

DESCRIPTION**Title: METHOD FOR TREATING A PART MADE OF IRON ALLOY FOR IMPROVING THE ANTI-CORROSION PROPERTIES THEREOF**

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Technical field of the invention

The present invention relates to a method for treating a part made of iron alloy by nitriding and phosphating to improve the anti-corrosion properties thereof, as well as a part made of iron alloy treated by nitriding and phosphating.

10 **Prior art**

In automotive, aeronautical, or industrial applications, the mechanical parts are generally subjected to significant operational stresses.

Conventionally, the mechanical parts can receive one or more treatments, making it possible to improve some of their performance, among which, friction

15 properties, resistance to wear, resistance to fatigue, or also resistance to corrosion.

Among these different treatments, nitriding is an interesting choice. It consists of immersing a part made of ferrous metal in a medium which can transfer nitrogen, and the formation of iron nitrides on the surface of the part, as well as the diffusion of nitrogen from the surface to the core of the part leads to a significant superficial

20 hardening.

Nitriding includes nitrocarburising, which is a variant of nitriding, in which carbon penetrates into the part, in addition to nitrogen. The ARCOR method, developed by the Applicant and implemented by them for numerous years, and described below in the present text, is a preferred example of the nitrocarburising method.

25 Below in the present text, nitriding and nitrocarburising are grouped together in one single term of “nitriding”.

Nitriding can be done from a gaseous phase, a plasma phase, or from a liquid phase.

Liquid phase nitriding, also called salt bath nitriding, has the advantage of enabling a significant hardening over a thickness of several tens of microns in times of barely a few hours, which makes it a first-rate choice. Baths of molten salts are typically at temperatures of around 600°C, and contain, in practice, cyanates and carbonates, and also contain cations which are usually alkaline metal cations, such as lithium, sodium, or also potassium, for example.

Nitriding makes it possible to harden the surface of the part, and to thus improve its resistance to wear. It can also improve the sliding and gripping properties.

It is often combined with another treatment, for example, if a good resistance to corrosion is needed.

Phosphating is, for example, such a treatment, making it possible to improve the performance of the parts in terms of resistance to corrosion.

The performance of the parts having undergone phosphating, whatever their application, mainly depend on two features: crystallinity and the adherence quality on a substrate of the phosphated layer.

Generally, it is therefore sought to obtain, during the phosphating step, a fine and regular crystallisation, leading to a phosphate layer which is as dense as possible.

These two features are directly dependent on the quality of preparing the metal surface of the substrate, before the strictly speaking phosphating step. The physico-chemical state of this surface indeed conditions its reactivity with respect to active agents of the phosphating bath, as well as the growth of the phosphated complex layer.

It is implicit that the parts can be washed, degreased and dried before the nitriding and/or phosphating steps. These routine steps do not modify neither the chemistry, nor the structure of the parts to be treated. In certain cases, however, other pretreatment steps are implemented.

It is thus known by a person skilled in the art, that the crystallinity of the phosphate layer can be improved by a pretreatment which consists of depositing titanium compounds finely dispersed on the surface to be phosphated. The Applicant has also demonstrated, in patent EP 0560641, that a nitriding in the presence of sulphur
5 species allows to facilitate phosphating, and thus guarantee a fine crystallinity.

However, the content of sulphur species must be low (around ten ppm), and controlling and maintaining the good content of sulphur species increases the complexity and the cost of such a nitriding.

The cost can thus become prohibitive for treating inexpensive materials, for
10 example, very low-alloy steels or cast irons.

In the particular case of cast irons, grey cast iron is a cast iron, in which carbon crystallises in the form of graphite inclusions, which can take the form of long and narrow graphite lamellae, nodules (spheroids), or vermicules. These inclusions, when they open onto the surface of the part, can disrupt surface treatments and
15 thus form primer points for corrosion. Thus, in order to improve resistance to corrosion, it has been proposed to perform a degreasing treatment before nitriding (described in document WO2016143712). However, such a pretreatment also increases the duration and the overall cost of treating grey cast iron.

