Patented Dec. 2, 1941

2,264,431

UNITED STATES PATENT OFFICE

2,264,431

HARDENING OF STEEL ARTICLES

Harold Bradley, Frodsham, England, assignor to Imperial Chemical Industries Limited, a corporation of Great Britain

No Drawing. Application March 28, 1940, Serial No. 326,467. In Great Britain April 4, 1939

9 Claims. (Cl. 148—15)

This invention relates to hardening steel articles, and more particularly to hardening articles of high carbon steel.

It is well known to modify the characteristics of steels by immersing them in baths of molten salts. Thus it is known to caseharden articles of iron, steel and alloys thereof by immersing them in a molten bath containing in addition to a cyanide a mixture of alkali metal and/or alkaline earth metal chlorides, and also an alkali metal carbonate. Again molten salt baths, such as fused mixtures of alkali metal and alkaline earth metal chlorides have been used to effect purely physical changes in the properties of iron or steel articles, as for example high carbon steels. Thus high carbon steels, i. e. steels containing more than approximately 0.6% carbon, are worked in a soft condition, and in order to harden them subsequently they may be heated for a suitable time in such a fused salt bath maintained at a suitable temperature and then quenched by immersion in brine, or otherwise. Usually small amounts of cyanogen compounds, e. g. alkali metal cyanides are also added to the bath to prevent superficial decarburisation of the articles during hardening, and baths have also been described which in addition contain small amounts of alkali metal carbonate to increase its fluidity at a given temperature. More than small amounts of carbonates have, however, been considered deleterious because they were considered liable to bring about decarburisation.

In use such baths tend to alter in composition through decomposition of the cyanide resulting in an accumulation of unwanted carbonate and also to decrease in volume through drag-out losses.

In order to maintain the bath at a comparatively constant composition it has been necessary to withdraw quantities of the fused salt bath in addition to the drag-out losses and to make up the volume of the bath by the addition of mixed chlorides, thereby readjusting the carbonate content to its initial small value; in addition it has been necessary to add quantities of cyanide from time to time to make up for that decomposed to carbonate. The quantities of the mixed chlorides and of the cyanides which have to be added can only be determined by periodic analyses of the fused salt bath and thus almost daily skilled supervision is required for a process which otherwise could be carried out by an unskilled operative. Even so it becomes necessary in time to reject the whole of the bath and recommence operation with a fresh charge of fused salts.

It is an object of the present invention to provide an improved salt bath for treating high carbon steel articles. It is a further object of the invention to provide an improved salt bath for treating high carbon steel articles which can be maintained in a satisfactory condition for use for much longer periods of time. It is a still further object of my invention to provide an improved process for hardening high carbon steel articles. Other objects of the invention will be apparent hereinafter.

I have found that by operating with baths containing a high carbonate content it is possible to omit the separate step of withdrawing part of the salt bath periodically prior to making up the volume of the bath, the accumulation of carbonate being prevented solely by the drag-out losses; moreover, in spite of what would have been expected from the prior art, I have not found that the high carbonate content has caused decarburisation to occur. It is thus possible to maintain the composition and the volume of the bath merely by adding the appropriate mixture of chlorides in the ratio in which they are present in the bath, with a small amount of cyanide to compensate for the loss through decomposition. Moreover, the bath can be maintained in a usable condition for much longer periods than hitherto.

According to the present invention, therefore, a fused salt bath for treating high carbon steel articles consists of a mixture molten at the temperature of operation and containing between 1 and 10% by weight of an alkali metal cyanide and between 60 and 75% by weight of an alkali metal carbonate, the remainder being one or more alkali metal chlorides and/or alkaline earth metal chlorides. Suitably the alkali metal carbonate is sodium carbonate, and the mixture of chlorides consists of two or more of the group consisting of sodium, potassium, barium and calcium chlorides.

According to a further feature of the invention I provide a process for hardening high carbon steel articles, i. e. steel articles containing at least 0.6% carbon, which comprises immersing the articles in such a fused salt bath until they have attained the temperature of the bath, and then quenching the articles, e. g. in brine.

A typical bath consists of 5% sodium cyanide, 67% sodium carbonate, 7% sodium chloride, 7% potassium chloride and 14% barium chloride.

In using such a bath it is maintained at a

suitable temperature for hardening high carbon steels, e. g. between 750° and 850° C. or preferably between 780° and 800° C. and the articles are immersed in the bath until they have attained the temperature of the bath and are then withdrawn and quenched in e. g. brine.

For small articles such as files the necessary time of immersion in the bath may be only a matter of seconds, e. g. 40 to 80 seconds while in other cases, depending on the size of the articles, times of the order of 2 to 3 minutes are suitable; in the case of large articles still longer times may be necessary. For the subsequent quenching brine is particularly suitable and articles with a clean dull appearance free from adherent salts are obtained. Other quenching media however, may be used satisfactorily, such as aqueous solutions of caustic soda, sodium cyanide, sodium carbonate and potassium carbonate.

