

The invention concerns a coating on a substrate for conferring good tribological properties on it, consisting of a non thermodynamic equilibrium chromium-nitrogen alloy. The invention also concerns a method of obtaining such a coating.

The tribological properties of a surface or coating refers to the properties which determine the friction behaviour of this surface over time. The parameters which express this behaviour are essentially the wear rate under friction and the coefficient of friction.

The friction referred to here is true friction between two surfaces, and not lubricated friction where a film of lubricant is interposed between the two solid surfaces and where the relative movement essentially occurs between the layers of lubricant in the film.

In particular, under severe friction conditions, with a high load per unit area, resistance to wear implies a high hardness of the rubbing surface. However, increasing the hardness of a friction coating frequently increases in its fragility, with the risk of premature wear through erosion.

There is a definite correlation between wear rate and coefficient of friction because increasing the coefficient of friction, all other things being equal, leads to an increase in degraded energy and the wear rate is in direct proportion to this degraded energy.

In many applications the energy degraded by friction represents only a minor part of the energy involved; it is then more important to attempt an overall reduction in the wear rate, which depends on the hardness, the fragility and the coefficient of friction combined, rather than to reduce the coefficient of friction alone.

In what follows, the expression "good tribological properties" thus means essentially good resistance to wear, including the wearing of fragile coatings by erosion. The typical test will involve measuring the rate of wear or removal of material on a plane coating in contact with a high-speed steel ring with a load of 20 daN and sliding at 0.55 m/s on the plane coating in water.

The interrelated documents FR-A-2 512 070 and EP-A-0 074 322 describe alloys with good tribological properties comprising chromium and an alloying element, either carbon or nitrogen, where this alloying element is in metastable interstitial solution in the chromium at concentrations between a minimum representing saturation of the solid solution of the alloying element in the chromium in thermodynamic equilibrium and a maximum representing saturation of the interstitial solution.

In the context of the present invention only the chromium-nitrogen system is considered. In this system the nitrogen content is expressed as the number of atoms of nitrogen per 100 atoms of chromium-nitrogen alloy.

In the thermodynamic-equilibrium diagram of the chromium-nitrogen system, moving in the direction of increasing nitrogen contents, there is a solid solution region with 0 to 0.15 atoms of nitrogen per hundred of alloy, followed by a Cr_2N nitride with 33.3 atoms of nitrogen per hundred, followed by a CrN nitride with 50 atoms of nitrogen. The Cr_2N nitride has a hexagonal crystalline structure and the CrN nitride has an NaCl type cubic structure. The latter CrN nitride has all the characteristics of a ceramic. Moreover, two-phase chromium-nitrogen alloys are routinely obtained with a cubic chromium phase and a hexagonal Cr_2N nitride phase.

The prior art documents cited above, and EP-A-0 074 322 in particular, disclose saturation of metastable interstitial solutions of nitrogen in the chromium to 3.5% by weight of

nitrogen, which represents substantially 12 atoms per hundred of nitrogen. These documents disclose that the interstitial solutions have a hardness very much greater than that of chromium (a Vickers hardness of up to 2200, for example, as compared with 600 for chromium) and that, for concentrations of alloying elements greater than the saturation of the interstitial solution, the composition of the alloys was as might be predicted from the thermodynamic equilibrium diagrams.

These interstitial solutions are obtained by fast cathodic sputtering using a chromium cathode on a substrate in a reduced-pressure atmosphere consisting of a rare gas containing the alloying element in the combined dissociable state or in the free state.

It is also found that metastable interstitial solutions cause distortion of the cubic crystal lattice of the chromium, which could account for the increased hardness.

The applicant has discovered that, contrary to what might be expected from the prior art, it is possible in the chromium-nitrogen system to obtain metastable alloys comprising more nitrogen than the interstitial solutions mentioned above and which have better tribological properties than interstitial solutions, combined with a reduced wear rate, freedom from fragility and a relatively low coefficient of friction.

