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كلية العلوم والتكنولوجيا
قسم الهندسة الميكانيكية

Course Handout

SURFACE TREATMENTS

Intended for: 1ST Year Master Students
Materials Engineering

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PREFACE

Surface treatments and coatings currently constitute one of the essential means of improving the functional properties of metals, in particular resistance to oxidation and corrosion, resistance to fatigue in all its forms (mechanical fatigue, thermal fatigue, surface fatigue), thermal insulation, electrical conductivity, resistance to friction and wear, without forgetting the color and appearance, biocompatibility or adhesion of another class of materials (ceramic or polymer). In 2017, they represented between 8 and 9% of the overall turnover of industrial metalworking subcontracting and up to 15% if we include their share in integrated workshops.

Among the different surface treatment processes, it is possible to distinguish four families: structural transformation treatments of mechanical or thermal origin, diffusion or thermochemical treatments, conversion treatments and coatings. The main sectors of activity are automobiles, construction, public works, mechanics, aeronautics and space, weapons, electrical equipment and biomedical.

This handout entitled “surface treatments” is intended for first-year Masters in Materials Engineering students. The aim of this handout is to describe the different surface treatments and coatings based on improved functional properties based on numerous industrial examples. The improvement of these properties is directly a function of the internal health of the deposits or surface layers modified by the treatment. The document will address in a final chapter the different means of destructive and non-destructive control.

It is written in a simplified manner with examples introduced after having given concepts so that the student can assimilate the course content and have a clear vision of its application in the industrial sector.

Dr. BOUBAAYA Rabah

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Chapter I

Specific properties of surfaces

I.1. Introduction

In a majority of cases, as soon as the problem of optimizing the properties of a material, metallic or not, arises, it appears that surface phenomena play a determining role in this approach. Some industrial examples illustrate this strong influence: saving of materials and respect for the environment through the choice of materials with increased resistance to attacks suffered in service, optimization of the catalytic properties of the surfaces involved in the chemical engineering processes, reduction of friction and wear in power transmission used in the transportation industry, biocompatibility and wear resistance of prosthetic biomaterials, structure and properties of interfaces in active and passive constituents of microelectronics.

Many metallurgical phenomena are linked to a determining role of surfaces, we can cite as an indication:

- in development, the solidification process, crystal growth, sintering and making a deposit,
- in evaluation of the properties of use, the modes of cracking and rupture in mechanical or thermal fatigue, the resistance to erosion and cavitation, the mechanical resistance and its evolution with the temperature, the ability to machining with or without chip removal, friction and wear behavior, adhesion and bonding ability, influence of lubrication,
- in physicochemical reactivity, corrosion and oxidation, coloring and appearance, catalysis, recrystallization, phase transformation and coalescence processes, ceramic metal or polymer metal bonding, biocompatibility,
- in evaluation of physical properties, reflectivity and resistance of contact, thermal or electrical conduction.

All these specific surface criteria linked to the properties of implementation and use of materials can be represented schematically in Figure I.1.

The surface is effectively a discontinuity in the arrangement of the atoms of a solid, which gives it an energy greater than that of the volume; this results in a great reactivity of the atoms and a rearrangement of their distribution, with formation of geometric figures such as for example the striations which appear in the first stages of oxidation, segregations of residual elements or minor additions which will migrate from the volume towards the surface, such as for example tin which can disrupt the diffusional phenomena linked to a thermochemical treatment such as carburizing or carbonitriding.

The concept surface is therefore inherently multidisciplinary; it concerns the mechanic, the chemist, physicist and metallurgist. Only a global approach allows to arrive at a complete description of a surface and to understand all of its functional properties.

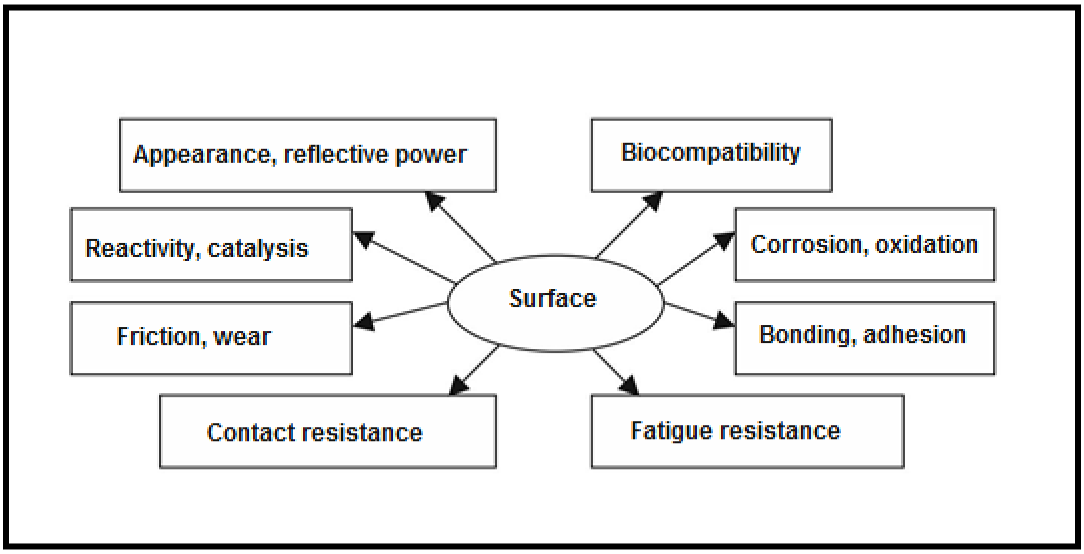


Figure I.1. Functional properties of a surface.

The subject of this introductory chapter dealing with specific criteria for surfaces is to define their main characteristics with a multidisciplinary approach.

The following points will therefore be examined successively:

- a geometric and crystallographic description, making it possible to characterize the the most generally accepted models of atomic structure,
- a physical description, with in particular a definition of the electrical structure tronic,
- a thermodynamic and energetic description, including the notion of surface tension, as well as segregation and adsorption phenomena.

I.2. Surface structure

The surface of a body corresponds to a discontinuity in the periodic arrangement of the atoms of the latter; on the surface, the number of the nearest neighbors of an atom is weaker than in volume, as shown in Figure I.2, relating to a centered cubic structure. In this example in fact, if we cut the crystal with a plane {100} passing through the common vertex of eight adjacent cubes, the number of more close neighbors that are in the center of the cubes goes from eight to four. To restore the balance of the force fields to which they are subjected, the atoms on the surface will tend to exchange new connections with the closest neighbors, either on the surface, or in the underlying volume, or with atoms, molecules or even ionized species from the surrounding environment. This results in a high reactivity of the surface atoms, which will depend on the orientation of this surface. The structure of materials affects the nature and arrangement of atoms in a given cutting plane; this takes on its full importance in polycrystalline materials, which are by far the most common case in practice. Certain properties, such as reactivity, in connection with corrosion and oxidation mechanisms, depend on the orientation of the grains on the surface.

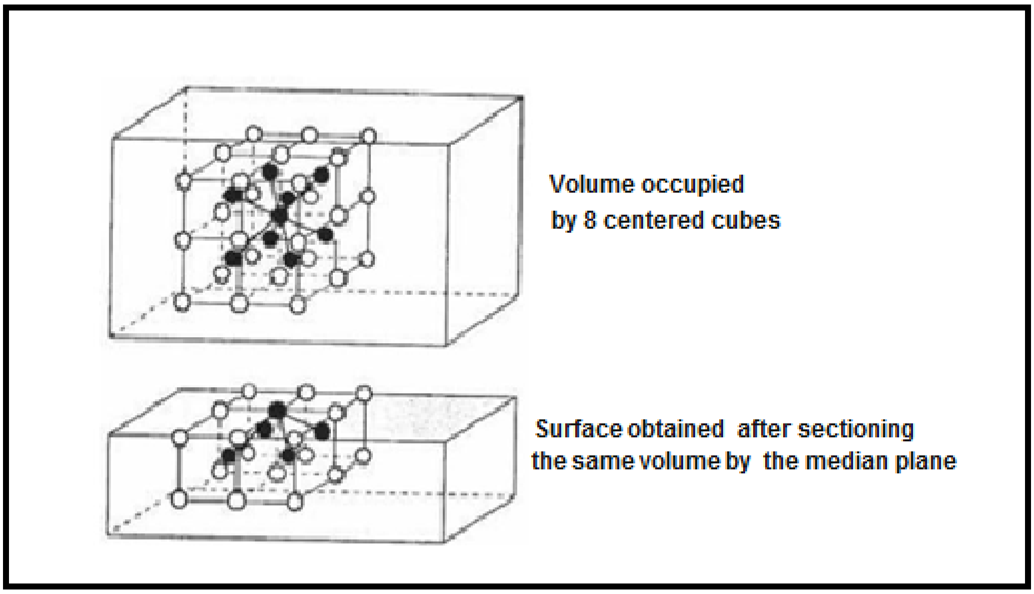


Figure I.2. Close neighbors of an atom in the centered cubic structure: in volume (upper part) and in surface (lower part).

These differences in reactivity constitute a very useful means of revealing the structure of metals and alloys, during metallographic observation. The attack in a given reagent makes it possible to reveal the grains each of which, in connection with its own orientation, will have its own potential, which will lead to the existence of local galvanic couples and to differences in attack, which can be amplified by selective etching of areas close to grain boundaries. This last phenomenon can even be amplified by the segregations of residual elements, which have diffused from the core towards the joints.

