

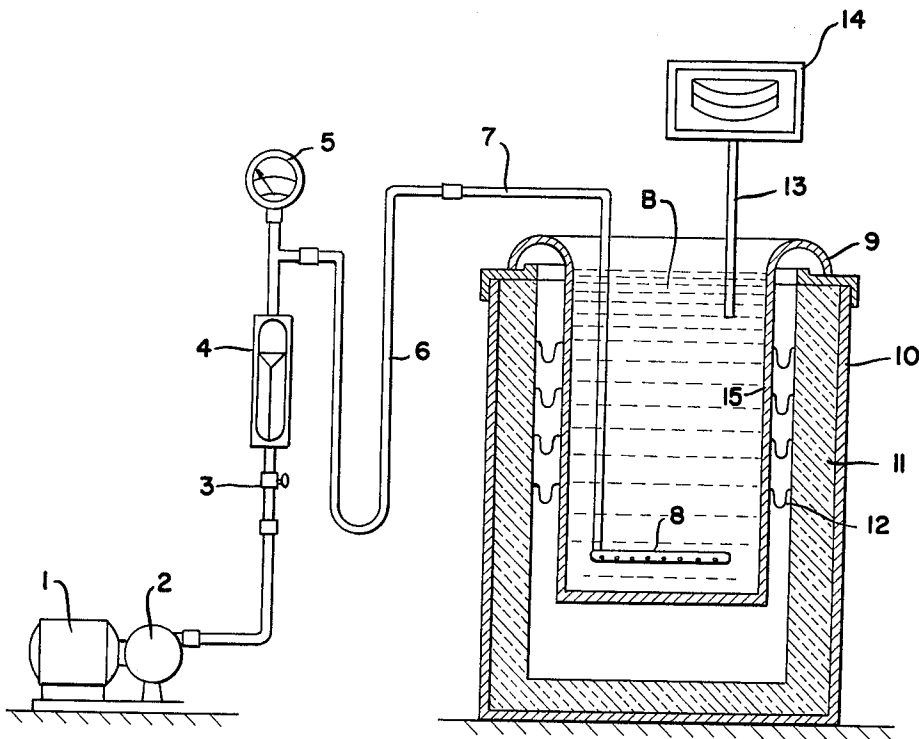
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APPARATUS FOR NITRIDING OF METALS

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**APPARATUS FOR NITRIDING OF METALS**  
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This invention relates to nitriding of ferrous metals in a fused cyanate-cyanide bath, usually with aeration, and particularly to nitriding of the ferrous metal in a bath wherein the dissolved iron content thereof is maintained low.

In the nitriding of ferrous metals, as practiced in the art, particularly of low and medium carbon steels, as well as alloy steel and tool steels, the preferred nitriding, now commercially known as TUFFTRIDING, has been practiced by immersing the metal in a molten salt bath comprising a mixture of alkali metal cyanate, cyanide and carbonate in which the cyanate is controlled between about 25% and 40%, and preferably about 32% to 38%, and maintaining the temperature in the range of 500 to 600° C. The ferrous metal is immersed in such bath for several hours, about thirty minutes to three hours, preferably while continuously aerating by passing finely divided air bubbles evenly through the molten salt bath.

It is found that the metal, so treated, often forms porous or double compound layers comprising a mixture of ferrous carbide and nitrides on the surface of the treated metal which impart inferior strength characteristics to the metal and often spall off. This is evidenced by occasionally reduced wear resistance as well as lower fatigue strength than is often obtained and commonly expected of ferrous metal which has been TUFFTRIDED. Particularly it will be noted that a well nitrided metal has a compound layer of several microns in thickness, variable with the treating time, comprising essentially lower nitrides of iron such as Fe<sub>3</sub>N admixed with Fe<sub>3</sub>C and a dissolved nitrogen content probably in the same ferrous nitride form extending beneath the compound layer indefinitely. It is to this composite nitrided surface that the improved nitrided metal qualities were attributed.