Thus the invention proposes a coating on a substrate for conferring good tribological properties on it, consisting of a non thermodynamic equilibrium alloy of chromium and nitrogen, characterised in that the alloy contains, per 100 atoms, from 87 to 68 atoms of chromium and from 13 to 32 atoms of nitrogen, and in that it consists of two phases, a cubic microcrystalline chromium phase containing included nitrogen and a quadratic chromium nitride phase with a nitrogen content which is stoichiometrically deficient relative to the Cr_2N

nitride.

The two-phase alloy with these characteristics has a high hardness (a Knoop hardness of approximately 2000); it has important advantages as compared with known chromium-nitrogen alloys of comparable hardness:

- its wear rate is up to three times lower than that of interstitial solutions of nitrogen in chromium close to saturation;
- its wear rate is substantially the same as that of the CrN and Cr₂N nitrides and of two-phase compounds consisting of chromium and Cr₂N nitride, but it is considerably less fragile. It shows no scaling due to friction and therefore has a service life much longer than that of thermodynamic-equilibrium nitride compounds;
- using physical vapour-phase deposition, the fineness of grain is not influenced by the angle of incidence of the deposition on the substrate. This contrasts with conventional deposition using the same process where the grain size varies greatly with angle of incidence. This independence of the grain size and angle of incidence facilitates deposition on substrates of relatively complex shape without it being necessary to perfect arrangements whereby all parts of the surface of the substrate receive the deposit with the same angle of incidence.

The differences between the thermodynamic-equilibrium Cr₂N nitride and the metastable nitrides in accordance with the invention are confirmed by examination of the crystal structure, by X-ray diffraction for example, and by the distinctly different properties of the two-phase alloys depending on whether the nitride phase is quadratic or hexagonal, even when their overall composition is the same. However, it has not at present been possible to determine the

chemical composition of the quadratic nitride. In particular, it will be understood that the metastable nature of this nitride makes phase separation very difficult, entailing the risk of bringing about rearrangements in composition. In any event, it will be noted that the chemical composition of the nitride is a matter for scientific curiosity only, given that it cannot contribute in practice to the identification or obtaining of the nitride.

It is not even certain that quadratic metastable nitrides are all of the same clearly defined type. The crystal lattice parameters must be between 1.02 and 1.5, without any preferred values having been noted within this range.

The thickness of the coating is preferably between 0.1 and 50 μm , and more particularly between 5 and 20 μm . This thickness depends on the wear rate, the intended application and the permissible tolerances. With thinner coatings the grain size of the alloy has to be taken into consideration.

In another aspect, the invention proposes a method of coating an electrically conductive substrate, intended to confer good tribological properties on this substrate, according to which chromium is sputtered in a reactive atmosphere of nitrogen in a rare gas confined at low pressure in a chamber equipped with so-called magnetron sputtering equipment with, in combination with a magnetic field, an electric field established between the anode substrate and a cathode chromium target and generating a plasma under operating conditions such that a deposit of a non thermodynamic equilibrium alloy of chromium and nitrogen is formed, a method characterised in that the nitrogen partial pressure in the rare gas is set to a value between a predetermined minimum pressure at which the single-phase alloy is saturated with included nitrogen and a predetermined maximum pressure at which hexagonal chromium nitride Cr_2N begins to form, the alloy then containing, per 100 atoms, from 87 to 68 atoms of chromium and from 13 to 32 atoms

of nitrogen and having two phases, a cubic microcrystalline chromium phase and a quadratic chromium nitride phase with a nitrogen content which is stoichiometrically deficient relative to the hexagonal chromium nitride.

It will be understood that the formation of metastable alloys which correspond to relative internal crystallisation energy minima separated from the absolute minimum corresponding to the thermodynamic-equilibrium alloy by energy barriers that cannot be crossed at the temperatures used implies a sufficient rate of deposition for the arrangements of atoms in the crystals to be fixed in their deposition configuration.