Another example of illustrating the difference in reactivity depending on the orientation of the grains is the revelation of the structure by oxidation. For short exposure times, the thickness of the generally epitaxial oxide films depends on the orientation of the grains; this results in colorings, due to interference phenomena, which vary depending on the orientation of the grains.

This effect of grain orientation is put into practice in the case of rolling thin mild steel sheets (centered cubic structure) for cans.

These products are given, through appropriate thermomechanical treatment, a strong texture in order to minimize possible risks of grain attack and significant differences in reactivity with respect to the environment during subsequent coatings. .

Topographically, an ideal surface, as it can appear using powerful detection tools such as the scanning tunneling microscope, corresponds to the section of a crystal whose orientation is well defined in relation to the crystallographic axes. Depending on the orientation of this plane in relation to a plane of high atomic density, we can consider three categories of surfaces:

- **so-called singular surfaces**, atomically plane, whose surface energy is minimal; this is for example the cutting (111) of CFC crystals for metals or semiconductors with a covalent structure of the diamond type, this is also the case for ionic crystals of the NaCl type which are found in ceramics and for which the minimum energy surfaces are those which correspond to strict electrical neutrality (see figure I.3a);

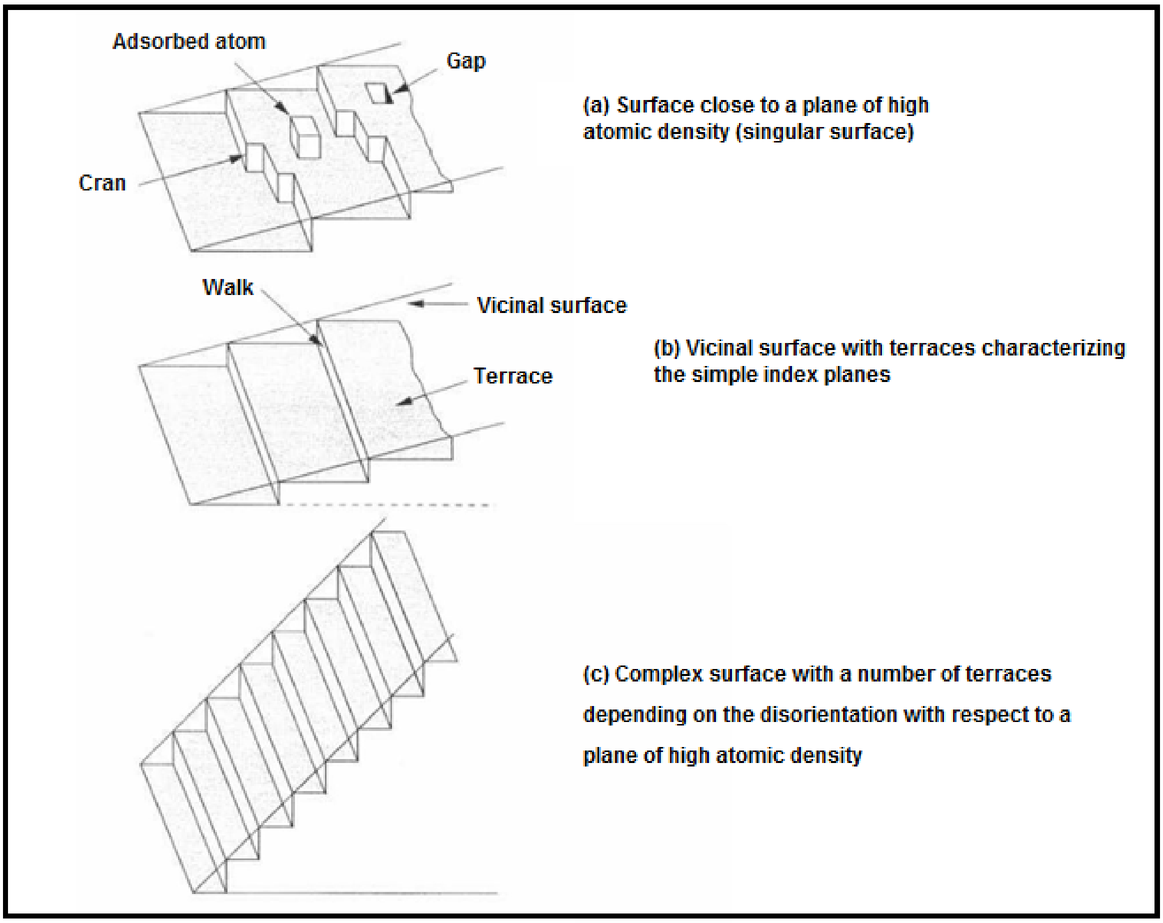


Figure I.3. Defects of a slightly disoriented vicinal surface with schematization of the TLK model.

- **so-called vicinal surfaces**, slightly disoriented in relation to the planes of great density, which appear formed of ranges of highly developed singular surfaces separated from each other by monatomic steps. They can be described by the TLK (Terrace Ledge

Kink) model or (terrace, step edge, step or step) and whose number of steps increases with the angle of disorientation (see figure I.3b);

- complex surfaces that are strongly disturbed and characterized by a natural roughness not described by previous models. This roughness on the atomic scale is completely different from the roughness on the µm scale, which results from preparation by abrasion or machining (see figure I.3c).

Thus, in the general case, at the atomic scale, the surface already has a certain roughness, which increases with disorientation relative to a plane of high atomic density. Each step and each notch constitute so many sites with stronger reactivity. Thus, a surface is all the more reactive the rougher it is on the atomic scale. A curved surface has a greater reactivity as the density of surface defects (and in particular notches) is greater and its radius of curvature is smaller. This reactivity will reach its maximum for areas with a very small radius of curvature such as the “tips”. In addition to the defects defined previously such as adsorbed atoms or vacancies, walking or separation, other linear or planar defects must be added such as the emergence of dislocations or sliding planes, sub-boundaries and grain boundaries, which contribute to modifying the reactivity of the surface.

Tangential relaxations can occur with changing angles of edges and notches, as well as deformations in the vicinity of surface steps.

If the tension stresses developed on a flat surface by tangential relaxation are too high, a reconstruction of the latter can occur with multiplication of defects, pseudo epitaxy or even development of a layer in discordance with the substrate. These very varied reconstructions, whose amplitude is of the order of the atomic distance, disappear for the most part by raising the temperature, multiplying the steps or doping. The resulting surface diffusion of atoms leads to a rearrangement which results in the formation of facets and streaks.

I.3. Electronic properties

The creation of a surface, in addition to the structural aspects, leads to an alteration of the electronic properties of the material. Atoms in the last shell have unpaired electrons in atomic orbitals; their wave functions interfere with those of other atomic orbitals of neighboring atoms. This results in a kind of double-layer type structure, with an electron excess and deficit, respectively above and below the surface. These disturbances in the electronic structure of atoms are all the more important as the number of broken bonds is high. We can deduce from this that ideally flat surfaces (singular surfaces) are not very reactive and characterized by a low level of electron extraction work; on the other hand the steps, notches, gaps that we encounter on local or even complex surfaces constitute sites reagents for elements like oxygen or sulfur. This adsorption of atoms on the surface will result in a strong reduction in the level of extraction work electrons.

The existence of broken bonds and modifications of the associated electronic densities takes on its full importance in the case of semiconductor materials.

Such as silicon, germanium and gallium arsenide. In these materials for which the bonds are strongly covalent and therefore directed, the creation of a surface cannot modify the lengths of these bonds and the hybridization angles of the orbitals must be respected. The dangling connections thus created will not not cause relaxation phenomena such as those previously defined, but rather a reconstruction with modification of the electronic structure in surface. Thus, different models have been proposed to remove the maximum amount of pendant bonds in the sections along the {111} or {100} planes of silicon, with intervention of adsorbed atoms and even stacking faults.

It should be noted, however, that the effects linked to the existence of a surface are limited to one or two atomic layers in metals, due to the high mobility and of the abundance of electrons, which very effectively screen the external fields.

