Patented Sept. 25, 1951 2,568,860

UNITED STATES PATENT OFFICE

2,568,860

PROCESS FOR THE CARBURIZATION OF FERROUS METALS

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No Drawing. Application January 22, 1948, Serial No. 3,828

3 Claims. (Cl. 148—15.5)

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This invention relates to the carburization of ferrous metals, including iron steel, and iron and steel alloys, and more particularly it relates to the carburization of ferrous metals in a fused salt bath.

Many different kinds of fused salt carburization baths have been suggested heretofore for use in the carburization of ferrous metals. The most commonly used bath of this type is composed of inert alkali or alkaline earth metal salts, such as alkali metal or alkaline earth metal chlorides or alkali metal or alkaline earth metal carbonates, and a carburizing material in the form of a cyanide. In these baths, the cyanide is decomposed and the carbon and nitrogen of the same penetrates into the surface of the objects to be hardened or carburized. The addition of carbon to a cyanide case hardening bath decreases its carburizing action. Cyanide-containing fused baths are, however, objectionable in view of the relatively high cost of the cyanide with which the bath must be constantly replenished and the toxic properties of cyanides.

Cyanide-free, fused salt, carburization baths have also been used heretofore, for example, a fused, inert, salt bath containing silicon carbide. Baths of this latter type have been found objectionable in that not only do they produce very poor carburization, but the silicon carbide must be constantly replenished and the metal silicates formed in such baths cause objectionable sludging.

It is an object of this invention to provide an improved process for the carburization of ferrous metal articles.

It is another object of this invention to provide a fused, carburization bath that is capable of producing a nitrogen-free, carburized case.

It is still another object of this invention to provide a cyanide-free, fused, carburization bath which is not subject to objectionable sludge formation.

It is yet another object of this invention to provide a cyanide-free, fused, carburization bath which is not subject to frequent replenishment of molten bath ingredients.

It is a still further object of this invention to provide a cyanide-free, fused, carburizing bath that is non-corrosive and washes freely from the carburized articles, and which is capable of producing an active carburization at a comparatively low temperature, between 1550° F. and 1750° F.

Other objects of the invention will appear hereinafter.

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The objects of this invention can be achieved by preparing a fused salt bath composed essentially of alkali-metal carbonates and chlorides, and finely divided carbon, and passing through the bath an oxygen-containing gas taken from the group consisting of carbon monoxide and gases capable of reacting with carbon to form carbon monoxide in the fused salt bath.

Ferrous structures or articles, i. e., structures or articles composed of iron, steel, and iron and steel alloys, when immersed in the above-described bath at a temperature of 1550° F. to 1750° F. for a period of fifteen minutes or longer will be actively carburized.

The carburizing bath of the present invention is preferably prepared as follows:

A mixture of alkali metal (sodium or potassium) carbonate and alkali metal (sodium or potassium) chloride, preferably, not necessarily, containing 25% to 75% of the carbonate and 25% to 75% of the chloride, is melted and held at a temperature of about 1500° F. to 1700° F. for several hours. Finely divided carbon is added to the fused carbonate-chloride bath in an amount in excess of that which will remain dispersed in the bath, and is thoroughly mixed into the bath. A stream of a gas taken from the group consisting of carbon monoxide and gases capable of reacting with carbon to form carbon monoxide, for example, carbon dioxide, oxygen, nitrous oxide, nitric oxide, steam, air, or mixtures thereof, is bubbled through the carbon-containing, fused bath at a rate between 50 and 500 cc. N. P. T., i. e., measured at 0° C. and 760 mm. Hg, per 100 pounds of the bath. The carburizing activity of the bath increases gradually for a period of twenty to twenty-four hours, after which it levels off and remains substantially constant.

This carburizing bath is operative to case harden ferrous structures within a temperature range of 1550° F. to 1750° F. when immersed in the bath.

The fused carburizing bath, as above stated, preferably should contain 25% to 75% of the alkali metal carbonate and 25% to 75% of the alkali metal chloride to obtain the best carburizing conditions. These proportions are not, however, essential since carburization will take place in the absence of one or the other substance. For optimum carburizing conditions, it is also desired that at least 25% of the mixture be composed of potassium salt. The presence of at least 25% of potassium salt appears to induce more active carburization than where the entire amount of the salt is composed of sodium salts.

