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CASEHARDENING

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This invention relates to case hardening steel and more particularly to case hardening steel by treatment in a fused salt bath containing alkali metal cyanide.

A common method of case hardening steel consists in treating steel in a fused bath of alkali metal cyanide, with or without diluent salts such as alkali metal carbonates, halides and the like. Such a bath gives a carburized case having a relatively high nitride content. For many purposes, it is desirable to decrease the amount of nitriding and increase the amount of carburizing in such operations. It is also desirable to accelerate the carburizing activity of such baths, to obtain deeper cases in shorter time of treatment.

One object of the present invention is to provide an improved method of case hardening by means of a fused cyanide bath. A further object is to modify a cyanide case hardening operation so as to decrease the nitriding effect and increase and accelerate the carburizing effect. A further object is to provide case hardening compositions and case hardening baths suitable for obtaining the above objects. Still other objects will be apparent from the following description of my invention.

The above objects may be attained in accordance with the present invention by the addition of a small amount of titanium cyanonitride, titanium carbide or a mixture thereof to a molten salt bath containing alkali metal cyanide. Titanium cyanonitride (also known as "titanium carbonitride") is a known commercial product comprising a compound of titanium with varying amounts of carbon and nitrogen, as described in the textbook "Titanium" by W. M. Thomton, Chemical Catalog Co., 1927, page 53.

Typical analysis of a commercial titanium cyanonitride follows:

	Per cent
Ti	80.0
C	3.0
N	6.8
O	6.6
Fe and other impurities	4.2

The combined oxygen is present as titanium oxide impurity in the cyanonitride. My invention is not restricted to the use of the particular grade of titanium cyanonitride shown by the above analysis but I may use various grades of cyanonitride which may be free of oxide or contain up to 10% by weight of oxide and in which the carbon and nitrogen contents may vary over in a wide range. Thus, for the purpose of defining my invention, titanium cyanonitride may be considered as a compound of titanium with variable amounts of carbon and nitrogen and it may be pure or more or less contaminated with oxide or other impurities.

In practicing my invention, I prepare a molten alkali metal cyanide bath of the conventional type containing 10 to 50% by weight of cyanide and add to this a small amount of titanium cyanonitride or titanium carbide as activator. I prefer the activator in finely-divided form, for example, 100 mesh size or smaller, in an amount from 1 to 10% by weight of the bath. Generally I have obtained the best results by adding 2 to 5% by weight of the activator in finely-divided form. However, it is not essential to add finely-divided material, as I may obtain equivalent results by adding granular material of relatively large mesh size or even large pieces or briquets of cyanonitride but in such cases larger amounts usually are required. I have found that when a large amount of the activator is added, a relatively small amount, for example, in the neighborhood of around 5% by weight, dissolves in the cyanide bath, while the excess slowly dissolves and maintains continuous bath activity.

In order to obtain good results, I have found it necessary to maintain in the case hardening bath an alkali metal cyanide concentration of not less than 10% by weight. I prefer to maintain a cyanide concentration of 20 to 30% by weight and to dilute the bath with alkali metal carbonates or halides or both. However, if desired, pure alkali metal cyanide may be used to practice my invention. I prefer to utilize case hardening baths which are substantially free from alkaline earth metal compounds, including magnesium compounds or which contain not more than about 5% by weight of alkaline earth metal compounds.

The temperature of the bath preferably is maintained as in conventional cyanide case hardening operations, for example, at 700 to 900° C. For example, I have obtained excellent results by operating the bath to case harden steel at temperatures in the neighborhood of 800 to 860° C. However, my invention is not restricted to these temperatures, as I may operate at any temperature suitable for cyanide bath operations.

I have found that the addition of cyanonitride to the case hardening bath also increases the activity of the bath resulting in more rapid carburization to produce a deeper effective carbon

case in a shorter time than a plain cyanide bath.

In a preferred mode of practicing my invention, I melt a mixture of sodium cyanide and sodium carbonate containing about 30% of the cyanide and bring it to the temperature desired for case hardening, for example, at 820 to 850° C., and then add thereto 1 to 2% by weight of finely-divided titanium cyanonitride which has been screened to finer than 100 mesh. The bath is analyzed for cyanide from time to time and cyanide is added as required to maintain the cyanide concentration at 20 to 25% by weight. Also, during the operation the activity of the bath is maintained by hourly additions of from 0.01 to 0.10% by weight of the titanium cyanonitride.