I.4. Energy properties, surface phenomena

I.4.1. Surface energy and surface tension

Surface energy is the most important quantity used in thermodynamics of surfaces. This is the excess free energy that must be provided to a surface to increase its area by an increment dA, taking account of the need to rebalance the surface atomic bonds and in assuming that the temperature, the volume of the solid and the number of constituents (in the sense of the phase rule) remains constant. The unit of surface energy is joule per square meter; for practical reasons, we often use a submultiple:

$$\mathbf{1\ mJ \cdot m^{-2} = 10^{-3}\ J \cdot m^{-2} = 1\ erg \cdot cm^{-2}\ (CGS\ system)}$$

In the case of solids and liquids, the notion of surface tension γ is often used, characteristic quantity of the surface and linked to the thermodynamic potential. The unit of surface tension is newtons per meter, but as previously, a submultiple is more frequently used:

$$\mathbf{1\ mN\ .\ m^{-1} = 10^{-3}\ N\ .\ m^{-1} = 1\ dyne\ .\ cm^{-1}\ (CGS\ system)}$$

The Gibbs procedure consists of introducing into the classical expression relating the internal energy **E** to the entropy **S**, the pressure **P** on the volume **V** and the chemical potentials μi of different constituents $\mathbf{N_i}$, recalled below:

$$\mathbf{E = TS - PV + \Sigma\, \mu i\, .\, N_i}$$

An excess quantity linked to the mechanical energy to be provided to break the bonds and create a surface A, that is to say γA. The fundamental Gibbs equation is therefore expressed, in the presence of a flat surface, at constant T, P, γ and μi, by the following relation:

$$\mathbf{E = TS - PV + \gamma A + \Sigma\, \mu i\, .\, N_i}$$

By removing from this expression the contribution of the massive phases, there remain the superficial quantities of excess which take for the total area created the values:

$$\mathbf{E_\sigma\ (surface\ energy) = TS\sigma + \gamma\, A + \Sigma_2{}^n \mu_\sigma{}^i \cdot N_\sigma{}^i}$$

$$\mathbf{F_\sigma\ (surface\ free\ energy) = E\sigma - TS\sigma\ (surface\ entropy)}$$

In the case of a single component (n = 1), then $F_\sigma = \gamma$ A car $\Sigma_2{}^n \mu_\sigma{}^i \cdot N_\sigma{}^i = 0$. In the previous relation for the definition of E, we see that γ is in fact the partial derivative of E with respect to the area A, at constant S, V and N_i. The surface energy appears as the reversible work necessary to increase the surface area by a unit area, at constant S, V and N_i, which corresponds well to the definition given previously.

These theoretical considerations allow us to draw some practical consequences in surface engineering. First of all, an “ideally clean” surface is unstable because the energy evolution will be in the direction of a reduction in the product γA. In the absence of any chemical species in the surrounding environment (ultravacuum), it is the term A which will be modified with surface restructuring effects. In the presence of foreign molecules, there will be adsorption or reaction with the formation, for example, of a layer of contamination (oxides, organic molecules, etc.). It will be necessary to resort to surface modifications using suitable methods (ion bombardment for example) to treat these surfaces in order to give them other functional properties.

Table I.1. Surface energy of some characteristic materials.

Material class	**Nature of the material**	**Surface energy (erg · cm^{-2})**
Metals	Lead	450
	Magnesium Tin	560
	Tin	570
	Cadmium	620
	Zinc	790
	Aluminum	900
	Copper	1100
	Titanium	1200

	Chromium	1400
	Zirconium	1400
	Iron	1700
	Nickel	1700
	Cobalt	1800
	Molybdenum	2300
	Tungsten	2,300
Oxides, carbides	ZrO_2	530
	Al_2O_3	740
	Tic	900
	V_4C_3	1250
Polymers	PTFE	20
	HDPE	35
	Polyamide	50

In general, the highest surface energies (up to several thousand ergs.cm^{-2}) correspond to metals and covalent solids, the lowest (less than 100 ergs.cm^{-2}) to organic molecules (polymers and in particular fluorinated compounds), while ionic compounds (oxides) are at intermediate levels, i.e. a few hundred ergs. cm^{-2}. Table I gives as an indication some values for the most common materials of the main families.

Surface energy influences the dry friction behavior of materials (adhesion forces, friction coefficient). The correlation between surface energy and adhesion ability of materials appears clearly in Table I.1 through the use of fluorinated materials (PTFE) whose frictional ability is well known.

The notion of surface tension also influences the behavior of materials in the lubricated regime through the wettability phenomena which occur in numerous stages of metal processing: hot and cold production and transformation, brazing, welding, galvanizing, electrolytic deposits, embrittlement by liquid metals, metal-polymer adhesion and its consequences for bonding ability.

I.4.2. Wettability

- **Definition of wettability**

Surface tension concerns all interfaces: liquid-gas, solid-gas and solid-liquid. The solid-liquid interface is the most important on a practical level because it concerns many metallurgical applications. When a drop of liquid is deposited on the surface of a solid, it will spread out and adopt an equilibrium configuration. The system is traditionally represented by the sectional diagram in Figure I.4. The contact angle θ results from the balance of the tensions of the three solid-liquid interfaces γ_{SL}, liquid-vapor γ_{LV} and solid-vapor γ_{SV}. These quantities are linked together by the Young relation:

$$\gamma_{LV} . \cos\theta = \gamma_{SV} - \gamma_{SL}$$

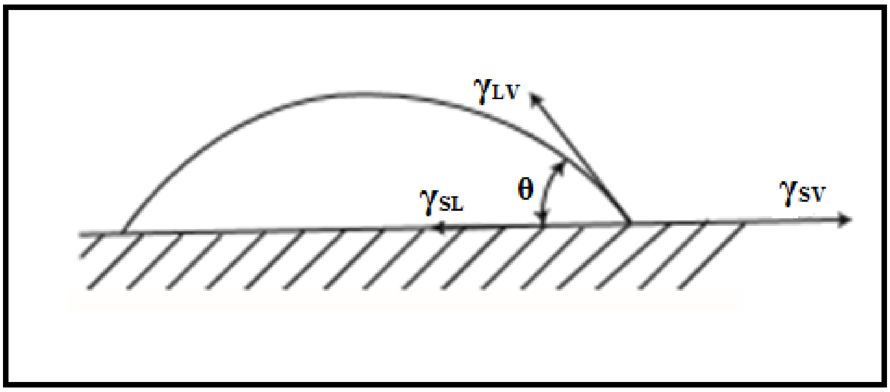


Figure I.4. Schematic representations of the different tensions acting on a drop of liquid in equilibrium on a solid.

Four scenarios must be considered:

- **θ = 0** : this is perfect wetting and the liquid spreads spontaneously
- **0 < θ < 90°** : wetting is good (general case of metals)
- **90° < θ < 180°** : wetting is poor (example θ = 110° with PTFE)
- **θ = 180°** : there is no wetting at all.

The contact angle θ reflects the energy supplied during the spreading of the drop. For a unit of surface area, the work necessary to reversibly separate the solid from the liquid is written as:

$$W_{SL} = \gamma_{SV} - \gamma_{SL} + \gamma_{LV}$$

By combining this relation with that of Young, we obtain that of Dupré:

$$\cos\theta = W_{SL}/\gamma_{LV} - 1$$

This relationship shows that wetting results from the competition between two types of forces: those which govern the cohesion of the liquid which are translated by its surface tension γ_{LV} and those of attraction of the atoms of the liquid by the solid, expressed by the adhesion energy liquid solid W_{SL}.

The wetting ability of a solid can be strongly influenced by a certain number of parameters, in particular the topographical characteristics of the surface: roughness, morphology of the surface layers, and presence of porosities or micro-cracks. The improvement of wetting characteristics by these surface structures can go as far as real impregnations by liquids in connection with capillarity phenomena.

- **Determination of wettability**

Determining wettability consists of measuring the contact angle θ. There are two types of methods, static and dynamic.

- **Static measurement (placed drop method)**

The experiment consists of directly measuring the contact angle of a drop of liquid deposited on the surface of the metal, using an optical sighting method. The measurements must be repeated due to dispersion due for example to roughness and heterogeneities, either in structure or in chemical composition. This method, used industrially, provides practical information regarding surface cleanliness. It also makes it possible, during development, to characterize the behavior of refractory materials in contact with liquid metals and to predict the risks of reactivity between the solid and the liquid.

- **Dynamic measurement (tensiometric method)**

This method consists of immersing a solid in a liquid, then emerging it and measuring the force F exerted on the arm of a balance during the emergence phase (see figure I.5). This force is expressed by the relation:

$$\mathbf{F = \gamma_{LV} \cdot L \cdot \cos\theta}$$

With: **L**: perimeter of the sample, γ_{LV}: surface tension of the liquid in the air.

As the solid-liquid relative speed is very low (< 1 mm/min), it is possible to consider that the system is in equilibrium. The measured force must be reduced by the apparent weight p of the sample in air. It is then worth:

$$\mathbf{\gamma_{LV} \cdot L \cdot \cos\theta - \rho \cdot g \cdot S.\ L}$$

(**ρ:** specific mass of the solid, **g:** acceleration of gravity, **S:** contact area).

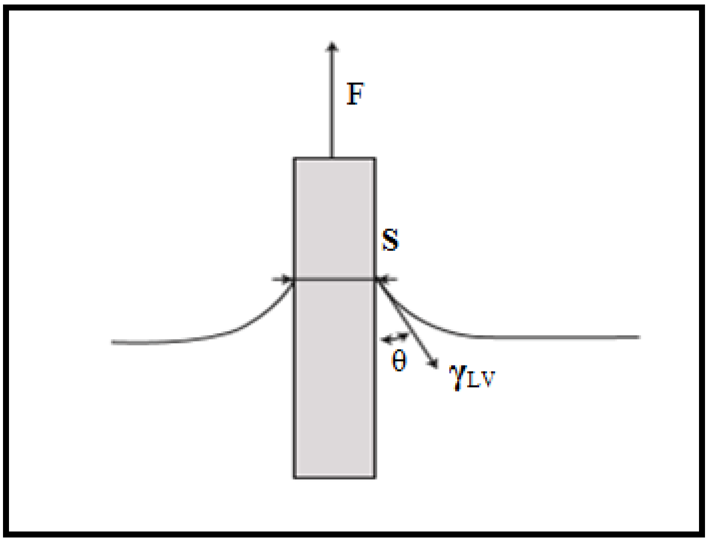


Figure I.5. Schematic diagram of a surface tension measurement using the tensiometric method.

