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CASE HARDENING

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This invention relates to case hardening of fer-  
rous metals and particularly to improvements in  
the use of molten cyanide baths to produce a hard  
case on finished or partly finished articles of iron,  
steel, or alloy steels.

The ordinary case hardening of ferrous articles  
in molten baths is accomplished by immersing the  
object in a molten bath containing a cyanide  
compound; many varied bath compositions have  
been proposed for this purpose. During treat-  
ment, transfer of carbon and some nitrogen to the  
ferrous article takes place in the bath and a  
"case" is produced; this is commonly called car-  
burizing from the fact that predominantly carbon  
is transferred to the article. It has been pro-  
posed to case harden by means of a bath contain-  
ing small amounts of compounds of boron, nitro-  
gen and carbon, whereby a case containing these  
three elements is produced. Carburization has  
likewise been accomplished by heating ferrous  
metal articles and sprinkling them with a coat-  
ing of aluminum sulfate, borax, and potassium  
cyanide. When this mixture is employed as a  
bath however, it forms a viscous mass which oxi-  
dizes rapidly, deposits metallic aluminum on the  
metal being treated therewith and is expensive to  
maintain.

Nitriding is the production of a high nitrogen  
case on ferrous articles. This is done, for exam-  
ple, by treating alloy steels with gaseous am-  
monia. This is also accomplished by treating al-  
loy steels in fused salt baths of high metal cyanide  
content at temperatures below 600° C.; this  
method, however, produces a relatively shallow  
or thin case and is not applicable to plain carbon  
steels.

An object of this invention is to produce a tough  
case having a high nitrogen content on ferrous  
metal articles, and, specifically to produce such a  
case by treatment in a fused salt bath. A still  
further object is to provide means whereby such  
case may be produced on iron or plain carbon  
steel, as well as on alloy steels. Other objects  
will be hereinafter apparent.

I have discovered that the above objects may  
be attained by treating ferrous metal articles in  
a fused salt bath which contains at least 5% of  
cyanogen compounds; for instance metal cyanide,  
a small amount of a boron compound and sub-  
stantially no alkaline earth compounds.

The presence of the boron compound decreases  
the carburizing action of a bath containing cyan-  
ogen compounds and increases the nitriding ef-  
fect. However, if substantial amounts of alka-  
line earth compounds are present, or if the cyano-  
gen compound content is below 5% by weight,  
the boron compound has substantially no effect  
on the case hardening properties of the bath.

I have found that quite varied amounts of  
boron compound added to the cyanide contain-

ing melt will give this control of the case. I have  
used up to 20% by weight of boron compound,  
calculated as B<sub>2</sub>O<sub>3</sub> with excellent results; pref-  
erably I use about 1% by weight B<sub>2</sub>O<sub>3</sub>. I have  
added the boron in the form of various com-  
pounds soluble in the bath, such as sodium borate  
and boron oxide; preferably I use boron oxide.  
I do not wish to be limited however in the  
amounts stated nor the compounds, since larger  
amounts and other compounds of boron may be  
used for the purpose stated within the scope of  
my invention.

I have obtained improved nitriding action upon  
steels with cyanide baths containing boron op-  
erated at from 550° C. to 860° C. The best bal-  
ance between nitrogen content and diffusion  
depth is ordinarily obtained at 790–845° C. At  
860° C. the effect of the boron is still in evidence  
but at this temperature the surface nitrogen con-  
tent is markedly lower than that obtained at  
825° C. At 550° C. there is a noticeable nitriding  
action with baths containing boron but a rela-  
tively shallow case is obtained. The results in-  
dicate that temperatures less than 550° C. could  
likewise be used but that in such cases very shal-  
low nitrogen penetration would be obtained.

I have used boron oxide as an addition agent  
in fused salt baths containing from 5% to sub-  
stantially 100% of metallic cyanide in the ab-  
sence of alkaline earth metal compounds and in  
each case I have thereby increased the nitriding  
action of the bath.

The following examples serve to illustrate my  
process.