For replenishing the bath, I prefer to prepare a composition containing from 60 to 98% of sodium cyanide and 2 to 40% by weight of titanium cyanonitride or titanium carbide, with or without diluent salts such as alkali metal halides or carbonates and to add this composition at hourly intervals or as required to maintain the desired degree of activity caused by the addition of the cyanonitride. As such replenishing mixture, I generally prefer to use a mixture containing approximately 10 parts by weight of sodium cyanide to one part by weight of titanium cyanonitride.

Example 1

A mixture of sodium cyanide and sodium carbonate containing 30% by weight of the cyanide was melted and bars of S. A. E.-1020 steel were carburized by treating the molten bath for 1 hour at 840° C. This bath had a low cyanate content and during the operation described below, an effective scum was maintained on the bath surface to prevent increase in the cyanate content. The bath was then activated by the addition of 2% by weight of titanium cyanonitride which had been ground to 100 mesh size or finer and other bars of the same steel then were treated in the bath for 1 hour.

The carbon and nitrogen gradients of the treated bars then were determined by cutting successive layers 0.004 inch thick from the bars and analyzing each layer for carbon and nitrogen. While the bars were being treated, samples of the bath were taken and analyzed for cyanide and cyanate. The following results were obtained:

Cut	Before adding the cyanonitride		After adding the cyanonitride	
	Percent C	Percent N_2	Percent C	Percent N_2
1	0.27	0.25	0.64	0.40
2	0.27	0.02	0.50	0.04
3	0.25	0.01	0.31	0.02
4	0.22	0.01	0.25	0.01
5	0.23		0.22	
6			0.22	
Percent NaCN in bath	28.22		27.30	
Percent NaCNO in bath	0.97		0.95	

Example 2

A molten bath was prepared as in Example 1, containing about 2% by weight of titanium cyanonitride. This bath was operated over a period of two days at a temperature of about 840° C. to carburize S. A. E.-1020 steel bars, the bars being treated for one hour in the bath. Carbon and nitrogen gradients and the cyanide content of the bath were determined as in Example 1. The following results were obtained:

Cut	Steel bar samples					
	A		B		C	
	Percent C	Percent N_2	Percent C	Percent N_2	Percent C	Percent N_2
1	0.71	0.55	0.75	0.58	0.79	0.43
2	0.63	0.09	0.61	0.09	0.74	0.10
3	0.43	0.02	0.39	0.04	0.47	0.03
4	0.28	0.01	0.30	0.02	0.33	0.01
5	0.24		0.24		0.25	
6	0.23		0.23		0.22	
Percent NaCN in bath	24.86		24.37		25.59	
Percent NaCNO in bath	1.26		0.92		1.14	

Example 3

A molten cyanide bath was prepared as in Example 1 and activated by the addition of 2% by weight of titanium carbide. This bath was operated over a period of 5 days, during which time sodium cyanide was added as required to maintain the sodium cyanide content at approximately 23% by weight, and bath activity was maintained by hourly addition (during daily 8 hours of operation) of 0.02% by weight of titanium carbide. Carbon and nitrogen gradients were determined as in the preceding example. Following are typical results obtained in the treatment of S. A. E.-1020 steel bars; the data being arranged chronologically, from left to right:

Cut	Steel bar samples							
	A		B		C		D	
	Per cent C	Per cent N_2	Per cent C	Per cent N_2	Per cent C	Per cent N_2	Per cent C	Per cent N_2
1	0.76	0.32	0.74	0.37	0.72	0.32	0.68	0.44
2	0.52	0.02	0.55	0.02	0.54	0.02	0.44	0.02
3	0.32	0.01	0.35	0.01	0.31	0.01	0.30	0.01
4	0.25		0.27		0.25		0.24	
5	0.22		0.23		0.23		0.22	
Per cent NaCN in bath	23.05		23.17		21.94		23.19	
Per cent NaCNO in bath	1.89		1.38		1.15		0.88	

An advantage of my invention is that it produces a deeper carbon case than a plain cyanide bath and in shorter time. At the same time, the solidified bath adhering to treated work is entirely water-soluble and easily washed off, the washing characteristics being equally as good as the ordinary plain cyanide bath.