- **Dynamic measurement (Meniscographic balance method)**

This method is widely used in industry to monitor wettability during surface treatment operations on flat products, for example during immersion in liquid metals (dip or scroll processes). It consists of rapidly immersing a sample to a given depth and following, as a function of time, the result of the forces exerted on the arm of the balance reduced by the apparent weight of the sample in the air (4). We obtain curves like the one shown schematically in Figure I.6, which give access to three parameters:

- the interfacial tension: $\gamma_{LV} = F_R \cdot g/L$

- the contact angle θ defined by: $\cos\theta = (F_{max} + \rho \cdot g \cdot S \cdot d)/L \cdot \gamma_{LV}$

- the wetting speed: $d\theta/dt = 180 - \arccos[(F_3 + \rho Sd)/F_R]$

With **S**: area of the section of the test piece, **ρ**: density of the liquid, d depth of immersion, **L**: perimeter of the solid. The method also makes it possible to monitor the reactivity between the steel and the liquid zinc and to take into account the influence of the addition elements in the bath.

Classical approaches to wettability assume not only that the system is in equilibrium, but also that there is no chemical transfer at the interface. However, this is not always the case, particularly when the tests are carried out at high temperature, as in galvanizing or aluminizing studies. Under these chemical non-equilibrium conditions, variations in free energy of the system are associated both with variations in interfacial area and with variations in liquid-solid interfacial tension. Great precautions are then necessary to exploit the results obtained using the meniscographic balance (figure I.6).

I.4.3. Adsorption on surfaces

- **General information on adsorption phenomena**

Given what has been said previously about the geometric and crystallographic approach to surfaces, the latter are very reactive. They quickly become covered, even in a rarefied atmosphere, with foreign atoms which will profoundly modify their properties, despite the very small thickness of these adsorbed layers (one or more atomic layers depending on the temperature, the type of atmosphere and the nature of the substrate).). These processes are of great importance in metallurgy where they are involved in particular in oxidation or aqueous corrosion, in surface treatments, in the reactivity of catalysts and during treatments in atmospheres under very low residual pressure. Several teams around the world have contributed to the study of these adsorbed layers. It was demonstrated that the adsorption phenomenon was reversible and could respond to the laws of thermodynamics.

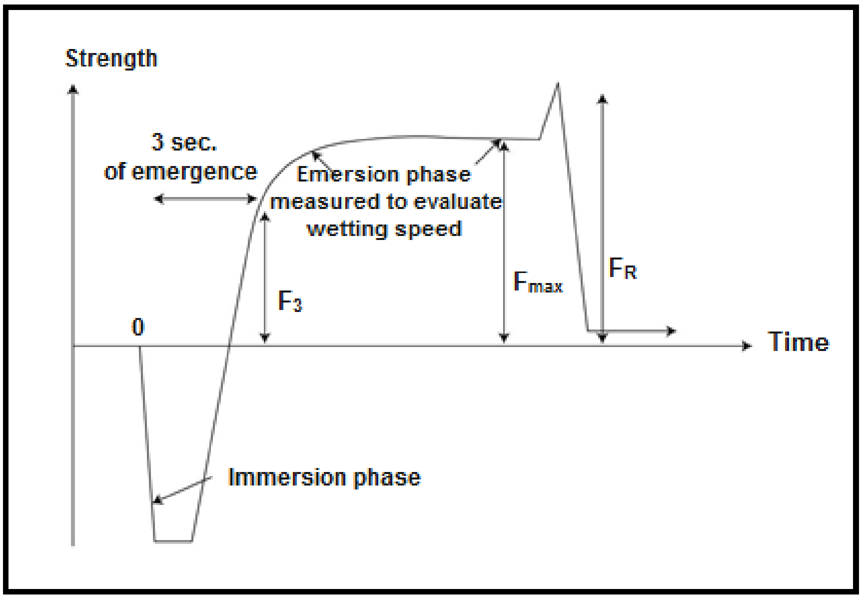


Figure I.6. Monitoring, as a function of time, of the force exerted on a steel blade immersed in a zinc bath using the meniscographic method.

In the presence of adsorbates, the electronic structure of a surface is modified. Depending on the binding energies used, adsorption can be classified into two areas:

- The **physisorption domain** for binding energies E < 0.5 eV; the bonds are of the Van der Waals or hydrogen type and there is little interaction of electronic origin.
- The **domain of chemisorption** for binding energies E > 0.5 eV; there is sharing or transfer of electrons and the bonds are strong.

The thermodynamic study of adsorption leads to the search for a simple description in which the adsorbed species is considered as a single-component system in equilibrium with its vapor, thus identifying the substrate as an inert solid. The most usual approach consists of characterizing the **coverage rate τ** of the surface, which is equal to the ratio between the real surface atomic fraction and the maximum surface atomic fraction of the species considered. This rate depends on the activity of the species in the surrounding environment (i.e. a partial pressure for a gas and a concentration for a liquid) or in the solid (concentration):

$$\boldsymbol{\tau_i = A/(1 + A)}\text{, with :}$$

$$\mathbf{A = (p_i/p_t) \,.\, exp(-\,\Delta G_i^{ads}/RT)}\text{ for a gas}$$

($\mathbf{p_i}$ **:** partial pressure of species i, $\mathbf{p_t}$ **:** total pressure,

ΔG_i^{ads} **:** change in free enthalpy of adsorption)

$\tau_i = B/(1 + B)$, with :

$B = C_i \, . \exp(-\Delta G_i^{seg}/RT)$ for a liquid

(C_i **:** concentration of species i in the liquid, ΔG_i^{seg} **:** change in free segregation enthalpy).

Adsorption can profoundly modify the properties of surfaces, for example:

- the work of extracting electrons.
- electrical and magnetic conductivity.
- faceting and striation, allowing free energy to be minimized.
- reactivity, that is to say the kinetics of surface germination and growth reactions which will contribute to the creation of one or more new phases (oxidation, electrochemical corrosion and passivity).
- packaging operations, particularly before gluing.
- surface treatments to ensure new functionalities.

- **Examples of surface behavior modified by adsorption**

There are many examples showing the impact of the adsorption of different species on the functional properties of metals. We can cite in particular:

- the inhibition of carbon and nitrogen loading on the surface of the steel after adsorption of sulfur or oxygen, during a thermochemical treatment.
- the very high sensitivity of friction resistance properties to the presence of adsorbed atoms: self-lubrication of tungsten by surface segregation of impurities.
- the chemisorption of fatty acids on metallic surfaces during the implementation phase by stamping or by rolling with a thin film of lubricant which does not make it possible to avoid metallic contact between the two opposing surfaces, but which substantially improves the resistance to galling.
- surface striation and faceting, induced by the instability of certain crystalline planes and the obtaining of new equilibrium profiles, which accompany the first stages of oxidation of metals such as iron or copper, strictly two-dimensional stages before the formation of oxides.
- the formation of a passive layer on the surface of stainless steels immersed in aqueous solutions of oxidizing acids (nitric, sulfuric), through germination and growth phenomena.

- the adsorption of fluorinated species during the chemical polishing of metals and alloys in a fluonitric bath which can have consequences on the aging ability of bonded structures.

I.5. Industrial surface area

I.5.1. Introduction

The characteristics of industrial surfaces are far from those of the model surfaces which have just been described in order to present a global approach.

In fact, a three-dimensional representation is necessary to describe such surfaces, because it is the properties of the surface layers which will determine the suitability for subsequent transformations, in particular by surface treatment or the addition of a coating. An industrial surface retains the imprint of the implementation process: tool machining, grinding, cold rolling with cylinders textured by shot peening or laser ablation and lubrication, surfacing operation by skin pass without lubricant with cylinders having undergone a mirror polished… Observations with a scanning microscope make it possible to clearly distinguish these surfaces: coarse and regular scratches by turning or regular and crossed by milling, fine scratches by grinding, surface punctuated by rolling with a laser textured cylinder and irregularly broken up by rolling with a shot-blasted cylinder…

I.5.2. Schematic representation of an industrial surface

After it has been conditioned by various thermal treatment, machining and mechanical, chemical or electrochemical polishing operations, a surface placed in its working environment, apparently clean, is in fact the succession of a series of layers above the healthy metal, which can range from a few atomic layers to several hundred nanometers, or even several µm.

Figure I.7 shows what a surface represents on the scale of the metallurgist with in particular physisorbed and chemisorbed layers which are the consequence of the adsorption on this surface of molecules contained in the environment: O_2, N_2, CO_2, SO_2, Cl_2 and other organic molecules. Below these adsorbed layers, there are strata which are the result of interactions between the material and its environment during the development phases (between 10 and 100 nm), then a zone which can reach several µm which results mechanical and thermal modifications during the material implementation phases.

The presence of adsorbed layers concerns almost all surfaces of metals, ceramics and polymers. Depending on the nature of the elements present, the bonds may be of a physical (physisorption) or chemical (chemisorption) nature, with the chemisorbed layers being characterized by the greatest bonding forces.