Lamellar cast iron, in which the inclusions are in the form of lamellae, has the
20 advantage of being cheaper than other cast irons. Spheroidal cast iron requires the addition of a crystallising element (rare earth, lithium, magnesium), which increases its cost.

Generally, grey cast iron is a quite inexpensive material, but rather difficult to protect against corrosion.

25 With grey cast iron being an inexpensive material, it is used for manufacturing motor vehicle brake discs. Often, the brake discs are not treated and have a very

low resistance to corrosion. During braking, corrosion attacks on the surface of the discs are abraded by platelets, and are therefore removed.

However, with the emergence of electric vehicles and electrical energy recovery upon braking, mechanical brakes are less and less stressed, and possible corrosion attacks present on the surface of the discs are now no longer removed: corrosion, unsightly and damaging for braking quality, propagates over the brake discs.

In addition, in case of storing the vehicle for a long duration before it is sold, the presence of unsightly corrosion on the brake discs damages the appearance of the vehicle and can prevent it being purchased.

Therefore, mechanical parts should be proposed, in particular, brake discs which are inexpensive, but resistant to corrosion. In the case of brake discs, phosphating alone is not sufficient, as upon first braking, the phosphated layer is removed.

Brief description of the invention

Faced with this situation, the Applicant has sought a solution to simplify the methods for treating mechanical parts by nitriding and subsequently phosphating, quite specifically in view of the constraint of preparing the surface before the strictly speaking phosphating step, which increases production costs.

The method must preferably be adapted to treating grey cast iron, despite the intrinsic constraints of this material. However, it must be able to be applied to any cast iron or low-alloy steel, even in theory, to all iron alloys.

To this end, the invention proposes a method for treating a part made of iron alloy, to improve its anti-corrosion and mechanical strength properties, comprising:

- a molten salt bath nitriding or molten salt bath nitrocarburising step, to form a combination layer on the part, and subsequently
- a step of phosphating the part, to form a phosphating layer on the surface of the part,

mainly characterised in that the bath of molten salts contains chlorides, and the phosphating step is carried out in a phosphating bath which contains zinc ions and/or manganese ions, and iron ions.

The Applicant has noticed that the carrying out of a nitriding step in the presence
5 of chlorides (i.e. Cl^- chloride ions, and by extension, chemical species containing chloride ions, such as chlorine salts), and subsequently a phosphating step with zinc and iron (of the zinc/iron, Zn/Fe type), or with manganese and iron (of the manganese/iron, Mn/Fe type), or with zinc and manganese and iron (of the zinc/manganese/iron, Zn/Mn/Fe type), makes it possible to obtain a part having
10 good anti-corrosion and good mechanical strength properties.

Furthermore, in the particular case of a part made of grey cast iron, the method of the invention not only leads to the abovementioned advantageous mechanical properties, in particular, a mechanical strength which is relatively similar to the current standard for grey cast irons, namely nitriding and subsequently gaseous
15 phase oxidation, but also makes it possible to avoid a prior degraphitising. For applications requiring a low friction coefficient, zinc can be replaced at least partially with manganese.

Conversely, in the case where it is sought to preserve a relatively high friction coefficient, for example for brake discs, thus the presence of manganese ions in the
20 phosphating bath should be avoided.

The phosphating bath therefore comprises, in addition to usual PO_4^{3-} phosphate ions, Zn^{2+} zinc ions, and/or Mn^{2+} manganese ions, as well as Fe^{2+} iron ions.

As indicated above, the method for treating a part according to the invention does not comprise any step of degraphitising the part, prior to phosphating, i.e. before
25 phosphating, or even before nitriding.

The absence of degraphitising makes it possible to reduce time and production costs, without however degrading the quality of the part obtained, in particular its good hardness, resistance to wear and resistance to corrosion properties.

The method according to the invention therefore advantageously applies, but not exclusively, to iron alloy parts which usually require a degraphitising, in particular grey cast iron parts.