A further advantage, not possessed by plain unactivated cyanide baths, is that the bath may be operated with a protective covering of graphite or carbonaceous scum floating on the bath surface, which protects the bath from the air. The use of such protective floating layers is very desirable, having a number of advantages and represents a preferred mode of practicing my invention. The protective layer decreases the formation of disagreeable fumes of finely-divided sodium carbonate which often arise from cyanide baths. More important, it decreases heat radiation from the bath, thus resulting in a saving of fuel required to heat the bath and often prevents overheating, thus materially increasing the effective life of the bath container and furnace. The

protective layer, by exclusion of air, also greatly decreases the rate of cyanide decomposition, thus making the operation more economical and facilitating control of cyanide concentration. In operating a plain cyanide bath, not activated by my method, good results usually are not obtained with such protective layer. In such bath, the protective layer acts to markedly decrease the carburizing activity of the bath. I have found that the activity of my herein-described bath depends on the amount of titanium cyanonitride or carbide added and is substantially independent of the presence of a protective layer of carbon or the like.

I claim:

1. The process for case carburizing steel which comprises treating steel articles in a molten bath containing 10 to 50% by weight of alkali metal cyanide and a small amount of a titanium compound selected from the group consisting of titanium cyanonitride and titanium carbide, the remainder of the bath being composed chiefly of at least one salt selected from the group consisting of alkali metal carbonates and halides.

2. The process for case carburizing steel which comprises treating steel articles in a molten bath containing 10 to 50% by weight of alkali metal cyanide the remainder composed chiefly of at least one salt selected from the group consisting of alkali metal carbonates and halides and a small amount of a titanium compound selected from the group consisting of titanium cyanonitride and titanium carbide, said bath containing not more than about 5% by weight of alkaline earth metal compounds and being maintained at a temperature of about 700 to 900° C.

3. The process for case carburizing steel which comprises treating steel articles in a molten bath containing about 20 to 30% by weight of sodium cyanide the remainder composed chiefly of at least one salt selected from the group consisting of alkali metal carbonates and halides and about 1 to 10% by weight of titanium cyanonitride, said bath containing not more than about 5% by weight of alkaline earth metal compounds and being maintained at a temperature of about 700 to 900° C.

4. The process for case carburizing steel which comprises treating steel articles in a molten bath containing about 20 to 30% by weight of sodium cyanide the remainder composed chiefly of sodium carbonate and about 1 to 10% by weight of titanium carbide, said bath containing not more than about 5% by weight of alkaline earth metal compounds and being maintained at a temperature of about 700 to 900° C.

5. The method for activating a molten alkali metal cyanide case carburizing bath composed chiefly of at least one salt selected from the group consisting of alkali metal cyanides, carbonates, and halides which comprises adding thereto a small amount of a titanium compound selected from the group consisting of titanium cyanonitride and titanium carbide.

6. The method for activating a molten alkali metal cyanide case carburizing bath composed chiefly of at least one salt selected from the group consisting of alkali metal cyanides, carbonates, and halides which comprises adding thereto titanium cyanonitride at a rate sufficient to maintain a concentration of at least 1 to 5% by weight of said cyanonitride in said bath.

7. The method for activating a molten alkali metal cyanide case carburizing bath composed chiefly of at least one salt selected from the group consisting of alkali metal cyanides, carbonates, and halides which comprises adding thereto titanium carbide at a rate sufficient to maintain a concentration of at least 1 to 5% by weight of said carbide in said bath.

8. A case carburizing composition comprising 10 to 50% by weight of alkali metal cyanide and a small amount of a titanium compound selected from the group consisting of titanium cyanonitride and titanium carbide, the remainder of said composition being composed chiefly of at least one salt selected from the group consisting of alkali metal carbonates and halides.

9. A case carburizing composition comprising about 20 to 30% by weight of alkali metal cyanide and 1 to 5% by weight of titanium cyanonitride, the remainder of said composition being composed chiefly of at least one salt selected from the group consisting of alkali metal carbonates and halides.

10. A case carburizing composition comprising about 20 to 30% by weight of alkali metal cyanide and 1 to 5% by weight of titanium carbide, the remainder of said composition being composed chiefly of at least one salt selected from the group consisting of alkali metal carbonates and halides.

11. A composition for replenishing and activating a cyanide case carburizing bath comprising 60 to 98% by weight of alkali metal cyanide and 2 to 40% by weight of a titanium compound selected from the group consisting of titanium cyanonitride and titanium carbide.

12. A composition for replenishing and activating a cyanide case carburizing bath consisting essentially of a mixture of approximately 10 parts by weight of sodium cyanide and one part by weight of titanium cyanonitride.

13. A composition for replenishing and activating a cyanide case carburizing bath consisting essentially of a mixture of approximately 10 parts by weight of sodium cyanide and one part by weight of titanium carbide.

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