I.6. Functional criteria for industrial surfaces

I.6.1. Introduction

To the extent that the industrial surface is the result of mechanical conditioning (implemented by machining, rectification or deformation by different types of tools), metallurgical (heat or thermochemical treatment), in connection with different types of gaseous atmospheres or lubricants, their characteristics call upon different areas of expertise to evaluate them. Metallurgical support will be required to know the structural changes and possible texture effects brought about by the different ranges of treatments carried out. Mechanical support will also be required to measure the deformations and deduce the state of the residual stresses, as well as the application load in conjunction with geometric criteria such as the drawing of the roughness profile, which will make it possible to define the notion of lift. Finally, physico-chemistry support will be required, on the one hand to determine the reactivity of a real metallic surface, in conjunction with the adhesion mechanisms, on the other hand to know the nature of the chemical elements present on the surface, their concentration and as far as possible the nature of their relationship.

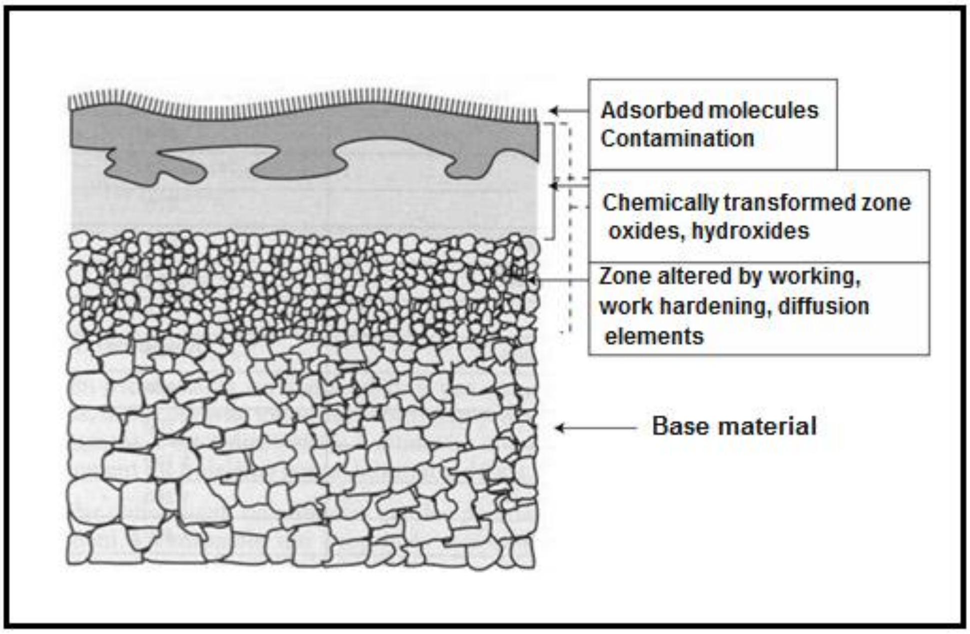


Figure I.7. Schematic representation of the structural and analytical state of a surface after preparation by different methods.

I.6.2. Physico-chemical criteria

The physico-chemical characteristics of surfaces, linked to the presence of adsorbed layers and a sub-layer, which can be grouped under the name of superficial films, play a fundamental role in numerous surface degradation phenomena such as wear or corrosion. The formation of these surface films is linked to chemical criteria, such as the kinetics of oxidation, the possibilities of reaction with polymer films, lubricants, as well as the affinities between alloy elements constituting the two antagonistic surfaces. The formation of these films is also linked to physical criteria such as thermal conductivity and reflective power.

- **Chemical criteria**

In practice, a metallic surface has specific properties linked either to the presence of surface layers of an ionic or covalent nature (oxide, organic film), a consequence of the manufacturing range of the product, or to the existence of heterogeneities in the surface chemical composition such as the precipitation of impurities in grain boundaries, segregations of residual elements, or the presence of chemisorbed foreign species. This situation results in imbalances in the surface electronic population, which translate energetically into the formation of electrostatic charges, which modify the distribution of isopotential lines on the surface of the solid. The electrostatic fields thus created contribute to the activation of superficial reactive sites by a modification of their electronic affinity (reinforcement of the electron donor or acceptor character). It follows from these considerations that the surface of a real metallic solid can be described as a complex set of sites characterized by different reaction affinities (acceptor, neutral or electron donor). The relative density and reactivity of these sites are linked, on the one hand to the chemical nature of the metallic solid and on the other hand to its range of preparation.

The reaction possibilities of a metal surface with polymers or lubricants are a direct consequence of the formation of this complex set of reactive sites. Indeed, many organic molecules are characterized at the level of their molecular skeleton by the presence of a functional group inducing a permanent dipole moment. As a result, under the influence of superficial electric fields, orientation phenomena will occur and lead to the selection of sites likely to interact. It is thus created between the reactive sites on the surface and those of the organic molecule in contact with donor-acceptor pairs, which can interact, by an acid-base type process in the sense of Lewis, if the energy conditions are favorable.

Oxidation kinetics is also a criterion associated with the chemical reactivity of the metal surface. The important criterion in this case is all of the rheological characteristics of the oxide layers as a function of temperature. Certain oxides can behave as real lubricants, and protect the metal surface against any degradation through wear. This is for example the case of iron oxide FeO unlike magnetite Fe_3O_4, which is hard and fragile, as shown by the curves in Figure I.8.

The presence of adsorbed layers is also a limiting factor in the work of adhesion in the contact of two opposing surfaces. The adhesion energy is lower as the sum of the surface energies of the two antagonist surfaces is lower. For metallic couples, the strongest adhesion energies correspond to the contact of identical metals with values that can reach several thousand ergs.cm^{-2}. The affinities between alloy elements of the two antagonistic surfaces therefore constitute a chemical criterion responsible for the risks of adhesion between two metallic elements in contact.

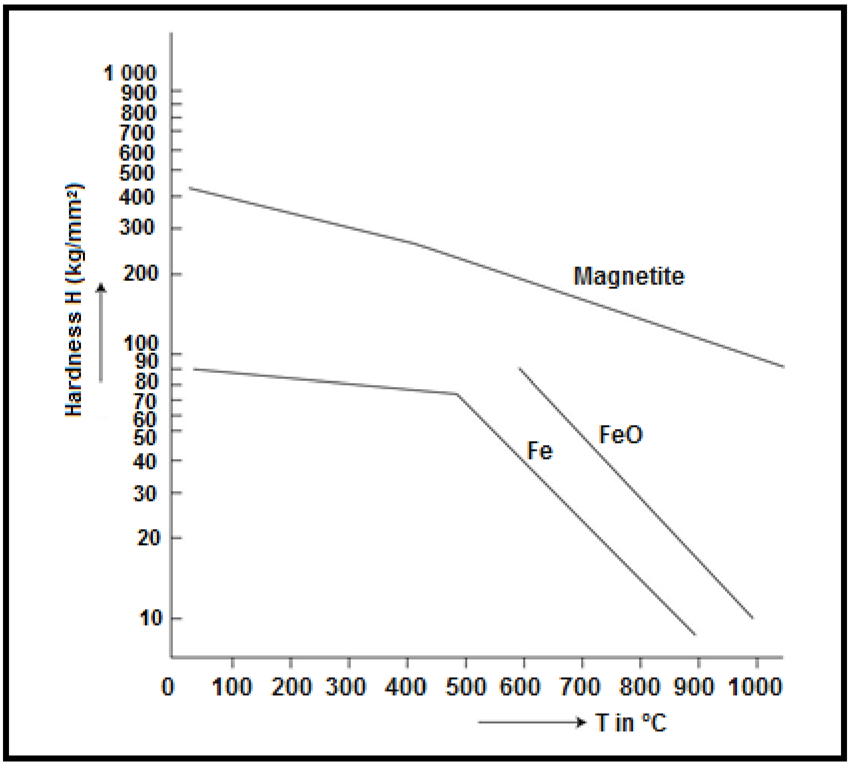


Figure I.8. Hardness of iron oxides as a function of temperature.

- **Physical criteria**

The most representative physical criteria of a metal surface are thermal conductivity and reflective power. These criteria are decisive, the first to evacuate a thermal flash within the material by thus reducing the temperature gradient and the second to limit the impact of this same thermal flash in the material. For example, a laser beam will be perfectly reflected by a metallic surface of polished stainless steel and there will be practically no laser-material interaction. Reflective power is also a major criterion in all fields of application where the visual perception of the material is one of the selection criteria, such as in architecture or in the automotive industry. Good thermal conductivity will make it easier to evacuate calories from the tools when using plastic materials. It is for this reason that the plastics industry is using more and more aluminum alloy molds, particularly for medium series because the gain in industrial productivity compared to steel is close to 70%.

I.6.3. Geometric criteria

The complete description of the real geometry of a surface is relatively complex since it must involve all the identifiable defects from the part scale to the atomic scale. The topography of a surface brings together all the factors characterizing the geometric irregularities or deviations from the ideal surface, which range from the microscopic domain defined more generally by roughness to the macroscopic domain corresponding to the contact geometry.

Macrogeometric irregularities correspond to large amplitude deviations generally due to geometric defects of the generating machine: shape deviations (1st order) and undulations (2nd order) are part of such irregularities. These include profiles generated for example by heat treatment (1^{st} order corrugations) or by rough tool machining (2^{nd} order corrugations).

Microgeometric irregularities include small amplitude deviations due to machining (mechanical finishing phases), abrasive grains, sandblasting or shot blasting particles or possibly vibratory mechanisms. These are small irregularities, which belong to 3^{rd} order deviations from the geometric surface, as shown in the illustrations in Figure I.9.