According to other aspects, the treatment method according to the invention has the following different features taken individually or according to their technically possible combinations:

- 10 - the bath of molten salts does not contain sulphur;
- the chlorides comprise alkaline metal chlorides;
- the alkaline metal chlorides are lithium, sodium and/or potassium chlorides;
- the bath of molten salts comprises CNO^- cyanate ions, $(\text{CO}_3)^{2-}$ carbonate ions, and alkaline ions, preferably chosen from among Li^+ lithium ions, and/or K^+ potassium ions, and/or Na^+ sodium ions;
- 15 - the bath of molten salts for nitriding comprises:
 - 25% to 60% of alkaline metal chlorides,
 - 10% to 40% of alkaline metal carbonates,
 - 20% to 50% of alkaline metal cyanates,
 - 20 • 3% or less of cyanide ions,
 the percentages being expressed by weight with respect to the total weight of the bath;
- the content of zinc, manganese and iron ions in the phosphating bath is adjusted as follows, according to the alloy of the treated part and the expected performance:
 - 25 • when the phosphating bath contains zinc ions, but no manganese ions, said zinc ions are present at a mass concentration of between 1 g/l and 40 g/l (grams per litre), preferably between 5 g/l and 20 g/l, with respect to the total volume of the phosphating bath;

- when the phosphating bath contains manganese ions, but no zinc ions, said manganese ions are present at a mass concentration of between 1g/l and 40g/l, preferably between 5g/l and 20g/l, with respect to the total volume of the phosphating bath;
- 5 • when the phosphating bath contains zinc ions and manganese ions, the total of these ions is present at a mass concentration of between 1g/l and 40g/l, preferably between 5g/l and 20g/l. Furthermore and optionally, the manganese ions can represent between 10% and 90% by weight, preferably between 25% and 75% by weight, and advantageously between 40% and 60% by weight of the total
- 10 weight of the zinc ions and manganese ions;
 - the iron ions being, in any case, present in a phosphating bath at a mass concentration of between 1g/l and 8g/l, preferably between 1g/l and 6g/l, and more preferably between 1g/l and 5g/l;
 - the bath optionally comprising nitric acid or nitrates;
 - 15 • the rest of the bath being mainly formed of water.
 - the phosphating layer has a thickness of between 3μm and 40μm, preferably between 5μm and 30μm, and even more preferably between 5μm and 20μm;
 - the combination layer measures between 5μm and 40μm thick, and preferably between 15μm and 25μm;
 - 20 - the part is made of grey cast iron.

The method of the invention, in the case where the phosphating bath does not contain manganese ions, applies quite specifically to a brake disc. The invention therefore also relates to a method for treating a part made of grey cast iron to improve its resistance to corrosion, the method being such as described above.

- 25 Another aim of the invention is a part made of iron alloy which can be obtained by the treatment method described above, comprising:
 - a nitriding layer on the surface of the iron alloy, comprising a combination layer containing nitrides,

- a phosphating layer arranged on and in contact with the nitriding layer, comprising metal phosphates, mainly characterised in that the metal phosphates comprise zinc and/or manganese, and iron.

5 The invention also relates to a part made of grey cast iron which can be obtained by the treatment method described above, comprising:

- a nitriding layer on the surface of the grey cast iron, comprising a combination layer containing nitrides,
- a phosphating layer arranged on and in contact with the nitriding layer,

10 comprising metal phosphates, mainly characterised in that the metal phosphates comprise zinc and/or manganese, and iron.

Preferably, the phosphating layer has a thickness of between 3µm and 40µm, preferably between 5µm and 30µm, and even more preferably between 5µm and

15 20µm;

Preferably, the combination layer has a thickness of between 5µm and 40µm, preferably between 15µm and 25µm.

The part has graphite inclusions at a surface of the part on which the combination layer is formed, insofar as it has not undergone prior degraphitising. These

20 graphite inclusions are located at least at one surface of the part on which the combination layer is formed.

The part is preferably a brake disc. In this case, the phosphating is a zinc/iron phosphating. The invention therefore also relates to a brake disc having the features of the part made of grey cast iron described above.