As disclosed in U.S. Patent 3,022,204, such qualities were obtainable where the cyanate content was rigidly maintained as stated below 40% and preferably in the range of 32% to 38%. It was found also that the temperature of the bath required very close control to the stated range. Any excessive temperature tended to destroy the quality of the bath, too radically reducing its cyanate content. For instance, treating the bath at temperature of about 700° C. very rapidly destroyed the cyanate, so that it was sometimes used as a control procedure for that very purpose. The cyanate content with desirable aeration tends, however, to continuously increase, making the close quality control difficult. It was considered, for instance, to operate above about 40% cyanate would fail to give the high quality surface compound layer upon the metal characteristic of well-nitrided metal. Particularly in the treatment of high carbon or alloyed steel, little desirable effect of nitriding could be produced therein, despite observance of such close controls.

The failure of improved nitriding is observed in producing a surface nitrided layer which is highly porous and sometimes in the spalling of the layer, and several undesirable effects are exhibited by poorly nitrided metal, particularly as regards to its wearing as well as high fatigue resistance.

According to the present invention, it is found that the several critical controls such as the quantity of cyanate and temperature, are rendered less critical, and an improved treatment which imparts high wearing and fatigue qualities to a wider range of ferrous metals is made available

by conducting the nitriding in such molten nitriding salt bath, maintained with a low iron content and preferably substantially free of iron compounds. By substantially "free of iron" it is meant to maintain the bath invariably, despite continuous use with iron work pieces immersed therein over long time periods, reduced in iron content, substantially below 0.5% iron. The optimum and preferred condition of the bath is about 0.1% iron or less.

The iron content of the bath is maintained low despite use of the bath for substantial periods for treatment of ferrous metals. This result is obtained by maintaining the molten salt in a container usually referred to as a pot, whose exposed surface composition in contact with the molten salt is free of metallic iron or compounds of iron. For this purpose the pot is formed or is lined with non-ferrous metal; or the pot is provided with a surface coating of ceramic materials which are free of ferrous metal. Useful non-ferrous pot, pot liner or pot-coating metals are those of Groups IVb through VIIIb of the periodic system, preferably titanium, zirconium, vanadium, chromium, molybdenum, cobalt, nickel and alloys thereof; metallic iron, it will be noted, being excepted. In addition, it is found that metallic aluminum outside of this grouping also forms a useful container or container lining or coating metal for such molten salt container pot. Instead of or in combination with these metals, it is also possible to use oxides of such metals such as aluminum oxide, zirconium oxide, titanium oxide as well as others listed including oxide mixtures, all excluding iron or iron oxides. Again, even auxiliary apparatus, such as heating electrodes, where the pot is electrically heated inlet tubes and protective sheaths about various elements such as thermocouples and the like, which normally are brought into contact with the molten salt of the bath, must also be sheathed or coated with one of said metals or metal oxides as listed. In this manner the apparatus comprising the pot and auxiliary elements associated therewith which are usually brought into contact with the molten salt are protectively encased or coated with a metal or metal oxide which is resistant to (insoluble and not corrodable by) the molten salts of the bath and, being free of iron, will consequently supply no iron thereto. The bath is therefore maintained molten in an iron-free pot of this type by protective sheathing to exclude the iron from its lining material which prevents a substantial accumulation of iron in the bath despite its continuous use in the treatment of ferrous metals with substantial immersion contact time for the nitriding thereof.

Operated in this manner, the conventional alkali metal cyanate-cyanide ratio of the bath, usually maintained between 30% and 40% cyanate can be brought up to about 50% and more cyanate, the balance being cyanide or cyanide and carbonate. Moreover, the temperatures heretofore held in the range of 500 to 600° C., for the nitriding of metal can be increased non-critically, such as up to 700° C., the former controls of salt composition and temperature being of lesser criticality, providing, of course, that the iron content of the bath is maintained low, such as below 0.5% and ideally about 0.1% or less.

The nitriding effect upon the ferrous metal is improved whether the bath is aerated, as is preferred, or not, over the prior nitriding of metals. Moreover, the types of ferrous metals that can be improved are more extensive, including various alloys as well as high carbon steels.

Again, notoriously improved, is the high wear resistance and fatigue strength or endurance upon the wider range of ferrous metals. For instance, the somewhat porous compound layers that sometimes formed in the prior nitriding, even when the cyanate content of 40% was not exceeded, is not formed in the bath. Rather, the compound layers are maintained hard and thick in contrast

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to the porous layers often formed. The actual wear resistance and fatigue strength are considerably improved, and the range of materials include high carbon and alloy steels not heretofore substantially improved by former practices which are likewise greatly improved in this treatment.