Standard NF E 05 015 of December 1982 retains a certain number of criteria to characterize these geometric profile deviations: geometric requirements according to standard NF E 04 552 of November 1983 for deviations of the 1^{st} and 2^{nd} order (deviations in shape and undulations), the symbolization of geometric deviations from the 2^{nd} to the 4^{th} order (undulations, periodic or pseudo periodic streaks and furrows, aperiodic pitting) according to standard NF E 05 016 of June 1978. The processing procedure consisting of breaking down the profile into a succession of elementary patterns (roughness patterns) composed of two peaks surrounding a hollow and to associate undulation patterns corresponding to the envelope curve summits was used to establish a European standard NF EN ISO 12085 in March 1998.

The main parameters, which are defined by two-dimensional profilometry, are the arithmetic average roughness R_a, the maximum roughness R_t which represents the difference in level between the highest peak and the lowest valley of the material over the length of the measurement or the roughness R_z which is calculated on the arithmetic mean of 5 successive undulations. A schematic representation of R_a and R_z is given in Figures I.10 and I.11.

The geometric irregularities of the 1st and 2nd order influence the following functionalities: sliding and rolling friction, static and dynamic tightness, unit load in connection with the notion of lift. Irregularities of the 3rd order influence fluid flows, resistance to fatigue in all its forms (fatigue in the mass, surface fatigue, thermal fatigue) and irregularities of the 4th order influence the resistance of a coating or polymer-metal adhesion. It should be noted that 4th order irregularities are not taken into account in the roughness criteria previously defined, but that they can be identified qualitatively on the profilometric surveys previously defined.

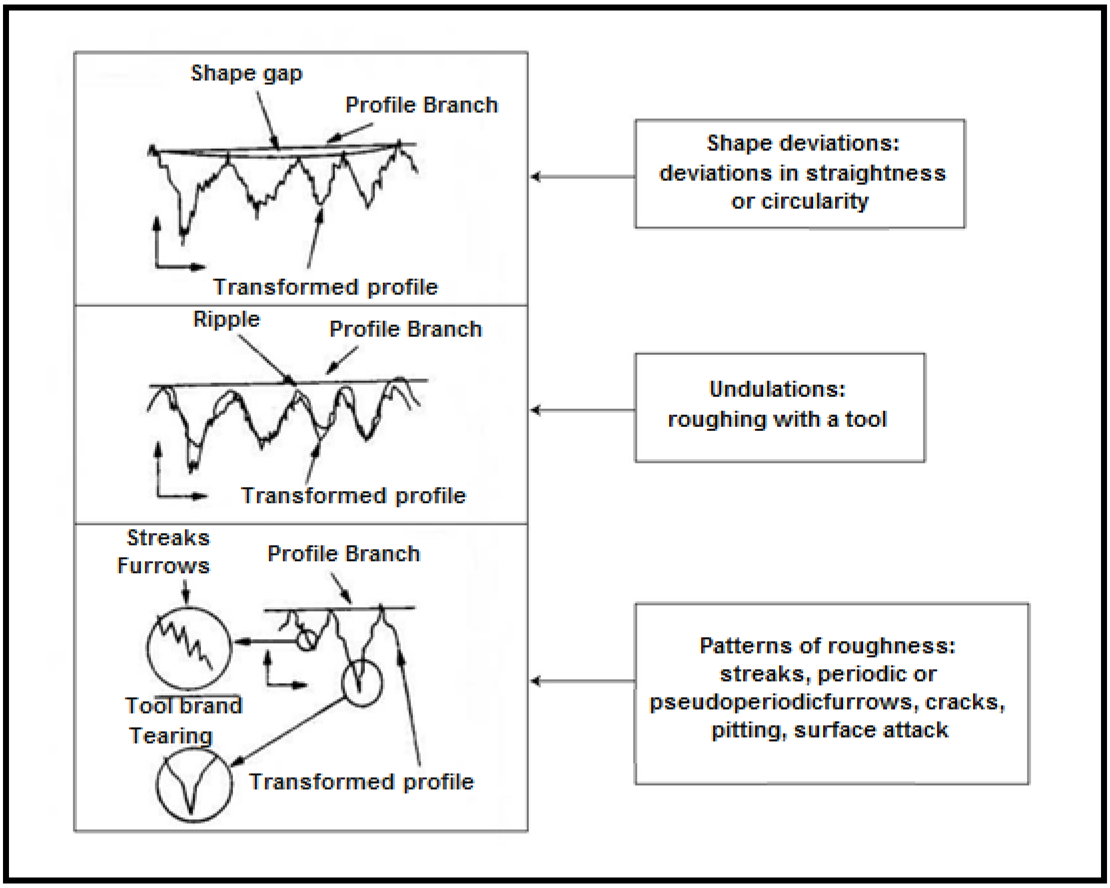


Figure I.9. Classification of geometric deviations of a surface according to standard NF E 05015 of December 1982.

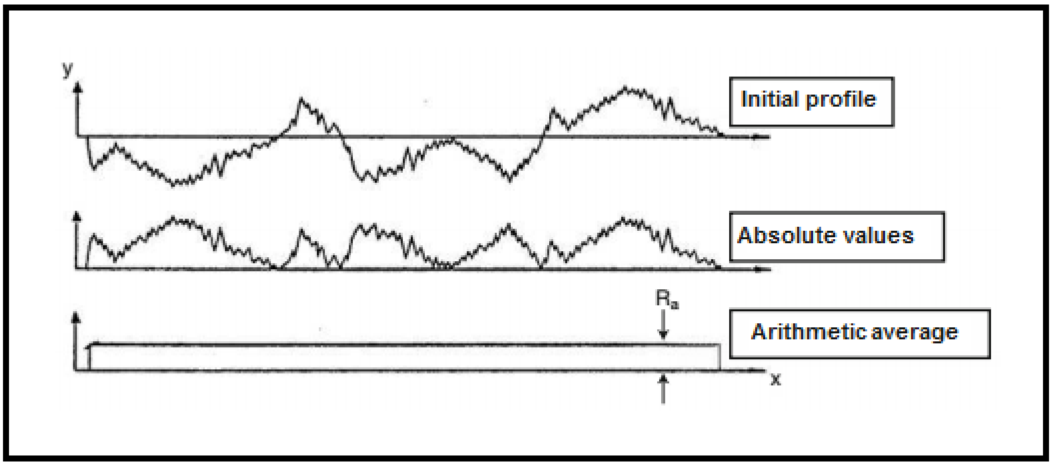


Figure I.10. Determination of root mean square roughness

$$\mathbf{R_a = 1/n \cdot \Sigma_1^n|yi|}$$

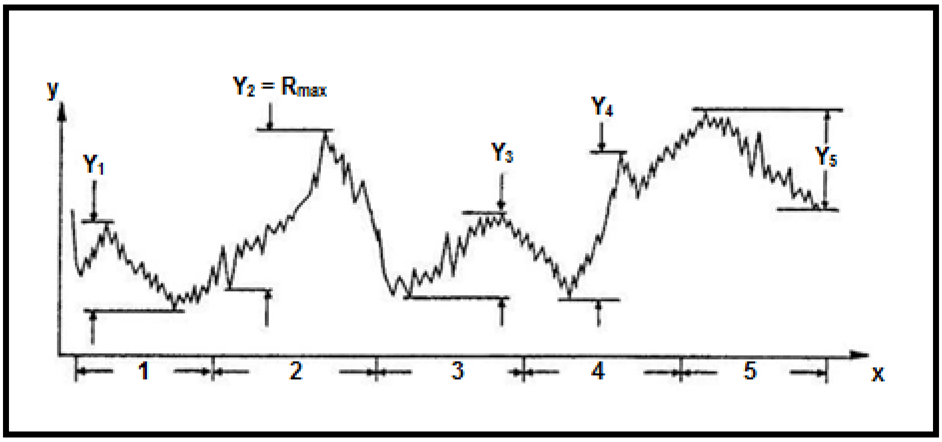


Figure I.11. Determination of roughness R_z on the average of five successive undulations.

$$\mathbf{R_z = 1/5 \cdot \Sigma_1^5 Yi}$$

I.6.4. Mechanical criteria

These criteria must be taken into account in the contact of two metallic surfaces, where the notion of lift comes into play, that is to say the contact between peaks of roughness. These are essentially the modulus of elasticity, the level of hardness and the resistance to cracking, as well as the state of residual stresses.

- **Mechanical resistance**

This is the rigidity and toughness of the geometric irregularities of the surface defined previously. Indeed, the deformation capacity of the roughness patterns can have a favorable impact for hydrodynamic lubrication conditions (running-in of a surface), by increasing the contact surface and reducing the unit application load. However, the deformation of the roughness patterns can promote adhesion phenomena in the absence of lubrication or in “limit” lubrication conditions, which do not prevent metallic contact between opposing surfaces. The mechanical resistance of the surface and the ductility of the material are in this case very important mechanical criteria because they will control the behavior of the roughness patterns upon deformation. These criteria also have a very great influence on the initiation of cracks during a fatigue process (in the mass or on the surface).

These same temperature characteristics are also of great importance for severe metal contact conditions (high application loads or high sliding speed) due to the rise in contact temperature, or when a metal surface is in contact with a heated material for a shaping process (case of forging or extrusion tools and molds for casting metal alloys). The temperature behavior of the roughness patterns will also be very influential on the initiation of thermal fatigue cracks.

