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(54) Process suitable to give a direct protection against the wear corrosion of metallic pieces

(57) In a process suitable to give a direct protection against the corrosion of metallic pieces, a nitrogen diffusion area is realised on the outer layer with a maximum depth of 0.1 mm, and with a nitrogen weight % lower than 2-4%, depending on the steel to he treated. The nitrogen is diffused into the piece and fills the imperfections and the empty areas of the crystal lattice. The temperature at which this first phase takes place goes from 480 to 525°C depending from the steel type and the maximum duration is of 10 hours. Then, both the temperature values and the gas mixture, by introducing an oxidising atmosphere, are changed and the nitrogen diffusion is fully stopped by the oxygen action of the oxidising atmosphere against the iron atoms of the surface. Layers of Fe_3O_4 at 95-99% content are obtained, practically FeO/Fe_2O_3 oxides free, which are formed at temperatures comprised between 505 and 545°C and which are comprised between 2 and 4 μm and containing an oxygen weight % between 25% and 30%. A strong barrier and insulation effect is thereby obtained directly within the steel.

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Description

[0001] The present invention refers to a process suitable to give a direct protection against the wear corrosion of metallic pieces, in particular without producing polluting materials.

[0002] Processes and treatments to realise a protection against the corrosion of metallic pieces are generally known, as for instance the processes described in the previous patents FR 2 672 059, US 5.346.560 and GB 2 298 434.

[0003] In general, these systems provide the production of magnetite layers on the steel which has to be protected. These known processes use salt dipping with cyanides, cyanates and a post-oxidation.

[0004] For instance, the French patent 2 672 059 shows, as known and available systems or treatments for increasing the corrosion resistance of metallic pieces, salt baths or environments with an oxidising ionised atmosphere (plasma-ionic environments), in particular at page 2 of the description.

[0005] In this way it is not possible to realise a barrier which can withstand the wear and the corrosion in a particularly efficient and resistant way, above all said barrier is limited in dimensions and geometry. In fact, the barrier is obtained by dipping the metallic parts to be treated in liquid salt baths containing carbonates - nitrides - hidroxides and oxygenated alcali metals (for the oxidation phase).

[0006] The morphology of the so obtained protective layers is not compact enough because of the high level of porosity (up to 50%). Said porosity currently requires, to obtain a perfect insulation, a saturation with polymeric resins or waxes in order to close said porosity; otherwise preferred paths are present which will start the corrosion.

[0007] The above mentioned and to date used thermochemical means can not realise a thickness with a defined and constant chemical composition.

[0008] Said protection means are particularly weak and inefficient for corrosion protection in aqueous environment containing salts, for protection during dipping in solutions of melted light alloys and said protection means have a very low wettability associated to layers which have been subjected to hardening through nitride precipitation.

[0009] Further, the limits of these known processes and treatments are significant and are also related, in particular, to the dimensions of the steel elements or products to be subjected to treatment.

[0010] In fact, the above mentioned processes can only treat products with small dimensions and with simple geometry without cavities and without deep holes.

[0011] Further it has to be pointed out the significant environmental limits and problems for the storage and disposal of salty compounds with high toxic emissions and fumes which are derived and developed from the known processes.

[0012] The purpose of the present invention is to define a process which can solve the above mentioned technical problems.

[0013] Said purpose, according to the present invention, is achieved by realising a process suitable to give a direct protection against the wear corrosion of metallic pieces as disclosed by claim 1 in the following claims.

[0014] The characteristics and the advantages of a process suitable to give a direct protection against the corrosion of metallic pieces according to the present invention will be better understood from the following description, which is given as a non limiting example.

[0015] In a process suitable to give a direct protection against the corrosion of metallic pieces according to the present invention, a pure magnetite layer as it will be shown in details hereinafter, will be realised for at least the first 3-5 μm on the surface of a metallic piece to be treated, as for instance on a tool steel or on a hardened and tempered steel and on low-alloy steel as well as on sheet steel.

[0016] It has to be pointed out that the process does not require any particular preventative preparation of the pieces to be treated and further that the so obtained oxide layer is produced without releasing or producing any toxic or polluting residual.

[0017] The process suitable to give a direct protection against the corrosion of metallic pieces according to the present invention is an innovative gaseous process. This fact allows to eliminate any geometric and/or dimensional restriction since the convection puts the reacting agents in contact with the entire surface of the piece to be treated for protection.

[0018] In particular, the invention allows the application of a layer of iron oxide, Fe_3O_4, even on parts with a vertical length of up to 10 meters or with 2.5 meter diameter. The process residual gases are directed to a post-combustor which releases only N_2 - H_2 - O_2 in totally neutral gases into the environment.

