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CASEHARDENING STEEL

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This invention relates to case-carburization of steel articles by treatment in molten cyanide case hardening baths and has as an object the increase in carburizing activity of such baths.

Cyanide case hardening baths basically are melts of substantially inert salts such as alkali metal carbonates or halides, containing an effective amount of alkali metal cyanide, e. g., 5 to 40% by weight.

Steel articles treated in such baths at temperatures around 1500 to 1800° F. acquire a mixed carbon-nitrogen case.

Several methods have been proposed for repressing the nitriding activity of cyanide baths and to accelerate the carburizing activity, so as to rapidly obtain a deep, carburized case, with little or no nitriding. The most successful results have been obtained by including alkaline earth metal salts in the melt. However, the concentration of alkaline earth metal salts required to successfully accomplish this object is large, consequently the cyanide replenishing agent used to maintain the bath at normal activity must contain in addition to the cyanide large percentages of alkaline earth metal salts, so that a high concentration of these will be maintained in the bath. Because of this, it is necessary to periodically bail out large parts of the bath in order to be able to replenish it with fresh salts. This is uneconomical. In addition, alkaline earth activated cyanide baths produce water insoluble residues on the treated work, interfering with the subsequent cleaning operations.

This invention has as an object to provide an improved process for case hardening ferrous articles. A further object is to provide a process for accelerating the carburizing action of molten cyanide case hardening baths. A further object is to provide an accelerated cyanide case hardening bath free from constituents that are or will form water insoluble materials upon work treated therein, i. e., an accelerated cyanide case hardening bath with easy washing characteristics. A further object is to provide an accelerated type cyanide case hardening bath which will minimize or eliminate the excessive bail-out of bath which is now necessary when replenishing the customary alkaline earth activated type accelerated bath. A still further object is to provide an accelerated cyanide case hardening bath in which the carburizing activity is markedly increased without significant effect upon the nitriding action of the bath, thus permitting one to obtain cases which are predominantly carbon in composition. Other objects will be apparent from the following disclosure.

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The above objects may be attained in accordance with my invention by adding to a carbonate containing cyanide bath an oxygen compound of boron or silicon and dispersing finely divided carbon throughout the bath. For example, the addition of 2% by weight of boron oxide (B_2O_3) to a standard cyanide case hardening bath containing normal concentrations of cyanide and carbonate (By the "standard" cyanide case hardening bath, I mean a bath composed of alkali metal cyanides, carbonates and halides, but not containing any catalysts to accelerate case hardening, such as for example, the alkaline earth metal salts. Normally, the cyanide content of these baths is held from 20 to 40% NaCN, the carbonate content will vary from 10 to 80% Na_2CO_3 with the balance alkali metal halide.) and added excess of graphite produced a marked increase in the carburizing action of the bath and had substantially no effect on its nitriding activity. Adding 5% of boron oxide produced an even more drastic increase in the bath's carburizing activity. Addition of boron oxide and carbon to a similar cyanide-carbonate bath, but with lower than the normal amount of cyanide present, also resulted in a drastic increase in the bath's carburizing activity. Prolonged operation of the bath at 1550° F. resulted in a slight falling off of its activity, thus necessitating small periodic additions of boron oxide to the bath to maintain its full activity.

The following examples serve to illustrate my invention:

Example 1

A cyanide bath containing approximately 25% sodium cyanide, 37.5% sodium carbonate and 37.5% sodium chloride was heated to 843° C. (1550° F.). Excess powdered graphite was next added until a layer about ¼'' thick remained on top of the molten bath. An SAE X1020 steel test bar (7'' long and 1'' in diameter) was immersed in the bath and treated for 1 hour, then removed from the bath and air cooled. An addition of

2% of the bath weight of boric acid anhydride was next added to the molten bath. A second SAE X1020 steel test bar was treated for 1 hour by immersing in the bath, following which it was removed and air cooled. The two steel test bars were washed free from adhering salt and six successive layers 0.004'' deep were cut from the periphery of each. The metal samples thus obtained were analyzed for both carbon and nitrogen. The results were as follows:

Cut No.	25% NaCN Bath With Added Graphite		25% NaCN Bath With Added Graphite and 2% B_2O_3	
	Per Cent C	Per Cent N	Per Cent C	Per Cent N
1	0.54	0.23	0.74	0.55
2	.41	.09	.59	.10
3	.29	.02	.38	.02
4	.24	.02	.29	.02
5	[1].23	[1].01	.24	[1].01
6	.23		[1].23	
Units	56	32	109	65

[1] Core.

Carbon and nitrogen "units" given in the above and succeeding tables herein are a measure of the amounts of carbon and nitrogen taken up by the steel. The carbon units are calculated by subtracting the percentage of carbon in the core from each of the percentages of carbon found in the successive 0.004'' radial cuts, adding the resulting figures and multiplying the sum by 100. The nitrogen units are calculated in the same way, using the results of nitrogen analysis.

Example 2

A cyanide bath containing about 33⅓% sodium cyanide, 33⅓% sodium carbonate, and 33⅓% sodium chloride was heated to 843° C. (1550° F.). Excess powdered graphite was added until a layer about ¼'' thick remained on top of molten bath. About 5% of the bath weight of boric acid anhydride was added to the molten bath. A bar of SAE X1020 steel (similar to those described in Example 1) was treated by immersing for 1 hour in the molten bath. After the bar was removed, air cooled, and washed, successive 0.004'' deep cuts were removed from the surface for carbon and nitrogen analysis. The results obtained were as follows:

Cut No.	Percent Carbon	Percent Nitrogen
1	0.80	0.46
2	.77	.05
3	.54	.01
4	.32	.01
5	.26	
6	.23	
Units	154	49

Example 3

A cyanide bath containing about 18% sodium cyanide, 37% sodium carbonate, and 45% sodium chloride was heated to 843° C. (1550° F.). Excess powdered graphite was added to the melt. Finally, 5% of the bath weight of boric acid anhydride was added to the bath. A bar of SAE X1020 steel was treated for 1 hour in the bath in a fashion similar to that described in Examples 1 and 2. Carbon and nitrogen analyses of the

gradient cuts removed from the surface of the test bar showed the following results:

Cut No.	Percent Carbon	Percent Nitrogen
1	0.78	0.32
2	.64	.04
3	.43	.01
4	.28	.01
5	.25	
6	.23	
Units	123	34

The specifications for SAE X1020 steel are:

0.15–0.25% carbon
0.70–1.00% manganese
0.045% phosphorus, maximum
0.055% sulfur, maximum

The SAE X1020 steel bars used in the above example contained 23% carbon, as shown by the results tabulated above.

In practicing my invention, I utilize carbonate-containing baths of molten alkali metal cyanide, e. g., cyanides of sodium, potassium, lithium or other alkali metals, with or without other alkali metal salts. I prefer to utilize mixtures of one or more alkali metal cyanides with an alkali metal halide (e. g., chloride, bromide or iodide) and an alkali metal carbonate, containing about 5 to 40% by weight of cyanide. I disperse in the melt not less than 1% by weight, and generally not more than 15% by weight, of finely divided carbon. This is best accomplished by adding an excess of the carbon to the bath, so that in addition to that dispersed, there is a layer of carbon floating on the baths. Any desired form of free carbon can be used, graphite being generally preferred. I also add to the bath 1 to 20% by weight of an oxygen compound of boron or silicon, preferably boron oxide (B_2O_3). In place of boron oxide, I may use other oxygen compounds of boron or silicon which are more acidic than alkali metal carbonates, for example, alkali metal borates, silica or alkali metal silicates.