- **Residual stresses**

It is also a determining criterion for the behavior of a mechanically stressed surface. These are the constraints existing in a part in the absence of any external constraint, the origin of which is linked to the preparation of the part.

These residual stresses can be compressive after a cold forming treatment, superficial plastic deformation (shot peening for example), after a thermal or thermochemical treatment, in this case they will be rather favorable unless the surface is subjected to strong application loads in which case there may be a risk of breaking the roughness patterns through compression.

These constraints can also be tensile in poorly suited machining conditions (for example severe grinding) or during welding and resurfacing operations involving strong thermal gradients. In this case, they will be rather unfavorable, particularly for the initiation of fatigue cracks (mechanical or thermal) in the hollows of the roughness patterns, areas where mechanical stresses are concentrated. They could also be the cause of stress corrosion phenomena in the presence of aggressive environments.

I.6.5. Metallurgical criteria

The crystallographic structure of the surface of a metal is also a determining criterion for its behavior in contact with another metal, in conjunction with environmental criteria such as temperature or the nature of the atmosphere.

- **Crystallographic structure**

The nature of the crystal lattice is an important parameter. For example, measurements of the adhesion coefficient of different metals on themselves have led to the following classification in descending order of adhesion ability:

- face-centered cubic systems,
- centered cubic systems,
- hexagonal systems.

In the latter case, the adhesion conditions can be minimized when the ratio of the crystal parameters c/a is close to 1.633 which characterizes the compact hexagonal system.

In connection with the crystallographic structure, other metallurgical criteria are important, in particular the texture which can result from the manufacturing range of the product, the grain size (grain boundaries are metallurgical discontinuities), the percentage of reinforcement phases (primary carbides for example in cobalt or nickel-based hardfacing alloys and certain tool steels), as well as the rate of residual austenite for ferrous alloys (the latter transforming into martensite by mechanical and/or thermal action).

- **Effect of environment**

The metallurgical criteria previously defined can be associated with environmental problems such as the gaseous atmosphere (which governs dry corrosion or oxidation), the fluid in contact with the surface (aqueous solution or lubricant) which contributes to corrosion, the temperature and the applied constraints, which will contribute to increasing the severity of the phenomena previously described.

Chapter II

Surface cleanliness

II.1. Reminder of the definition of an industrial surface

All the formatting or shapinging operations of a metal material play a decisive role in the nature of the superficial layers. This is the case, for example, in the case of half-products carried out by thermo-mechanical treatment where one can meet inlays of oxides. These inlays can belong to the basic metal or to alloy elements that migrated to the surface during hot rolling (example of magnesium in the form of MGO in aluminum alloys). This is still the case in the case of cold-laminated half-products where we can meet with adsorbed layers or reaction films as a result of an interaction with the constituents of the lubricant, in particular the "anti-rifle" or "extreme agents" or "extreme pressure ". This is also the case in operations that use cutting or electro-erosion, forge or cold strikes. All these processes lead to the formation of a general hydrocarbon contamination layer resulting from more or less significant adsorption phenomena depending on the temperature reached on the surface. This layer successively contains polar organic molecules, non -polar organic molecules and adsorbed gas molecules. Subsequent receipt operations to regenerate the structure of the material will cause chemical composition modifications to variable thicknesses of a few tens of nano meters to several microns on the surface, in connection with the differences in reactivity of the Vis- to the atmospheres used.

In general, an industrial surface has contaminations such as dust, metallic particles, and oxides, fatty body (oils and fats) sometimes cokéfiés, microorganisms, mineral salts and condensed vapors from atmospheres containing water vapor or carbon dioxide. These contamination can be defined as undesirable substances affecting the physical and chemical characteristics of a metal material and capable of affecting a measurement, such as surface energy, electrical characteristics, or a subsequent implementation process, as if by Example of thermal or thermochemical treatments, the realization of coatings or different assembly techniques. Dust originates the surrounding atmosphere and manipulators. They are embarrassing in microelectronics, in optics or for certain assembly techniques such as collage or brazing. They require precautions such as work in the white room. The metallic particles are present on the surface of flat products after cold rolling and reception; this is for example the case of iron fine on soft steel sheets. Oxides are always present on the surface of metal materials on sometimes very low thicknesses (2 to 10 nm), especially in the case of very easily oxidable materials such as stainless steels, titanium, aluminum and magnesium alloys; Their composition, their stocichiometry, their hydration rate are very dependent on environmental conditions and can vary in large proportions. Native oxides in particular characterized by very low thicknesses are always harmful because they are not mastered. Fatty substances or demonstrating agents such as traces of oil or grease, finger stains, silicones originally have packaging, manipulation and the environment; they also come from mechanical formation of material formatting such as machining, matrix or forging, as well as temporary protection during storage periods. They are extremely harmful because thicknesses of a few nanometers can compromise a surface covering or treatment process. Microorganisms and bacteria will be encountered, often in connection with corrosion products, on parts in service that we want to rehabilitate or strengthen by surface treatment, as well as on parts that have been stored. The mineral salts originated from the contact with the skin of manipulators (sweat), attack or cleaning baths; they are always annoying because it is residual contamination after the surface preparation cycle and can react with the substrate by causing localized tasks or damage. The condensed vapors finally, like the environmental atmosphere and its concentration of water vapor or carbon dioxide. They can cause the formation of very annoying oxides for certain surface treatments such as thermochemical treatments or certain types of coatings in the steam phase.

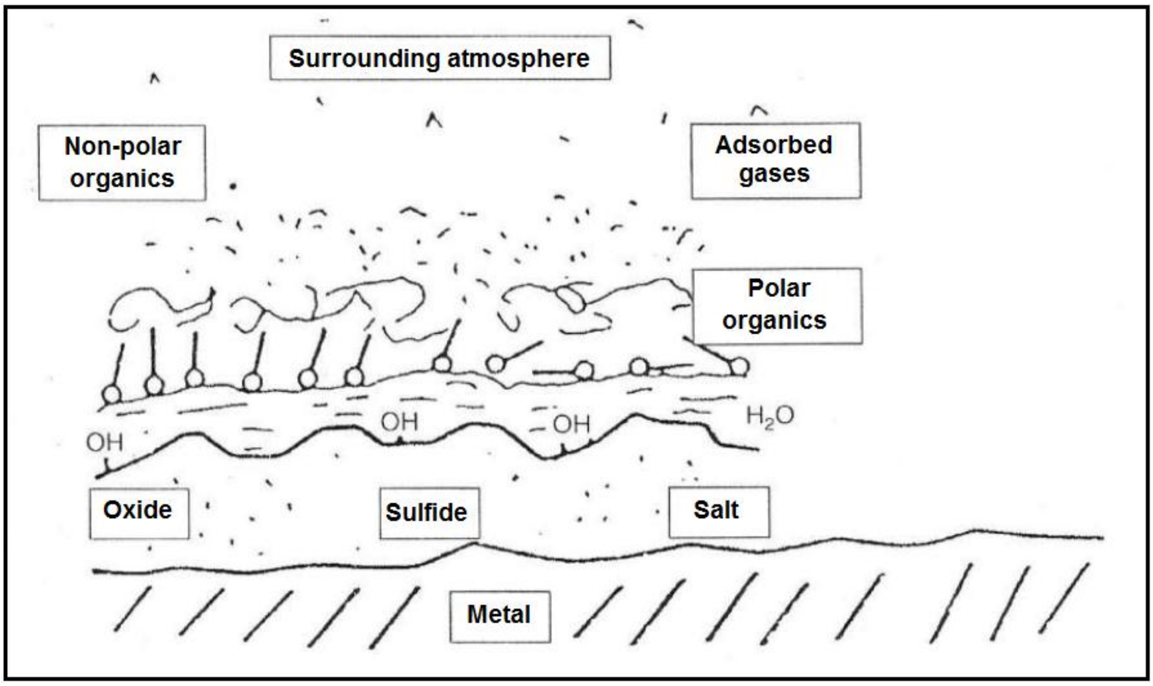


Figure II.1. Different types of contamination on a metal surface.

Figure II.1 schematically shows the hierarchy of contaminations that can be encountered on a metal surface after the different preparation cycles. The boundaries between the different areas are not always very marked, but one can estimate at a few tens of µm the thicknesses of layers of oxides coming from the hot implementation and at most at a few tens of nm the pollution from the Cold implementation.

II.2. Definition of a clean surface

A surface will be said to be clean when all or part of the unwanted contaminants has been eliminated in order to meet certain requirements and make the metal material capable of the application and treatment referred to. The operations carried out on the surface to eliminate these contaminants will act, either on geometric criteria such as roughness and reflective power, or on chemical criteria such as oxidation kinetics and reactions with polymer films or ceramic deposits, either on mechanical criteria such as the state of residual constraints, or on more specific criteria such as wetting or biocompatibility. Before the realization of a superficial treatment or a coating, the surface of a metal material must therefore be prepared and conditioned. This is the first essential step for obtaining quality treatment. A poor surface preparation is in most cases at the origin of a faulty surface treatment. Oxides of a few tens of µm thick can be eliminated by a preliminary stripping operation and the superficial pollution of a few tens of nm thick can be eliminated by preliminary degreasing operations. Finally, note that a "clean surface" must be subject to specific controls making it possible to assess certain properties such as the aspect or the reflective power, the wetting and the hardness. A clean surface is finally a transient quality and the packaging must be followed within the shortest time by the covering or the surface treatment.