Minor amounts, i. e., less than 25% of the weight of the inert salts in the bath, of other salts may be present without deleterious effect. For example, calcium, barium or strontium carbonates and chlorides, in a total amount of less than 25%, will have no harmful effect. Alkali metal or alkaline earth metal cyanides may be present in the bath, it being understood, however, that the presence of cyanides will cause nitriding along with the carburizing action.

The carbon employed should be finely divided, preferably 50 mesh or finer, so that it may be rapidly and uniformly dispersed throughout the melt. All forms of carbon are operative to produce useful carburization, preferably, however, finely divided graphite is employed because of the greater carburizing activity obtained with this material.

The amount of carbon mixed with the fused bath should be controlled within certain rather broad limits. It is preferably employed in an amount in excess of that amount which will remain dispersed throughout the bath, so that a certain excess will float on the surface of the bath. If too large an excess is employed, difficulty will be encountered from sludge formation; if too little is employed, maximum carburizing activity will not be obtained. The amount of carbon employed is dependent upon the temperature and composition of the fused bath. Depending upon these conditions, between 0.1% and 10% carbon may be usefully employed. For example in a 50% KCl–50% K_2CO_3 base melt having a temperature of 1700° F., the optimum amount of carbon employed should be between 0.5% and 10% by weight of the base melt. A 50% Na_2CO_3–50% KCl base melt having a temperature of 1600° F. will have optimum carburizing action if the carbon constitutes between 0.1% and 5.0% carbon.

Carbon monoxide or any oxygen-containing gas which is capable of reacting with carbon to form carbon monoxide at the above-mentioned temperature range may be used in the carburization with the above-described bath. The rate of gas flow to be employed will depend upon the kind of gas used, the composition of the base melt, the type of gas bubbling apparatus and the dimensions of the pot used, as well as the operating temperature of the bath. Generally, the carburizing activity of the bath will be found to increase with an increase in the rate of gas flow up to a definite maximum beyond which the carburizing activity falls off slowly. For example, when employing a base melt composed of 50 pounds Na_2CO_3 and 50 pounds KCl at a temperature of 1600° F. in a 12-inch diameter pot and a bubbler having uniformly dispersed holes over the bottom of the pot, the optimum rate of flow for carbon dioxide gas was found to be between 50 and 500 cc. per minute at normal conditions of temperature and pressure. Good carburization may, however, be obtained by use of gas flow as low as 25 cc. per minute, or by use of gas flow as high as 2000 cc. per minute, N. P. T., per 100 pounds of bath.

If simultaneous carburizing and nitriding is desired, ammonia may be added to one of the above-mentioned oxygen-containing gases.

The gas activated molten salt carburizing process of this invention may be used in the absence of other carburizing ingredients or it may be combined with other known methods of fused bath carburization to obtain an augmented effect. For example, the process of this invention could be employed in combination with a conventional alkali metal salt or alkaline earth metal salt, cyanide-activated, case-hardening bath, or other known molten salt type of carburizing bath.

Any desired apparatus may be employed in carburizing ferrous metals by the process of this invention, the only necessity being that the bath be maintained fused at a fairly constantly controlled temperature, and means be provided for passing the gas into the molten bath at the desired rate and fairly uniformly dispersed across the cross-sectional area of the pot. Preferably, the pot and bubbling means immersed in the pot are constructed of corrosion-resistant materials, for example, nickle, iron, chromium-nickel alloys, or compressed graphite.

Although we do not wish to be restricted by any theories underlying the principles of the present invention, it is believed that in the carburization of ferrous metals it is essential that two conditions be present: first, the presence of a supply of carbon monoxide, and second, a means of eliminating carbon dioxide formed during carburization. In the process of this invention, the supply of carbon monoxide is furnished by reaction between the oxygen-containing gas and the carbon present, and the means of eliminating excess CO_2 is present as the result of reaction between CO_2 and carbon dispersed in the bath.

The fused bath constituents and steps of the process of this invention appear to provide a well-balanced supply of CO and elmination of CO_2 whereby an exceedingly efficient and active carburization is produced without objectionable sludge formation, very infrequent replenishment of carbon, and under comparatively low temperatures.