Again, the bath is improved as to the amount of sludging that takes place, which formerly by large iron content appeared as insoluble precipitate, often interfering with the heating of the pot. With the low iron bath content, no depositing about the pot walls and bottom results because a comparatively smaller amount of sludge, about 10% of what is the normal high iron melt forms, and this sludge does not separate, but remains in relatively fine even suspension, whereby it does not interfere with the heat transfer into the salt melt.

The single figure of drawing, appended, illustrates diagrammatically, apparatus useful in the practice of this invention. The drawing shows an electric motor 1 which drives air compressor 2 for supplying air to the salt bath B. From the compressor 2 the air passes by way of valve 3, meter 4 for measuring gas quantity and manometer 5 for measuring the gas pressure, the gas entering by way of tubes 6 and 7 the bath. The air is preferably distributed evenly throughout the bottom of the molten salt bath by passing through perforated or porous annular tube 8 opening into the lower part of the pot 9 from which the air is emitted in numerous small bubbles passing upward and continuously aerating the molten salt. In detailed construction, pot 9 is supported within an outside shell 10 with intermediate insulating fire brick 11 upon which may be mounted numerous electrical heating coils 12 for supply of heat to the pot 9. A thermocouple 14 may have a heat sensing element 13 in contact with the molten salt for continuous temperature measurement thereof in a manner known in the art.

According to this invention the pot 9 is composed of a stable metal resistant to attack by the molten salts as listed above, free of iron. The pot 9 may be composed entirely of such metal; it may be merely lined with its inner surface 15 composed of such metal; or, it may be coated with such metal as by metallizing, whereby the surface of the metal in contact with the molten salt is one of the metals, as stated. As indicated further, the pot may alternatively have a ceramic oxide coating free of iron; for instance, such oxides as alumina, titania, zirconia and the like. Moreover, the coating, sheathing or substitution of metals in contact with molten salt in the pot will be extended to include such auxiliary metallic parts as sheathing about the thermocouple 13 or the porous gas emitting ring 8 or tubing 7, as well as such other incidental metallic operating parts as may be present, but not shown in the drawing. Hence, according to the invention, the molten salt in use is maintained substantially iron free by forming the parts normally contacted therewith, the pot and its appurtenances is formed of or carries a suitable metal or metal oxide coating which is free of iron which is relatively stable in the presence of the molten salts.

In operating, according to the invention, the molten bath salt comprises a mixture of a cyanide and cyanate of alkali metal such as sodium or potassium, together with up to about 25% of carbonates formed during the reaction. As pointed out in U.S. Patent 3,022,204, the 25% to 40% cyanate used is converted up to 99%, usually 90 to 99%, of iso-cyanate in use. While according to that disclosure the preferred cyanate range was 32% to 38% used at the temperature between 500 and 600° C., the quantity of cyanate tended invariably to increase rapidly so that it was always difficult to maintain a cyanate content even as low as 35% and almost impossible for as low as 32% except for a newly formed bath and under most careful continuous controlled conditions. However, operating with a bath having no more than about 0.5% iron, and preferably as low as 0.1%, the

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quantity of cyanate in the bath does not need to be so critically maintained. Indeed, fine nitriding effects result even when the cyanate content rises to as high as 50% and more. Moreover, the temperature of the bath itself, an important control element to maintain the desired cyanate-cyanide ratio, also is no longer critical. The following example illustrates the invention:

(a) *Prior art practice*

2500 lbs. of salt consisting initially of 950 lbs. of potassium cyanate and 1550 lbs. of sodium cyanide are fused at 570° C. into a molten salt bath apparatus as described in FIG. 1, using an ordinary cast iron pot and other iron containing metallic appurtenances and the melt is maintained at a temperature of 570° C. with continuous introduction of air bubbles. The bath was used for nitriding various ferrous metals treated for periods of about three hours, the metals treated being varied from low and medium carbon steels through alloy steels and cast irons, the treatment continuing at a rate of about 2½ tons of work per week. It was found by analysis of the bath after about 10 hours of use that it had a content exceeding about 0.6% iron in the form of alkali metal ferro-cyanides. The ferrous metal workpieces treated varied widely in the depth of the nitrided compound layer comprising mixed ferrous carbide and nitride, all varying in depth, porosity, and tendency to spall and scale off from the metal when worked. That variation in compound layers obtained was apparent even among treatments of exactly the same kind of metal for the same period of time, although the alloyed ferrous metals showed far greater variation in quality of compound layer. Indeed, it was only low and medium carbon steels that seemed to have any desirable effect of substantial consistency. Moreover, after use of the bath for about a week, about 1200 grams of sludge comprising such iron cyano compounds separated from the melt on the walls and bottom of the pot as a precipitate, greatly reducing the heat transfer into the pot.

(b) *Practice according to this invention*

The same molten salt bath was made up using a pot having a liner sheath of titanium metal, the thermocouple was sheathed in the same titanium metal, and also the air inlet tube and porous distribution ring were each formed of titanium metal. The bath was maintained at the same temperature with continuous aeration. Various ferrous metals ranging from low carbon through medium carbon, various cast irons, other high carbon steels are alloy steels including stainless steels were nitrided in the bath, each treatment comprising an average of about three hours immersion. Analysis of the bath after operating for a week showed that the iron content was approximately 0.1%. The sludge content of the bath was less than 120 grams, about 1/10 that of the prior practice, and such sludge as was present was finely dispersed, none tending to settle or interfere with the heat transfer. More important, however, the treated metal had compound layers formed of iron nitrides and carbides consistently free of porosity, double layers or any tendency to spall off, and were of greatly increased abrasion and fatigue resistance, the compound layers being many times as thick, as much as 30 to 40% thicker than the average compound layer of the prior practice. Moreover, alloying elements in the metal had improved properties, the compound layer being uninfluenced by alloy components, the nitrided alloys being produced from low alloyed structural steels such as 34Cr4, 42CrMo4 and even 34CrA16 (SAE 5134, 4142 and chrome aluminum alloyed medium carbon steel). Deep non-porous compound layers are also produced upon all kinds of cast iron which may be easily lapped.

Moreover, the compound layers produced, despite their increased thickness, have no porosity and do not tend to spall. Greatly increased fatigue strength is formed ac-

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ording to the following values which have been obtained by notched test bars of C15 (SAE 1015):

- (a) Steel pot/non-aerated bath, 34 to 36 Kp/mm.<sup>2</sup>.
- (b) Steel pot/aerated bath, 38 to 39 Kp/mm.<sup>2</sup>.
- (c) Titanium-lined pot/aerated bath, 42 to 43 Kp/mm.<sup>2</sup>.

It will be noted that while the metal as usual in an aerated bath is improved over a non-aerated bath in each case, the use of the titanium lined pot produces results which are highly superior to those formerly practiced in the art.

Various modifications will occur to those skilled in the art, such as to produce apparatus suitable for operating with an iron-free bath. While applicant has listed numerous preferred metals as linings and coatings for melting pots, others including oxides of metals and mixed amphoteric metal compounds resistant to dissolution in the bath may be used. Accordingly, it is intended that the above description be regarded as illustrative and not limiting except as defined in the appended claims:

I claim:

- 1. A process of nitriding a ferrous metal which comprises immersing the metal in a molten alkali metal salt bath comprising over 40 percent of a cyanate and the

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balance essentially a cyanide and a carbonate, said salt bath being contained in a metal pot constructed of one of the metals selected from the group consisting of titanium and aluminum, and aerating said bath.

2. A process according to claim 1 wherein the bath forms on the ferrous metal a thick adherent compound layer of ferrous nitride and ferrous carbide; and the dissolved iron content of the bath is maintained below about 0.5% by the use of the metal pot as above described.

3. A process according to claim 1 wherein an aerating gas is introduced into said pot, upwardly from its bottom.

4. A process according to claim 2 wherein an aerating gas is introduced into said pot, upwardly from its bottom.

References Cited by the Examiner

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3,022,204 2/62 Muller et al. ----- 148—15.5

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