The primary conditions which govern these configurations are apparently the respective fluxes of ionised chromium and nitrogen atoms which reach the substrate and the energy levels of these atoms. The laws are not well known, however, and in practice the operator can act only through the measurable deposition parameters, namely the total pressure of the atmosphere in the chamber, the nitrogen partial pressure, the potential drop across the discharge, the intensity of the discharge and, to some degree, the paths of the ions. However, these parameters are partially interdependent in the discharge area and the operator acts on global parameters.

In particular, the pressure adjustment process is essentially dynamic and result from the injection, at a controlled flow rate, of the gases into the chamber connected permanently to a pumping system. It will be understood that the pressure distribution cannot be uniform in the chamber. What is more, the various elements (target and substrate supports) in the discharge area and the presence of the discharge cause local pressure disturbances.

Consequently, the minimum and maximum pressures to either side of the deposition range according to the invention must be determined experimentally and will be valid only with a given

sputtering chamber and given deposition conditions.

For a given chamber and given operating conditions, in particular the total pressure in the chamber and the plasma discharge power, these minimum and maximum partial pressures are preferably determined so as to achieve an appropriate rate of deposition of the chromium onto the substrate, executing a multiplicity of depositions onto a number of substrates with staggered nitrogen partial pressures and carrying out a crystallographic analysis of the deposits obtained to determine the minimum and maximum nitrogen partial pressures for the particular chamber and operating conditions.

The rare gas pressure is preferably between 0.1 and 0.5 Pa and the nitrogen partial pressure is preferably between 0.01 and 0.1 Pa.

The discharge power is preferably between 250 and 1200 W per dm^2 of cathode area (the chromium target).

The preferred deposition rates are between 1 and 10 nm/s.

Secondary characteristics and advantages of the invention will moreover emerge from the following description, accompanied by examples.

Example 1: Determination of operating range

Direct-current magnetron cathodic sputtering vacuum metallisation equipment is used, with a metal vapour source and a 30 litre (0.03 m^3) chamber.

In the source a target cathode of 99.9% pure chromium with a surface area of 2 dm^2 is used. The atmosphere in the chamber consisted of a mixture of argon and nitrogen at a total pressure of 0.24 Pa.

Parallelepipedal steel substrates are used, disposed at 6 cm from the cathode and connected to earth. The cathode discharge power was set to 1800 W.

The substrate temperature was approximately 200°C.

With these conditions a coating 11 μm thick was obtained in one hour, representing a deposition rate of 3 nm/s.

A series of substrates were coated with the nitrogen partial pressure increasing in steps of 0.01 Pa from 0.03 Pa to 0.09 Pa. After deposition the coating was analysed by X-ray diffraction.

For the substrate coated at 0.03 Pa the diffraction diagram represented a cubic single-phase alloy with relatively high distortion of the lattice. This is a typical diagram for the alloy according to EP-A-0 074 322.

For the substrates coated at pressures from 0.04 to 0.08 Pa, the diagram represented a two-phase alloy with a cubic phase similar to the alloy formed at 0.03 Pa, with a broadening of the lines typical of fine crystallisation. The other phase had a quadratic structure with lattice parameters between 1.1 and 1.3.

For the substrate coated at 0.09 Pa, the diagram represented a two-phase alloy with a cubic phase corresponding chromium and a hexagonal phase corresponding to the known CrN nitride.

On the basis of these results it can be calculated that the minimum and maximum nitrogen partial pressures above and below the formation of a two-phase alloy with a chromium phase and a quadratic nitride phase were respectively 0.035 and 0.085 Pa. Chemical analysis of the coatings obtained with nitrogen partial pressures of 0.03, 0.04, 0.08 and 0.09 Pa show, allowing for the measurement accuracy possible, that the

proportions of nitrogen atoms corresponding to the limits are substantially 13 and 32 at %. It should be noted that the limit partial pressures determined in this way are valid only whilst maintaining the operating conditions defined with the scope of the present example.

