chloride
- 3 lbs. sodium cyanide
- 0.5 lb. silicon powder

The bath contents were maintained at a temperature of 950° C. and the surface covered with a layer of graphite carbon while steel articles remained immersed in the fused salt mixture for a period of two hours.

After treatment the steel articles were allowed to cool slowly and on examination showed the following results:

- Total case depth = 0.032" (8% silicon cyanide)
- Depth to 0.6% carbon = 0.016" (8% silicon cyanide)
- Eutectoid depth = 0.008" (8% silicon cyanide)

After the bath had been in use for some time its cyanide content was raised to 8% sodium cyanide and then allowed to fall in strength from day to day during continuous use until only 1% remained in the bath. During this period sludge was removed daily and 8 ounces of silicon powder was added each day of 8 to 9 hours to maintain the carburising potential of the bath. Mild steel test pieces were treated daily in the bath, slowly cooled and their case depths measured. It was found that with as little as 1% of sodium cyanide present appreciable carburisation of the steel took place. After 2 hours treatment in the bath at 950° followed by slow cooling the following results were obtained:

<table>
<thead>
<tr>
<th>% Sodium Cyanide</th>
<th>% Sodium Cyanide</th>
<th>% Sodium Cyanide</th>
</tr>
</thead>
<tbody>
<tr>
<td>Inches</td>
<td>Inches</td>
<td>Inches</td>
</tr>
<tr>
<td>Total Case Depth</td>
<td>0.09</td>
<td>0.08</td>
</tr>
<tr>
<td>Depth to 0.6% Carbon</td>
<td>0.019</td>
<td>0.017</td>
</tr>
<tr>
<td>Eutectoid depth to 0.6% Carbon</td>
<td>0.007</td>
<td>0.006</td>
</tr>
</tbody>
</table>

**Example 2**

A fused salt bath of the following composition was prepared and steel articles immersed therein:

- 22 lbs. sodium chloride
- 22 lbs. potassium chloride
- 2.5 lbs. sodium fluoride
- 3 lbs. sodium cyanide
- 0.5 lb. silicon powder

The bath was operated over a period of 5 days at 950° C. and sodium cyanide was added daily in amount sufficient to maintain the cyanide content of the bath at approximately 5% by weight.

Steel test pieces were treated in the bath for a period of 2 hours and after removal and cooling the following results were obtained:

<table>
<thead>
<tr>
<th>Day of Run</th>
<th>Total</th>
<th>Case Depth to 0.6% Carbon</th>
<th>Eutectoid 0.9% Carbon</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Inches</td>
<td>Inches</td>
<td>Inches</td>
</tr>
<tr>
<td>1</td>
<td>0.010</td>
<td>0.018</td>
<td>0.001</td>
</tr>
<tr>
<td>2</td>
<td>0.015</td>
<td>0.016</td>
<td>0.008</td>
</tr>
<tr>
<td>3</td>
<td>0.015</td>
<td>0.015</td>
<td>0.007</td>
</tr>
<tr>
<td>4</td>
<td>0.015</td>
<td>0.012</td>
<td>0.010</td>
</tr>
<tr>
<td>5</td>
<td>0.015</td>
<td>0.019</td>
<td>0.006</td>
</tr>
</tbody>
</table>

In this case only one 8 ounce addition of silicone was made to the bath in the entire period of five days and although the total contents of the bath were of the order of 50 lbs. it is clear from the results obtained that the carburising activity of the bath was maintained during the entire period of working.

We claim:

1. A salt bath which is fusible for the heat treatment of steels and alloy steels comprising a predominate amount of at least one alkali metal halide, a lesser quantity of alkali metal cyanide, and 0.25% to 5% by weight of silicon.

2. The bath of claim 1 wherein the silicon content is 0.25% to 1.5%.

3. The bath of claim 2 wherein the alkali metal halide contains alkali metal fluoride in an amount up to 10% by weight of the bath contents and wherein the alkali metal cyanide is present in amount up to 15%.

4. The bath of claim 1 wherein the silicon is finely divided.

5. The bath of claim 1 wherein the alkali metal halide contains a small amount of alkali metal fluoride up to 10% by weight of the bath contents and the alkali metal cyanide is present in an amount of from 1 to 10% by weight.

6. The bath of claim 5 wherein the silicon is present in an amount of from 0.25% to 1.5% by weight.

7. The bath of claim 1 wherein the alkali metal halide is a member of the group consisting of sodium chloride, potassium chloride, and mixtures thereof.

8. The bath of claim 7 wherein the cyanide is sodium cyanide in an amount up to 15%.

9. The bath of claim 8 wherein the sodium cyanide is present in amount from 1 to 10% by weight and the silicon is present in amount from 0.25% to 1.5%.

10. The bath of claim 1 wherein the alkali metal halide contains up to 10% by weight of alkali metal fluoride, the balance of the alkali metal halide being a member of the group consisting of sodium chloride, potassium chloride, and mixtures thereof.

11. The bath of claim 10 wherein the cyanide is sodium cyanide in amount up to 15% by weight and the alkali metal fluoride is a sodium fluoride.

12. The bath of claim 11 in which the sodium cyanide is present in amount of from 1 to 10% by weight and the silicon is present in amount from 0.25% to 1.5%.

13. A process for the heat treatment of a member of the group consisting of steel and alloy steel which comprises heating the said member of the group in a bath obtained by fusing a mixture containing a predominate amount of at least one alkali metal halide, a lesser quantity of alkali metal cyanide, and from 0.25% to 5% by weight of the silicon.

14. A process as in claim 13 wherein the bath is further characterized in that an alkali metal fluoride is present in amount up to 10% by weight of the bath contents and the alkali metal cyanide is present in amount up to 15%.

15. The process of claim 14 wherein the bath is at a temperature of 800° to 950° C.

16. A process for the heat treatment of a member of the group consisting of steel and alloy steel which comprises heating said member of the group in a bath obtained by fusing a composition comprising a predominate amount of a plurality of alkali metal halides in which one of the alkali metal halides is an alkali metal fluoride in an amount up to 10% by weight of the bath contents, a quantity of alkali metal cyanide up to 15% and from 0.25 to 5% by weight of finely divided silicon, dredging the bath at intervals to remove sludge and replenishing the bath by further addition of alkali metal halide, alkali metal cyanide, and finely divided silicon as needed.

17. The process of claim 16 wherein the cyanide is
present in amount from 1 to 10% and the silicon is present in amount from 0.25 to 1.5%.

18. The process of claim 17 wherein the bath is heated to a temperature of 800 to 950° C.

19. A member of the group consisting of steel and alloy steel treated by the process of claim 13.

References Cited in the file of this patent

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