25 **Description of the figures**

Other advantages and features of the invention will appear upon reading the following description given as a non-limiting, illustrative example, in reference to the following accompanying figures:

[Fig. 1] Figure 1 is a micrograph of a part according to an embodiment of the
5 invention, said part being a brake disc made of lamellar cast iron.

[Fig. 2] Figure 2 is a photograph of the part of figure 1 after nitriding/phosphating treatment and before a saline spray test.

[Fig. 3] Figure 3 is a photograph of a part not according to the invention, said part being a brake disc made of lamellar cast iron.

10 [Fig. 4] Figure 4 is a photograph of the part of figure 3 after nitriding/phosphating treatment and before a saline spray test.

Detailed description of embodiments of the invention

The approach of the Applicant has been to carry out several series of tests implementing different treatments of a part (P) made of grey cast iron.

15 The problem addressed consists of finding a method conferring a sufficient resistance to corrosion on the part (P), despite the fact that the nitriding bath does not contain sulphur and that in addition, said part is made of grey cast iron which is non-degraphitised, and therefore particularly difficult to protect from corrosion.

The treated parts (P) have been subjected to a saline spray, and their resistance to
20 corrosion is evaluated from the duration of appearance of a pitting and/or rust run-off threshold.

Then, the second problem has been to validate the correct operation of the part (P) thus treated, according to a particular use of the brake disc: comparative friction coefficient measurements have therefore been taken.

25 In particular, the Applicant has studied the effects of the two following steps.

In reference to the micrograph illustrated in figure 1, the ARCOR nitriding treatment (trademark filed by the Applicant) provides, from the surface to the part (P) core , a juxtaposed combination layer (1) and diffusion zone (1'). The combination layer (1) typically has a thickness of between 5 and 30µm, and is
 5 formed at the surface of the substrate (S) which composes the part (P).

The diffusion zone (1') typically has a thickness of a few tens or hundreds of microns, for example, 300µm, and is measured from the surface of the substrate (S) of the part (P), in the direction of the core of said part.

Nitriding has been carried out in a bath of molten salts.

10 Phosphating provides, on the surface of the part (P), above the combination layer (1), a metal phosphate layer (2). The metal phosphate layer (2) typically has a thickness of around 20µm.

On the micrograph of figure 1, an additional layer (a) can be seen: this is an aluminium layer not forming part of the part (P), but deposited in view of
 15 performing the cutting necessary for the micrograph.

Furthermore, the lamellar-shaped graphite inclusions (G) can be observed, which open on the surface of the part (P).

A first series of anti-corrosion tests has been carried out. The parts (P) manufactured as grey cast iron-based, and subsequently treated, are placed in an
 20 enclosure and subjected to a saline spray test.

The enclosure is then opened every 24 hours, in order to verify the appearance of corrosion points, which provide evidence of a start of localised corrosion. These points are counted, and if there is more of them than a predefined threshold, for example 50, then the part (P) is considered as corroded and the test is stopped.

The longer the duration is before the threshold is reached, the more resistant the part is to corrosion. A minimum resistance to corrosion is fixed by the Applicant to a duration greater than or equal to 96 hours.

The table 1 below illustrates the corrosion tests which are more relevant for
5 understanding the invention:

[Table 1]

No.	Pretreatment	Nitriding media	Nitriding salt	Post-treatment	Duration before corrosion threshold	Result
C4	Without	Liquid	ARCOR V	Oxidation 1	24 hours	NG
C5	Without	Liquid	ARCOR L	Without	24h	NG
C8	Without	Liquid	ARCOR L	Oxidation 2	24h	NG
C9	Without	Liquid	ARCOR L	Oxidation 1	48h	NG
C10 = P	Without	Liquid	ARCOR L	Ph (ZnFe)	>96h	OK
C13	Without	Liquid	ARCOR L	Ph (ZnCa)	24h	NG
C14	Without	Liquid	ARCOR L	Ph (Zn)	24h	NG
C16	Without	Liquid	ARCOR V	Ph (ZnFe)	24h	NG
C17	Without	Liquid	ARCOR V	Ph (ZnCa)	24h	NG

An “ARCOR L” nitriding is a ferritic nitrocarburising method with treatment temperatures being able to vary between 530°C and 650°C according to the steel to
10 be treated and to the requested specification. It corresponds to what is described in document FR2972459. The “ARCOR L” nitriding bath contains chloride ions.