The bath must contain at least one mole of carbonate for each mole of boron oxide or its equivalent added to the bath, and preferably a 5% excess over that amount. Larger amounts of carbonate may be used, as desired. For example, a bath consisting of sodium carbonate with 10–30% by weight of sodium cyanide and 1 to 20 by weight of boron oxide is suitable.

Steel articles are carburized according to my invention by immersing them in the bath, which is maintained at a temperature within the range of 1450 to 1850° F.

Since there is a slight decrease in carburizing activity when the bath is operated over a prolonged period of time, it will be necessary to replenish it periodically with fresh boron oxide or its equivalent, while maintaining a sufficient excess of carbon in the melt. Periodic replenishments of cyanide-rich material will also be necessary to maintain the cyanide content of the bath at 5–40%. Fresh carbonate may have to be added if there is an insufficient amount formed from the decomposition of the cyanide, but generally carbonate additions are not required, except as may be required to compensate for drag-out. The bath can be operated for prolonged periods of time with much less bail-out than with the alkaline earth metal salt activated cyanide baths.

One of the advantages of the process is that it permits one to obtain accelerated case hardening

in a molten cyanide bath by increasing the carburizing action of the melt instead of its nitriding activity. This is of particular value for those applications in which high nitrogen cases are detrimental. A second advantage of the process is that it permits one to obtain accelerated case carburizing in a cyanide-containing bath without introducing compounds which make subsequent washing of the treated parts difficult. Another advantage of the process is that it permits accelerated case carburizing without necessitating the bail-out of large quantities of the operating bath when making replenishments, as is necessary with some alkaline earth activated type accelerated cyanide case hardening baths.

I claim:

1. The case hardening process which comprises treating steel articles in a molten salt bath consisting of 5 to 40% by weight of alkali metal cyanide, 1 to 20% by weight of an oxygen-containing boron compound more acidic than alkali metal carbonates, at least one mole of alkali metal carbonate for each mole of said boron compound present, 1 to 15% by weight of finely divided carbon dispersed in the bath and any balance alkali metal halide, at a temperature of 1450 to 1850° F.

2. The case hardening process which comprises treating steel articles in a molten salt bath consisting of 5 to 40% by weight of alkali metal cyanide, 1 to 20% by weight of boron oxide, at least one mole of alkali metal carbonate for each mole of boron oxide present, 1 to 15% by weight of finely divided carbon dispersed in the bath and any balance alkali metal halide at a temperature of 1450 to 1850° F.

3. The case hardening process which comprises treating steel articles in a molten salt bath consisting of 5 to 40% by weight of alkali metal cyanide, 1 to 20% by weight of borax, at least one mole of alkali metal carbonate for each mole of borax present, 1 to 15% by weight of finely divided carbon dispersed in the bath, and any balance alkali metal halide, at a temperature of 1450 to 1850° F.

4. The case hardening process which comprises treating steel articles in a molten salt bath consisting of about 20 to 40% by weight of sodium cyanide, 1 to 20% by weight of boron oxide, at least 5% more than one mole of sodium carbonate for each mole of boron oxide present, 1 to 15% by weight of finely divided carbon dispersed in the bath and any balance sodium chloride at a temperature of 1450 to 1850° F.

5. The case hardening process which comprises treating steel articles in a molten salt bath consisting of about 20 to 40% by weight of sodium cyanide, 1 to 20% by weight of borax, at least 5% more than one mole of sodium carbonate for each mole of borax present, 1 to 15% by weight of finely divided carbon dispersed in the bath and any balance sodium chloride at a temperature of 1450 to 1850° F.

6. The case hardening process which comprises treating steel articles in a molten salt bath consisting of 20 to 40 parts by weight of sodium cyanide, 30 to 45 parts by weight of sodium chloride, 30 to 40 parts by weight of sodium carbonate, 2 to 5 parts by weight of boron oxide and having 1 to 15% by weight of finely divided carbon dispersed in the bath, at a temperature of 1450 to 1850° F.

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