Example 1

Two cyanide baths each containing approxi-  
mately 15% sodium cyanide, 65% sodium chlo-  
ride, and 20% potassium chloride, were heated  
to 825° C.; to one bath was added approximately  
1% by weight of boron oxide. These baths were  
aged for two hours at this temperature and a  
steel bar, S. A. E. 1020, (0.15–0.25% carbon) was  
suspended in each bath for one hour. The bars  
were removed, washed free from adhering bath,  
and four successive layers 0.004" deep were cut  
from the periphery of each. The eight samples  
of metal thus obtained were analyzed for both  
carbon and nitrogen. The results were as fol-  
lows:

Cut number	15% NaCN bath		15% NaCN bath+1% B <sub>2</sub> O <sub>3</sub>	
	Percent carbon	Percent nitrogen	Percent carbon	Percent nitrogen
1.....	0.30	0.85	0.14	1.84
2.....	0.28	0.37	0.24	0.93
3.....	0.25	0.12	0.13	0.26
4.....	0.24	0.04	0.14	0.03



*Example 2*

Two cyanide baths containing about 45% sodium cyanide and about 55% sodium chloride were heated to about 815° C. and allowed to stand at that temperature until the cyanide content of each was reduced to approximately 25%. To one bath was added approximately 1% by weight of boron oxide. These baths were maintained at about 815° C. and S. A. E. 1035 steel bars were suspended in each bath for thirty minutes. The bars were then cleaned and four cuts 0.003 inches deep from each were made as described in Example 1. These analyzed as follows:

Cut number	24% NaCN bath		24% NaCN+1% B <sub>2</sub> O <sub>3</sub>	
	Percent carbon	Percent nitrogen	Percent carbon	Percent nitrogen
1.....	0.52	0.47	0.44	1.74
2.....	0.47	0.05	0.41	0.53
3.....	0.39	-----	0.40	0.11
4.....	0.40	-----	0.40	-----

*Example 3*

Two cyanide baths containing about 47% potassium cyanide and about 53% sodium cyanide were heated to 555° C. To one of these baths was added approximately 1% by weight of boron oxide. Strips of steel 0.01 inches thick were suspended in each bath for two hours. The strips were cleaned, broken into small pieces and analyzed for carbon and nitrogen. The results were as follows:

47% KCN+53% NaCN bath		47% KCN+53% NaCN+1% B <sub>2</sub> O <sub>3</sub>	
Percent carbon	Percent nitrogen	Percent carbon	Percent nitrogen
0.20	0.10	0.20	0.16

*Example 4*

Two cyanide baths each containing approximately 20% sodium cyanide and 80% sodium chloride and sodium carbonate were heated to 815° C.; to one bath was added approximately 1% boron oxide. An alloy steel bar S. A. E. 5135 (0.8-1.1% Cr. 0.30-0.40 C., 0.3-0.4% Mn.) was suspended in each bath for one hour. The bars were removed, washed free from adhering bath, and four successive layers 0.004" deep were cut from the periphery of each. The samples of metal thus obtained were analyzed with the following results:

Cut number	20% NaCN bath		20% NaCN bath+1% B <sub>2</sub> O <sub>3</sub>	
	Percent carbon	Percent nitrogen	Percent carbon	Percent nitrogen
1.....	0.52	1.04	0.43	1.45
2.....	0.53	0.37	0.54	0.68
3.....	0.43	0.08	0.48	0.07
4.....	0.36	trace	0.36	Trace.

*Example 5*

Two 25% cyanide baths were made up; one containing 75% sodium chloride and carbonate, and the other 20% sodium borate and 55% sodium chloride and carbonate. A S. A. E. 1020 steel bar was suspended in each of these baths for one hour at 825° C. These bars were then

cleaned and four successive layers 0.004" deep were cut from the periphery of each. The samples thus obtained were analyzed with the following results:

Cut number	25% cyanide bath		25% cyanide+20% borate bath	
	Percent carbon	Percent nitrogen	Percent carbon	Percent nitrogen
1.....	0.46	0.87	0.36	1.31
2.....	0.32	0.20	0.33	0.41
3.....	0.20	0.08	0.22	0.06
4.....	0.17	0.08	0.19	0.05

By the use of my method it is possible to use a bath with a wide range of cyanide content, and obtain an increased nitriding action upon the ferrous metal treated therewith. I have obtained cases containing from 1.0-2.3% nitrogen in the first 0.004 inch layer and from 0.2-1.0% nitrogen in the second 0.004 inch layer.