An “ARCOR V” nitriding is a ferritic nitrocarburising method with treatment temperatures being able to vary between 500°C and 700°C according to the steel to be treated and to the requested specification. It corresponds to the nitriding part
15 which is described in document FR2812888. The “ARCOR V” nitriding bath does not contain chloride ions.

An “Oxidation 1” post-treatment is a method for oxidising in a bath of molten salts at a temperature of 450°C.

An “Oxidation 2” post-treatment is a method for oxidising in an aqueous solution with treatment temperatures being able to vary between 120°C and 140°C. The
5 salts are mainly formed of nitrates, nitrites and carbonates associated with Na⁺ alkaline cations.

A “Ph (ZnFe)” post-treatment is a method for phosphating with treatment temperatures being able to vary between 60°C and 70°C. The salts used are of the (H₂PO₄)₂Me type and comprise Zn²⁺ ions (Me = Zn). Iron is provided in iron
10 powder form.

A “Ph (ZnCa)” post-treatment is a method for phosphating with treatment temperatures being able to vary between 80°C and 90°C. The salts used are of the (H₂PO₄)₂Me type and comprise Zn²⁺ et Ca²⁺ ions (Me = Zn, Ca).

A “Ph (Zn)” post-treatment is a method for phosphating with treatment
15 temperatures being able to vary between 60°C and 70°C. The salts used are of the (H₂PO₄)₂Me type and comprise solely Zn²⁺ ions.

Based on the corrosion tests carried out, it is possible to draw the following conclusions.

In reference to the photograph of figure 2, it is seen that a part (P) according to the
20 invention has no corrosion point (photo taken at the end of 48 hours of testing).

In reference to the photograph of figure 3, a part (C14) not corresponding to the invention has, at the end of 48 hours of testing, more than 50 corrosion points (pc). The treatment referenced C14 is therefore not satisfactory.

In reference to figure 4, a micrograph of a part (C14) has been carried out after
25 treatment, and before the saline spray test. It is observed that the boundary between the phosphating layer (2) and the combination layer (1) is less clear than on the

parts (P) according to the invention. It can be assumed that the deposition of the phosphating layer (2) has attacked the combination layer (1), insofar as phosphating with Zn alone removes Fe ions in the substrate. Contrary to substrates made of zinc-phosphated iron alloy, but not having undergone nitriding, it is

5 observed that phosphating with zinc alone on nitrided parts does not give a good corrosion protection. A theory with this observation is that the dissolution of iron from the combination layer makes the surface of the substrate (S) too rough, which could increase the porosity of the phosphate layer.

This phenomenon is not observed when the phosphating bath comprises Zn^{2+} ions

10 and Fe^{2+} ions (test C10).

From all the different nitriding and phosphating/oxidising combinations tests on the parts (P) not having undergone degraphitising, only the combination of an “ARCOR L” nitriding and a “Ph (Zn and/or Mn) + Fe”) phosphating makes it possible to obtain a sufficient resistance to corrosion (test C10).

15 Other tests have then been carried out in order to verify that the features of the treated part (P) are compatible with a use as a brake disc.

It is observed that the presence of manganese ions in the phosphating bath confers a lower friction coefficient to the part (P), which is not compatible with a use as a brake disc.

20 However, a part (P) not having undergone degraphitising, and having undergone an “ARCOR L” nitriding and a “Ph (ZnFe)” phosphating is absolutely compatible with such a use.

In this regard, the friction performance of such a part (P) is close to that of the prior art. The method according to the invention is therefore particularly adapted to

25 the treatment of brake discs.

The method according to the invention is however less expensive than the solutions of the prior art, as it makes it possible to avoid degraphitising. The

nitriding step, in particular, is inexpensive, as the nitriding salts used (chlorides) are economical and their dosage is not critical.