[0019] The surface layer produced through the invention process has a nitrogen diffusion area with a maximum depth of 0.1 mm. Said diffusion has to have a nitrogen weight % lower than 2%, said percentage being different in function of the steel type of the piece to be treated. The nitrogen, during this phase, is diffused through the grain edge and fills the vacancies or the vacant areas formed by imperfections of the crystal lattice. As an alternative, the nitrogen atoms are trapped in the free interstitial gaps of the surface of the piece to be treated.

[0020] The temperature of this first phase of the process is comprised between 480 - 505°C for hardened and tempered steel, and between 500 - 525°C for tool steel.

[0021] The nitrogen weight % decreases while going towards the inner portion of the surface and it becomes almost zero at depth over 0.1 mm. The duration of this first phase is no more than 10 hours.

[0022] Then, both the temperature values and the gas mixture, by introducing an oxidising atmosphere, are changed.

[0023] During this second phase, the nitrogen diffusion is completely stopped by the adverse action of the oxygen comprised in the oxidising atmosphere against the iron atoms of the surface.

[0024] Layers of Fe_3O_4 at 95-99% content are obtained, almost FeO/Fe_2O_3 oxides free which have a higher oxygen content.

[0025] In fact, these latest oxides would be particularly disadvantageous as a protective and anti-corrosion agents since they have a high growth rate and therefore they can easily break.

[0026] According to the invention, layers of 2-4 μm thick iron oxide Fe_3O_4 are formed at temperatures comprised between 505 and 545°C, said layers contain oxygen weight % between 25% and 30%.

[0027] A very important factor is the stability of the above oxygen content inside the steel structure and inside the entire so obtained thickness.

[0028] The transition from the layer below is realised through a sudden decrease of the oxygen percentage from 25-30% to zero on a maximum depth of about 1 μm.

[0029] Therefore the integration of a layer with a high level of chemical stability, which makes the compound stable in a steel matrix previously hardened by a nitrogen diffusion of about 0.1 mm, makes available a barrier and insulation effect of a protective film directly from inside the steel. It is like having two different compounds integrated one into the other and exerting a mutually consolidating action. In fact, the steel supports and makes compact the oxide, while the oxide protects and insulates the steel.

[0030] This allows to have simultaneously a chemical barrier and a high temperature oxidation strength with characteristics of compactness, wear resistance, abrasion and glueing (adhesive wear).

[0031] In fact, the magnetite repellence towards all the liquid solutions is generally given by the compactness and by the compression level of the outer layers.

[0032] Said compression is due to the difference between the lattice structure of the oxide and the iron cell (body-centered cubic lattice).

[0033] If the ratio (between the iron lattice step and the oxide lattice step) is lower than 1, then the surface clearly compresses the lower layers; in this way, if the brittleness of these layers is not so high to cause cracks and flakings, we will obtain a mechanical closing action against any outside corrosive environment or alloying solution or light alloy mixtures (Al, Pb, brass).

[0034] It has to be pointed out that the magnetite has the following more interesting characteristics in order to assure the protection from environment corrosion and/or from melted metals:

- low electric conductivity which reduces the migration of the active ionised agents which further increase the oxide layer with consequent crumbling;
- high link energy which requires a higher amount of heat to destabilise the surface E=KT which withstands temperatures up to 900°C. This allows the use at high temperatures, notwithstanding the fact that the use in situations wherein the working temperatures is high is often accompanied by degenerative phenomena as for instance the wear and the abrasion;
- at this point also another characteristic of the magnetite becomes of interest, i.e. its compactness and its chemical stability which become a high hardness (850HV = 75 HRC);
- the hexagonal lattice structure gives additionally the possibility of a parallel sliding of the atomic planes one over the other; where there the planes with higher atomic compactness (Closed Packet).

[0035] This invention has produced the realisation of a magnetite layer in a gaseous environment, said realisation converts a 2-4 μm thick layer previously hardened through nitrogen diffusion into oxide.

[0036] The technical solutions and the great advantages consist in having the possibility to protect from the inside, without the application of any film or coating, the steel product without limits due to the dimensions and/or the shape.

[0037] For instance, the process of the invention is realised through a systematic and continuous control of the process parameters in function of the chemical analysis of a differential quantum-meter GDS versus the depth associated with more sporadic controls with X-rays.

[0038] A further parameter to be taken into account is the ratio between the linear thermal expansion coefficients of the oxide and of the metal contiguous thereto.