My invention is satisfactory for nitriding iron and the less expensive plain carbon steels as well as alloy steels. The deeper case produced by my method lends greater strength and wearing properties to the metal so treated than can be obtained in the ammonia nitriding process in the same length of time. This is due to the fact that the temperature of ammonia nitriding is definitely limited to the temperature at which the ammonia dissociates to such extent that the desired nitriding is obtained, while my process may be operated at much higher temperatures, which cause more rapid diffusion and deeper penetration of nitrogen into the metal. The case obtained by my process is not only deeper but also is more gradual than that produced by ammonia nitriding. At times the case produced by the ammonia method is so distinct from the rest of the metal that this case tends to break off, while by the use of my method the nitride case contains progressively more nitrogen nearer the surface of the metal. The results obtained by my method are also much more consistent than those obtained by the ammonia gas treatment so that one can more readily predict the depth of the case by my invention than by the use of gaseous ammonia. This fact is of great value in that a specified depth of case can be obtained by some predetermined length of treatment.

My invention may be carried out at higher temperatures than is possible with other methods of nitriding with fused salt baths, making possible a more rapid penetration of nitrogen. Thus it is not necessary to make up special, low melting salt mixtures to carry out my method. Since the amount of cyanide decomposition varies directly with the concentration of cyanide, nitriding by my method, using cyanide baths with low cyanide concentration is much more economical than using a high cyanide bath as required by prior methods. The case produced by my method shows much deeper nitrogen penetration in a much shorter time than has previously been possible.

A cyanide bath, as I refer to it in the following claims, is any bath of fused salts, which contains in excess of 5% of cyanogen compounds, for instance alkali cyanides or cyanates.

I claim

1. The process comprising treating ferrous metal articles in a cyaniding bath consisting of more than 5% by weight of an alkali metal cyan-



- ogen compound and a boron compound, the remainder of said bath being essentially made up of alkali metal salts commonly used in cyaniding baths.
- 5 2. The process comprising treating ferrous metal articles in a cyaniding bath consisting of more than 5% by weight of an alkali metal cyanogen compound and boron oxide, the remainder of said bath being essentially made up of alkali metal salts commonly used in cyaniding baths. 80
- 10 3. The process comprising treating ferrous metal articles in a cyaniding bath consisting of more than 5% by weight of an alkali metal cyanogen compound and 1-20% of a boron compound, the remainder of said bath being essentially made up of alkali metal salts commonly used in cyaniding baths. 85
- 15 4. The process comprising treating ferrous metal articles in a cyaniding bath consisting of more than 5% by weight of an alkali metal cyanogen compound and about 1% of boron oxide, the remainder of said bath being essentially made up of alkali metal salts commonly used in cyaniding baths. 90
- 20 5. The process comprising treating ferrous metal articles with a molten bath consisting of more than 5% by weight of sodium cyanide, a boron compound and the remainder of said bath being made up of alkali metal salts commonly used in the preparation of cyanide baths. 95
- 25 6. The process comprising treating ferrous metal articles with a molten bath consisting of more than 5% by weight of sodium cyanide, about 1% by weight of boron oxide and the remainder of said bath being made up of alkali metal salts commonly used in the preparation of cyanide baths. 100
- 30 7. The process comprising treating ferrous metal articles in a molten bath consisting of 5% to 99% by weight of an alkali metal cyanide, 20% to 1% by weight of a boron compound and 75% to 0% by weight of alkali metal salts commonly used as diluents in cyanide baths. 105
- 35 8. The process comprising treating steel articles in a molten bath consisting of 10-45% by weight of sodium cyanide, approximately 1% by weight of boron oxide and 89-54% by weight of alkali metal salts commonly used in cyanide baths and maintained at 780°-845° C. 110
9. A composition of matter consisting of more than 5% by weight of an alkali metal cyanogen compound and a compound of boron, and alkali metal salts commonly used in cyanide baths.
10. A composition of matter consisting of more than 5% by weight of alkali metal cyanide, from 1-20% by weight of a boron compound and alkali metal salts commonly used in cyanide baths. 115
11. A composition of matter consisting of more than 5% by weight of sodium cyanide, about 1% by weight of boron oxide, and alkali metal salts commonly used in cyanide baths. 120
12. A composition of matter comprising a mixture consisting of 5% to 99% by weight of alkali metal cyanide and 20% to 1% by weight of a boron compound, and 75% to 0% by weight of alkali metal salts commonly used as diluents in cyanide baths. 125
13. A composition of matter comprising a mixture consisting of 10%-45% by weight of sodium cyanide and about 1% by weight of boron oxide, and 89-54% by weight of alkali metal salts commonly used in cyanide baths. 130
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