Example 2

The operating conditions are as in Example 1, with an argon partial pressure of 0.2 Pa and a nitrogen partial pressure of 0.04 Pa.

The analysed coating contains 15 at % nitrogen.

The structure is two-phase, with a chromium phase with a highly accentuated microcrystalline character and a quadratic nitride with (absolute) lattice parameters as follows:

a = 285.7 pm
c = 330.6 pm
ratio 1.157

The measured Knoop hardness is 2100.

Example 3

The same equipment is used as for Examples 1 and 2, with the operating conditions slightly modified.

Argon partial pressure	0.3 Pa
Nitrogen partial pressure	0.06 Pa
Cathode discharge power	2200 W
Substrate temperature	350°C
Substrate bias	-100 V
	relative to
	earth
Source/substrate distance	5 cm

Duration 1 hour

Analysis of the coating obtained gives:

Composition: 20 at % nitrogen

Two-phase structure with a microcrystalline chromium phase and a quadratic nitride phase with lattice parameters as follows:

$a = 280.7 \text{ pm}$

$c = 350.4 \text{ pm}$

ratio 1.25

Knoop hardness: 2300

Example 4

A 1 m^3 vacuum metallisation chamber is used, fitted with a 14 dm^2 cathode.

The sputtering conditions were as follows:

Argon partial pressure	0.25 Pa
Nitrogen partial pressure	0.06 Pa
Cathode discharge power	6000 W
Substrate temperature	220°C

The substrates are mounted on a turntable biased at -100 V relative to earth.

Duration 3 hours

Analysis of the coatings gives:

Composition: 30 at % nitrogen

Two-phase structure with a microcrystalline chromium phase and a quadratic nitride phase with lattice parameters as follows:

$a = 286.5 \text{ pm}$

$c = 321.7 \text{ pm}$

Knoop hardness: 1800

Shiny appearance (indicating fine grains)

Example 5

These tests were applied to $10 \text{ }\mu\text{m}$ thick coatings on a parallelepipedal steel sample. The member rubbing on it was a high-speed steel ring, rubbing occurring in water at a sliding speed of 0.55 m/s and with a load of 20 daN . The contact between the rubbing parts was of the plane/cylinder type. The coefficient of friction and the wear rate were determined.

Three coatings were tested.

A) A coating of the type corresponding to Example 2.

B) A single-phase chromium-nitrogen alloy coating containing 2% by weight of nitrogen, ie 7 at %, in the form of a supersaturated solid solution, with a centred cubic structure (chromium).

C) A two-phase chromium-nitrogen alloy with a chromium phase and a hexagonal Cr_2N chromium nitride phase.

The results were as follows:

Table

	Wear rate	Coefficient of friction
A	0.83 nm/s	0.32
B	4 nm/s	0.27
C	0.83 nm/s	0.36

It should be noted that, after one hour of uneventful testing,

coating A had a polished appearance without defects in the friction area.

The test on coating B had to be interrupted before the friction had worn through the coating, which would have occurred in approximately 40 minutes.

The test on coating C had to be interrupted after 20 minutes, as localised binding had occurred. Profile measurements and examination of the friction area with a scanning electron microscope showed scaling of the coating which may be attributed to its fragile nature.

Moreover, the fragility of the type C layers was indicated by a qualitative, so-called scratch test which involves scraping the surface under test with a diamond indenter on which the load is progressively increased and measuring the level of noise emissions resulting from the scraping. With a type A coating there was no emission of noise until the indenter, passing through the coating, attacked the substrate. With the type C coatings, on the other hand, the indenter caused scaling which produced noise emissions.

The Applicant has carried out many tests which cannot be reported in detail here. These tests were concerned in particular with determining the bounds of the domain in which the quadratic nitride can appear and determined that the nitrogen concentrations ranged from 13 at% just after saturation of the interstitial solid solution of nitrogen in chromium, and that beyond 32 at % of nitrogen only the known and thermodynamically stable hexagonal Cr_2N nitride was formed. This suggests that the quadratic nitride may be stable only if it is associated with chromium.