[0039] For instance the value of FeO/Fe goes to 1.25 at temperatures up to 1000°C and to a 1.03 value for Fe_2O_3/Fe. The closer the value to 1 the safer the coupling of the metal-oxide even under stress and thermal tensions as the ones present in pressure die casting and in hot forging.

[0040] It has been previously pointed out that the thermochemical means used up to now have a chemical composition of the layer quite different from the one which is defined by an oxygen weight % comprised between 21 and 25% and constant over the first 4-5 μm as in the present invention.

[0041] The process of the invention produces this barrier which has a chemical identity with a defined and constant composition without changes into a transition composition with the base metal.

[0042] By using the process of the invention there is no porosity since the increase in gaseous agents is realised in a very diluted way so that no local high pressures are originated. In fact, the high local pressures, by effect of the gaseous atom coalescence within the host matrix, would be higher than the steel ultimate tensile stress and would therefore cause an opening towards the outside.

[0043] The extension of the above process to parts of any dimensions (up to 11 m height) and shape is the reason for this patent application to cover the formation of a magnetite (Fe3O4) layer through gaseous agents, i.e. by using convective heat plants wherein there is a light over-pressure of 25-30 mbar and the steel is the reaction catalyst.

EXAMPLE 1

[0044] X38CrMoV5.1 steel samples have been treated by diffusion during a first phase for 10 hours at a 525°C temperature.

[0045] In this way, a N_2 diffusion thickness of about 100 μm has been realised.

[0046] Then, the first nitrogen diffusion phase has been stopped and, during a second phase, an oxygen containing atmosphere has been introduced for 5-6 hours at a 545°C temperature.

[0047] In this way, a Fe_3O_4 thickness of about 3 μm has been realised.

[0048] We have therefore obtained a bar sample having perfect glueing strength characteristics and corrosion strength characteristics towards liquid Al at 700°C.

[0049] If said bar had been treated with a known method, as for instance the one according to the French patent 2 672 059, said bar would have been subjected to a salt bath for 10 hours.

[0050] Then the bar should have been treated with an oxidising bath. A bar sample would have been obtained with melted surface characteristics and with the formation of Fe-Al inter-metallic phases having a quick breaking action of the underneath matrix.

[0051] The advantages according to the process of the present invention are evident since there is a significant increase in the protection of the surface against the combined wear-corrosion action caused by Al alloys with silicates in suspension.

[0052] In fact, the oxidation according to the present invention does not jeopardise the previously acquired characteristics in terms of wear and seizing strength; on the contrary, especially in reference to this last feature, the oxidation greatly improves the friction and the plasticity coefficient of the hardened layers, thanks to the morphology of the hexagonal crystal lattice.

Claims

1. A process suitable to give a direct protection against the wear corrosion of metallic pieces wherein each metallic piece is subjected to nitriding with subsequent and integrated production of magnetite (Fe_3O_4), characterised in that said metallic piece, during a first phase, is treated in a gaseous environment with diffused nitrogen at a temperature between 480-525°C and for a 10 hour duration until said metallic piece reaches N_2 weight % no higher than about 4% in a diffusion layer of said metallic piece and, during a second phase, once the nitrogen feeding is stopped, the metallic piece is treated in a gaseous oxidising environment at a temperature between 505 and 545°C.

2. A process as claimed in claim 1, characterised in that said N_2 weight percentage is at about 4% for Al or Cr containing steels.

3. A process as claimed in claim 1, characterised in that said N_2 weight percentage is at about 2% for hardened and tempered steels and for low-alloy steels.

4. A process as claimed in claim 1, characterised in that a magnetite (Fe_3O_4) layer is formed and in that said layer is distributed on the surface of said metallic piece with a 3-5 μm thickness, wherein the transition gradient between the Fe_3O_4 layer (O_2 = 25-30%) and the N_2 diffusion layer ($O_2 \cong$ about 0%) is ≤ 1 μm so as to guarantee the chemical identity of the two areas having a complementary and integrated anti-wear anti-corrosion action.

5. A process as claimed in, claim 1, characterised by realising a primary diffusion layer having a thickness comprised between 0.05 and 0.1 mm by using controlled nitriding atmospheres with a nitriding potential comprised between 3 and 5.

6. A process as claimed in claim 1, characterised in that the O_2 weight percentage in the first 3-5 μm is steadily fixed between 25-30%, the rest being iron.

7. A process as claimed in claim 1, characterised in that it is easy to restore the protective action of Fe_3O_4 any time it is necessary to restore the surface which, during operations, is exposed to corrosion and wear.

8. A process as claimed in claim 1, characterised in that it is possible to apply the integrated magnetite-N_2 diffusion action even on parts already in an advanced state of use, after a cleaning operation and a surface mechanical activation.