In other words, the method according to the invention only requires a nitriding and a phosphating to modify the chemistry and the macroscopic structure of the part
5 (P), and thus confer it good mechanical properties, in particular of mechanical strength, resistance to wear, and resistance to corrosion.

In addition, with nitriding and phosphating both being carried out by bath, there is no need to change the mounting of the parts to move from one step to another, and industrialisation is facilitated. In particular, the time for carrying out the complete
10 treatment is broadly reduced with respect to an equivalent gaseous nitriding.

Other ferrous alloys can be considered to produce the part (P), such as steel or white cast iron. However, grey cast iron has the interest of being the least expensive material.

CLAIMS

1. Method for treating a part (P) made of iron alloy, to improve its anti-corrosion and mechanical strength properties, comprising:
 - 5 - a molten salt bath nitriding or molten salt bath nitrocarburising step, to form a combination layer (1) on the part (P), and subsequently
 - a step of phosphating the part (P), to form a phosphating layer (2) on the surface of the part,
 - characterised in that* the bath of molten salts contains chlorides,
 - 10 and the phosphating step is carried out in a phosphating bath containing zinc ions and/or manganese ions, and iron ions.
2. Method according to claim 1, wherein the bath of molten salts does not contain sulphur.
- 15 3. Method according to claim 1 or claim 2, wherein the chlorides comprise alkaline metal chlorides.
4. Method according to claim 3, wherein the alkaline metal chlorides are
 - 20 lithium, sodium and/or potassium chlorides.
5. Method according to any one of the preceding claims, wherein the bath of molten salts comprises:
 - 25% to 60% of alkaline metal chlorides,
 - 25 - 10% to 40% of alkaline metal carbonates,
 - 20% to 50% of alkaline metal cyanates,
 - 3% or less of cyanide ions,

the percentages being expressed by weight with respect to the total weight of the bath.

6. Method according to any one of the preceding claims, wherein:
- when the phosphating bath contains zinc ions but no manganese ions, said zinc ions are present at a mass concentration of between 1g/l and 40g/l, preferably between 5g/l and 20g/l, with respect to the total volume of the phosphating bath;
 - 5 - when the phosphating bath contains manganese ions but no zinc ions, said manganese ions are present at a mass concentration of between 1g/l and 40g/l, preferably between 5g/l and 20g/l, with respect to the total volume of the phosphating bath;
 - when the phosphating bath contains zinc ions and manganese ions, the total of
 - 10 these ions is present at a mass concentration of between 1g/l and 40g/l, preferably between 5g/l and 20g/l;
 - the iron ions being, in any case, present in the phosphating bath at a mass concentration of between 1g/l and 8g/l, preferably between 1g/l and 6g/l, and more preferably between 1g/l and 5g/l.
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7. Method according to any one of the preceding claims, wherein the phosphating layer (2) has a thickness of between 3 μ m and 40 μ m, preferably between 5 μ m and 30 μ m, and more preferably between 5 μ m and 20 μ m.
- 20 8. Method according to any one of the preceding claims, wherein the combination layer (1) has a thickness of between 5 μ m and 40 μ m, preferably between 15 μ m and 25 μ m.
9. Method according to any one of the preceding claims, wherein the part (P)
- 25 is made of grey cast iron.
10. Part (P) made of grey cast iron which can be obtained by the treatment method according to any one of the preceding claims, comprising:
- a nitriding layer in contact with the grey cast iron, comprising a combination
 - 30 layer (1) containing nitrides,

- a phosphating layer (2) arranged on and in contact with the combination layer (1), comprising metal phosphates,

characterised in that the metal phosphates comprise zinc and/or manganese, and iron.

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11. Part (P) according to claim 10, wherein the phosphating layer (2) has a thickness of between 3µm and 40µm, preferably between 5µm and 30µm, and more preferably between 5µm and 20µm.

10 12. Part (P) according to claim 10 or 11, said part (P) having graphite inclusions (G) at a surface of the part (P) on which the combination layer (1) is formed.

13. Part (P) according to any one of claims 10 to 12, said part being a brake disc.

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