The following examples are given to illustrate certain preferred methods of carburization of ferrous metals in accordance with this invention, it being understood that these examples are to be taken solely as illustrative and not limitative of the invention.

Example I

Fifty (50) pounds of Na_2CO_3 and 50 pounds of KCl were charged into a 35% Ni–15% Cr heat-resisting alloy pot 12 inches in diameter and 24 inches deep. The salts were melted and the temperature raised to 1600° F. The melt was held at this temperature overnight. Powdered graphite of 200 mesh and containing about 98% carbon and a maximum of 2% ash was then added to the bath and mixed therein. An excess was employed so that a layer of graphite remained floating on the top of the bath. The excess, however, was insufficient to produce sludge formation in the melt.

The bubbler was made of 1" nickel tubing of welded construction, having three horizontal equi-length legs (5") at angles of 120° with each other. Each leg was perforated on each side with six holes ($3\frac{3}{32}$" diam.).

Carbon dioxide gas was started through the bubbler, which had been preheated to remove all traces of moisture. The rate of flow was then adjusted to 200 cc. per minute N. P. T. and the pressure head was set at about 6 inches of mercury above atmospheric pressure. The bubbler was next slowly introduced under the surface of the molten bath. When it was properly positioned in the bath, the rate of flow was readjusted by means of pressure head and reducing valves.

After operating in this fashion overnight, an

S. A. E. X1020 steel test bar of 0.23% carbon was treated for one hour at 1600° F. This bar was then air cooled, washed free of adhering salt, and dried. Successive 0.004" cuts (on the radius) were removed from the periphery of the bar. These were analyzed for carbon, with the following results:

Cut	Per Cent C	Increase, Per Cent C	
#1	0.69	0.46	S. A. E. X1020, One hour, 1600° F.
#2	0.66	0.43	
#3	0.48	0.25	
#4	0.35	0.12	
#5	0.28	0.05	
#6	0.23	(core) 0.00	
Carbon units [1]		131	

[1] "Carbon units" are a convenient measure of the carbon picked up by the steel. They are determined by taking successive 0.004" cuts (on radius) from the surface of a one-inch diameter test bar, analyzing for carbon, subtracting the carbon found from the original or core carbon content, summing these carbon increments over the whole bar, and multiplying by 100.

For the purpose of comparison, a similar S. A. E. X1020 steel test bar was treated for one hour at 1600° F. in the standard 30% NaCN case hardening bath. This showed only 89 carbon units. In addition, 78 nitrogen units were also obtained, since cyanide-activated baths both carburize and nitride. Analysis of the first cut from the bar treated in the CO_2+C activated bath showed no increasse in nitrogen content.

An S. A. E. X1020 test pin that was water quenched from the above gas activated bath after one hour treatment at 1600° F. showed a Rockwell C hardness of 55. Case depth to 0.30% C on the test bar was 0.017", as revealed in the above gradient.

Test gears oil quenched from the above bath washed much more readily than similar ones quenched from an alkaline earth activated type cyanide bath.

Example II

This example illustrates the effect of variation in temperature using another base melt.

A mixture of 50 pounds of KCl and 50 pounds of K_2CO_3 was melted as described in Example I. After the addition of excess finely-powdered graphite, this bath was activated by a stream of CO_2 (500 cc. per minute N. P. T.) as previously described. Test bars of S. A. E. X1020 steel were treated for one, four, and sixteen hours, respectively, at 1600° F. Carbon gradients on the test bars indicated that the case depth to 0.30% C obeyed the following expression:

$$p_{30}=0.0096t^{0.56}$$

where

p_{30}=case depth in inches to 0.30% C, and
t=time of treatment in hours.

This same bath was then raised to 1700° F. with the same rate of CO_2 flow. Three more test bars were treated for one, four, and sixteen hours, respectively, at this elevated temperature. Analyses indicated that carburization at 1700° F. obeyed the following expression:

$$p_{30}=0.019t^{0.52}$$

Example III

This example illustrates the use of carbon monoxide gas.