Tests also showed that the quadratic nitride lattice parameter ratio a/c cannot be less than 1.05 or greater than 1.5.

At the same time the tests were concerned with the deposition conditions. Thus it was found that the rates of deposition, measured in terms of the rate of increase of thickness, ranged between 1 and 10 nm/s.

With these rates of deposition the appropriate discharge powers lie between 250 and 1200 watts/dm² of cathode (or target). The most suitable pressures are between 0.1 and 0.5 Pa for the total pressure and between 0.01 and 0.1 Pa for the nitrogen partial pressure.

In practice, coatings less than 0.1 μm thick are liable to wear out very quickly; in addition, their continuity may be suspect if the substrate is not perfectly polished. On the other hand, coatings more than 50 μm thick would generally be more than adequate to resist friction, but the time needed to obtain them would be excessively long. Such coatings are also likely to modify seriously the original dimensions of the substrate.

It may therefore be assumed that the thicknesses will frequently be between 5 and 20 μm .

CLAIMS

1. Coating on a substrate for conferring good tribological properties on it, consisting of a non thermodynamic equilibrium alloy of chromium and nitrogen, characterised in that the alloy contains, per 100 atoms, from 87 to 68 atoms of chromium and from 13 to 32 atoms of nitrogen, and in that it consists of two phases, a cubic microcrystalline chromium phase containing included nitrogen and a quadratic chromium nitride phase with a nitrogen content which is stoichiometrically deficient relative to the Cr_2N nitride.
2. Coating according to Claim 1, characterised in that the ratio of the quadratic nitride lattice parameters is between 1.02 and 1.5.
3. Coating according to Claims 1 and 2, characterised in that its thickness is between 0.1 and 50 μm .
4. Coating according to Claim 3, characterised in that its thickness is between 5 and 20 μm .
5. Method of coating an electrically conductive substrate, intended to confer good tribological properties on this substrate, according to which chromium is sputtered in a reactive atmosphere of nitrogen in a rare gas confined at low pressure in a chamber equipped with so-called magnetron sputtering equipment with, in combination with a magnetic field, an electric field established between the anode substrate and a cathode chromium target and generating a plasma under operating conditions such that a deposit of a non thermodynamic equilibrium alloy of chromium and nitrogen is formed, a method characterised in that the nitrogen partial pressure in the rare gas is set to a value between a predetermined minimum pressure at which the single-phase alloy is saturated with included nitrogen and a predetermined



maximum pressure at which hexagonal chromium nitride Cr_2N begins to form, the alloy then containing, per 100 atoms, from 87 to 68 atoms of chromium and from 13 to 32 atoms of nitrogen and having two phases, a cubic microcrystalline chromium phase and a quadratic chromium nitride phase with a nitrogen content which is stoichiometrically deficient relative to the hexagonal chromium nitride.

6. Method according to Claim 5, characterised in that, in a given chamber and under given operating conditions, in particular the total pressure in the chamber and the plasma discharge power, such as to obtain an appropriate rate of deposition of the chromium onto the substrate, a multiplicity of depositions are executed onto a number of substrates with staggered nitrogen partial pressures, and a crystallographic analysis of the deposits obtained is carried out to determine the minimum and maximum nitrogen partial pressures for the given chamber and operating conditions.

7. Method according to Claim 5 or Claim 6, characterised in that the rare gas pressure is between 0.1 and 0.5 pascals and the nitrogen partial pressure is between 0.01 and 0.1 pascals.

8. Method according to Claim 5 or Claim 6, characterised in that the discharge power is between 250 and 1200 W/dm^2 of cathode.

9. Method according to Claim 5 or Claim 6, characterised in that the rate of increase in the deposit is between 1 and 10 nm/s .