In contrast to many cyanide-containing fused salt baths used for heat treating iron and steel and alloys thereof, it is possible to maintain the constitution and volume of the salt baths according to my invention by the addition of a single salt mixture. In using fused salt baths drag-out losses invariably occur, and in addition where such baths contain a cyanide, the cyanide content drops through decomposition to carbonate.

In baths according to the present invention, the relative rates of accumulation of carbonate through decomposition and of diminution through drag-out losses are of the same order, and the bath can, therefore, be maintained substantially at its original composition for much longer than has hitherto been possible by the addition of a mixture of alkali metal chlorides and/or alkaline earth metal chlorides in the proportion in which they are present in the bath, with an amount of the alkali metal cyanide. The relative amounts of the cyanide and of the chlorides in the mixture will be determined by the rate at which the former is lost through decomposition and the latter through drag-out losses.

The composition and amount of the salt mixture which is used for making up the bath will depend on the use which the bath is given, and the rate at which cyanide is decomposed, but for normal usage it may be taken that drag-out losses may be of the order of between 1 and 2% of the weight of the bath each day, and the daily rate of cyanide decomposition will be approximately the same. The composition and volume of the original bath, can thus generally be restored by adding a salt mixture containing the percentage of alkali metal and/or alkaline earth metal chlorides present in the bath, the remainder being alkali metal cyanide. Thus a bath having the composition 5% NaCN, 67% Na_2CO_3 and 28% alkali metal and alkaline earth metal chlorides can be maintained at a substantially constant composition by replacing the drag-out by a mixture containing 28% chlorides in the proportion in which they are present in the bath, the remainder being sodium cyanide.

I claim:

1. A fused salt bath for heat-treating high carbon steel articles consisting of a mixture molten at the operating temperature and containing between 1 and 10% by weight of an alkali metal cyanide and between 60% and 75% of an alkali metal carbonate, the remainder being at least one salt selected from the group consisting of alkali metal chlorides and alkaline earth metal chlorides.

2. A fused salt bath for heat-treating high carbon steel articles consisting of a mixture molten at the operating temperature and containing between 1 and 10% by weight of an alkali metal cyanide and between 60% and 75% of sodium carbonate, the remainder being at least two salts selected from the group consisting of sodium chloride, potassium chloride, barium chloride and calcium chloride.

3. A fused salt bath for heat-treating high carbon steel articles consisting of a mixture molten at the operating temperature and containing 5% sodium cyanide, 67% sodium carbonate, 7% sodium chloride, 7% potassium chloride, and 14% barium chloride.

4. A process for hardening high carbon steel articles which comprises the step of immersing the articles in a fused salt bath molten at the hardening temperature and consisting of between 1 and 10% by weight of an alkali metal cyanide and between 60% and 75% of an alkali metal carbonate, the remainder being at least one salt selected from the group consisting of alkali metal chlorides and alkaline earth metal chlorides, withdrawing the articles when they have attained the temperature of the bath, and quenching the articles, e. g. in brine.

5. Process according to claim 4 in which the fused salt bath consists of between 1 and 10% by weight of an alkali metal cyanide and between 60% and 75% of sodium carbonate, the remainder being at least two salts selected from the group consisting of sodium chloride, potassium chloride, barium chloride and calcium chloride.

6. Process according to claim 4 in which the fused salt bath consists of 5% sodium cyanide, 67% sodium carbonate, 7% sodium chloride, 7% potassium chloride, and 14% barium chloride.

7. Process for hardening high carbon steel articles which comprises immersing the articles in a fused salt bath maintained at between 750 and 850° C. and preferably between 780 and 800° C. said bath consisting of between 1 and 10% by weight of an alkali metal cyanide and between 60% and 75% of an alkali metal carbonate, the remainder being at least one salt selected from the group consisting of alkali metal chlorides and alkaline earth metal chlorides, withdrawing the articles when they have attained the temperature of the bath, and quenching the articles e. g. in brine.

8. In a process for hardening steel articles which comprises maintaining at hardening temperature a fused salt bath molten at that temperature and consisting of between 1 and 10% by weight of an alkali metal cyanide and between 60% and 75% of an alkali metal carbonate, the remainder being at least one salt selected from the group consisting of alkali metal chlorides and alkaline earth metal chlorides, the step which comprises maintaining the volume and composition of the bath by intermittently adding to the bath a salt mixture containing alkali metal and alkaline earth metal chlorides of the kind present in the said bath, and in the proportion in which they occur therein, the remainder of the salt mixture being an alkali metal cyanide.

9. Process according to claim 8, in which the salt bath has the composition 5% sodium cyanide, 67% sodium carbonate, and 28% alkali metal and alkaline earth metal chlorides, and the salt mixture added contains 72% sodium cyanide.

HAROLD BRADLEY.