A charge of 50 pounds of Na_2CO_3 and 50 pounds of KCl was melted as described in Example I. Then, in the presence of excess finely-powdered

graphite, a stream of CO was bubbled through the melt at the rate of 300 cc. per minute N. P. T. A bar of S. A. E. X1020 steel containing 0.22% carbon was treated for one hour at 1600° F., and was analyzed for carbon as previously described. The following results were obtained:

Cut	Per Cent C	Increase, Per Cent C	
#1	0.54	0.32	S. A. E. X1020, One hour, 1600° F.
#2	0.47	0.25	
#3	0.34	0.12	
#4	0.27	0.05	
#5	0.23	0.01	
#6	0.22	(core) 0.00	
Carbon units		75	

Example IV

This example illustrates the use of nitrous oxide as activating gas.

A 50% KCl–50% Na_2CO_3 bath was started as described in Example I, but was activated with a stream of N_2O (instead of CO_2) at the rate of 50 cc. per minute N. P. T. A sample test bar of S. A. E. X1020 steel, treated at 1600° F. for one hour under these conditions, showed carbon pick-up of 51 units.

Example V

This example illustrates the effect of added NaCN upon the case hardening action of this type of bath.

Forty-four (44) pounds of Na_2CO_3+44 pounds of KCl were melted as in Example I. A heavy layer of finely-powdered graphite was added and 200 cc. per minute N. P. T. of CO_2 was passed through the melt using the nickel bubbler. The next morning a test bar of S. A. E. X1020 steel was treated therein for one hour at 1600° F.

Five (5) pounds of 96% NaCN were next added to the melt. Test bars were treated for one hour at 1600° F., one, five, and twenty-two hours after the cyanide addition. Carbon dioxide was bubbled throngh the melt throughout the entire experiment.

Gradient cuts were removed from the test bars as described in Example I. These cuts were then analyzed for carbon and nitrogen. Following are the results:

Remarks	NaCN	NaCNO	C units	N units
	Per cent	*Per cent*		
Before cyanide addition	0.0	0.0	111	0
1 Hr. after NaCN added	5.2	0.49	78	7
5 Hr. after NaCN added	4.8	0.65	94	13
22 Hr. after NaCN added	4.0	0.62	141	10

Two effects are apparent: First, the addition of cyanide causes nitriding; second, immediately following the cyanide addition, carburizing decreases slightly, then picks up to a value higher than without the cyanide present.

One advantage of the process of the present invention is that it permits one to carburize in a molten media free of cyanides and cyanogen compounds that are toxic, expensive, and cause simultaneous nitriding, which is often objectionable. A second advantage of the process is that it permits one to case carburize in a bath which does not contain compounds which make subsequent washing of the treated parts difficult. A third advantage of the process is that it produces consistently good carburizing with no salt replenishment required, except to take care of

dragout on the work. This eliminates entirely the necessity for bailing out a portion of the bath daily to make room for the replenishing agent, as must be done in the case of most other molten case hardening processes. A fourth advantage of the process is the elimination of objectionable thickening and sludge formation in the melt. Another advantage of the process is its economy. Still another advantage is the fact that this process enables one to case carburize with the above advantages in the lower portion of the normal case hardening temperature range, where direct quenching following carburizing is practical.

Throughout the specification and claims, any reference to parts, proportions and percentages refers to parts, proportions and percentages by weight unless otherwise specified.

Since it is obvious that many changes and modifications can be made in the above-described details without departing from the nature and spirit of the invention, it is to be understood that the invention is not to be limited to said details except as set forth in the appended claims.

What is claimed is:

1. The process of carburizing ferrous metal structures which comprises immersing said structures in a fused salt bath having an active carburizing action on ferrous metals, the carburizing action of which is produced by incorporating finely-divided carbon in a fused salt bath having a temperature between 1550° F. and 1750° F. and consisting essentially of at least one carbonate selected from the class consisting of sodium carbonate and potassium carbonate and at least one chloride selected from the class consisting of sodium chloride and potassium chloride, and passing into said bath a gas selected from the class consisting of carbon monoxide and an inorganic oxygen-containing gas which reacts with carbon to form carbon monoxide in said fused bath.

2. The process of carburizing ferrous metal structures as defined in claim 1 in which the fused salt bath contains between 25% and 75% by weight of one of said carbonates and between 25% and 75% by weight of one of said chlorides.

3. The process of carburizing ferrous metal structures as defined in claim 1 in which the fused salt bath contains between 25% and 75% by weight of one of said carbonates and between 25% and 75% by weight of one of said chlorides, at least 25% of said salt consisting of potassium salts.

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