II.3 .The main surface preparation operations

The main surface preparation operations can be classified into two categories: cleaning and raising techniques of the surface (degreasing, mechanical or chemical stripping) and techniques that improve the appearance (mechanical, electrolytic or chemical polishing, satin), all these operations are followed by washing, rinsing and drying. It is also necessary to point out the vacuum extraction of the distillation products of the residual organic contaminants and the gases or desired vapors, by the degassing operation.

Degreasing essentially aims to eliminate animal, vegetable or mineral fats as well as their degradation products and all the stains they retain. This operation is carried out, either by chemical or electrolytic route by means of organic solvents or in a lessivel aqueous environment, or by way more mechanical by means of supercritical fluids, ice balls, ultrasound and even cold plasmas.

The stripping is to eliminate adherent products from metal such as oxides from thermo-mechanical treatments or consecutive to corrosion phenomena and inlays of foreign bodies such as sand particles for foundry parts. The methods used are chemical, electrochemical or mechanical. It is also possible to use "ionic stripping" in equipment under reduced pressure (argon) or reducing (hydrogen) gas by subjecting the surface of the parts to the action of an ionized by cold plasmas. It is also possible to use the photomechanical action of an impulse laser on a surface.

The purpose of polishing is to eliminate geometric imperfections and master the surface appearance. This operation is carried out by fine abrasion, chemical or electrochemical dissolution. This operation must be added to this operation that can be applied, either to coated and put off parts, or to metal from an intermediate operation (masking). This operation, most often chemical, is specific to the metal to be eliminated.

The aim of washing is to eliminate soluble elements or little adherent particles from the surface, as well as the products that remain trapped by capillarity in certain areas that are difficult to reach (borgne holes, welding folds). This operation avoids transfers of matter and the risks of corrosion during subsequent treatments and even in service. This operation must be carried out as far as possible in demineralized water with drying within the shortest possible time, preferably in hot air.

The purpose of degassing is to remove adsorbed or dissolved gases from a metal material, as well as the distillation products of residual organic contaminants. These gases are likely to free themselves during a heat treatment under reduced pressure by causing layers of layers or a decrease in the ductility characteristics of the substrate. These are generally study or vacuum treatment operations (below 10-1 Pa) whose temperature and duration are adapted to the nature of the metal material.

Chapter III

Main surface preparation operations

III.1. Introduction

Before assembling or superficially treating metallic materials, their surface should be cleaned. This preparation is an essential element for the effectiveness of the treatment; neglecting it leads to serious disorders. Its purpose is to eliminate pollutants (grease, salt, scale, oxides, etc.). The main surface preparation methods are:

- Degreasing: Mandatory when the surface is soiled by fatty substances.
- Pickling: Very useful method for eliminating oxides and non-adherent scale for high-level anti-corrosion protection.
- Polishing: Process of finishing materials aimed at obtaining a beautiful appearance, a finish or a high quality surface condition (roughness, shine, and luster).

III.2. Degreasing operation

Degreasing is practiced both in the metal processing industry (after cold or hot machining or deformation, before and after heat treatments, before welding or diffusion brazing, etc.) and in a surface treatment workshop itself (before galvanization, metal deposits, enamelling, chemical or electrolytic conversions). Other more marginal applications such as cleaning before repair or assembly of electronic or electrotechnical parts may also require this step.

For chemical degreasing, there is a wide variety of products that can be classified into three families: aqueous solutions, halogenated organic solvents, and non-halogenated organic solvents. The main implementation techniques are as follows: Manual or automatic operation; dipping or spraying; hot or cold application. To treat small surfaces, a mechanical-chemical process is also applicable. In this type of treatment, the parts are agitated in contact with an abrasive, possibly in the presence of degreasing or stripping solutions.

III.2.1. Chemical degreasing in aqueous phase

These are complex mixtures containing phosphates, silicates, hydroxides, surfactants dissolved in water. The formulation of these products is generally adapted to the specific operation to be carried out. Aqueous solutions are effective for the majority of organic dirt. The two main processes are immersion or “dip” treatment and sprinkling. In the case of immersion, the pieces can be hung on a support, placed loose in a basket if they do not offer any possibility of retention (presence of cavities) or placed in a rotating barrel if they withstand light shocks. The baths are frequently heated between 50°C and boiling. However, there are degreasing products that act at low temperatures.

Immersion takes place in a dead bath or in a stirred bath. Agitation is ensured by different means such as a mechanical stirrer, a circulation pump and the injection of compressed air or the action of ultrasound. In the case of spraying, the degreasing solution is sprayed onto the parts in fixed installations such as enclosures or tunnels under a pressure of 1 to 4 bars, at a temperature close to 60°C. Spraying can also be done with a lance with detergent alone or by mixed projection of steam and detergent under 30 or 40 bar. After treatment it is often necessary to dry the parts. With regard to the environment, this method of degreasing involves significant volumes of baths which must be treated before discharge. Health risks are mainly linked to the caustic or irritating nature of these products. The risk is significant when handling concentrated products, particularly when preparing baths where splashes must be feared. Baths at 60°C and above emit alkaline aerosols which irritate the respiratory tract.

The preventive measures to be adopted are as follows:

- Install suction systems if the bath temperature is above 40°C or if mist forms.
- Prevent the risk of projections or splashes when preparing baths.
- Wear personal protective equipment (gloves, clothing, face shield, etc.).

III.2.2. Chemical degreasing in phase solvent

Their high oil dissolving power has made organic solvents preferred partners in the degreasing of metallic materials. The elimination of the adsorbed fatty film can be explained schematically by the breaking of the bond between the polar ends of the oil and the metallic surface for example, then the adsorption of the solvent in a reversible or non-reversible manner on the metallic interface. .

The first solvents used were derivatives of coal (benzol) or petroleum (white spirit, etc.). Their flammability has made them prefer chlorinated and/or fluorinated solvents, which are non-flammable and therefore do not require explosion-proof installations.

- **Halogenated organic solvents**

These are hydrocarbons containing one or more halogen atoms, mainly chlorine (Cl), fluorine (F) or bromine (Br). Chlorinated solvents are widely used industrially. They are excellent cleaners for mineral and vegetable oils and waxes, tars, polymers, etc. They dry quickly and are non-flammable. The most common for metal degreasing operations are: tetrachlorethylene or perchlorethylene; dichloromethane or methylene chloride; and hydrofluoroalkanes (HFA). They are implemented hot or cold, quenched, in the gas phase. After having experienced significant growth, their use is now limited, or even prohibited for some compounds, due to the harm they can cause both to the health of users and to the environment. It comes down to specific applications where their replacement could not be ensured.

- **Non-halogenated organic solvents**

These products act by dissolution or emulsion. Hydrocarbon solvents such as toluene, xylene, white spirit or kerosene had been gradually abandoned in favor of chlorinated solvents. Only white spirit and heavy hydrocarbons with a boiling temperature of at least 200°C and a flash point above 80°C remain. A return to petroleum solvents is currently underway. They are most often used in compositions in combination with other chlorinated solvents.

The preventive measures to adopt are as follows:

- Substitute the most dangerous halogenated solvents, if technically possible, with less dangerous solvents and processes.
- Work in closed, sealed machines.
- Ventilate work premises.
- Avoid manual work, otherwise carry it out at a workstation equipped with a device for suction of vapors at their emission sources.
- For products with a flash point above 60°C, hot application must be done exclusively in a closed machine.

III.2.3. Ultrasonic or vacuum assisted degreasing

- **Degreasing by ultrasound**

Ultrasonic degreasing is considered today to be the most modern and effective method in precision cleaning processes.

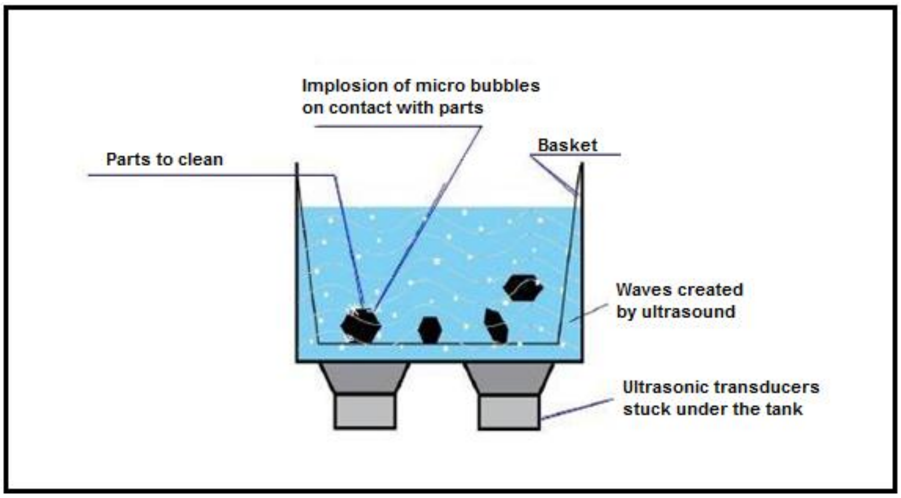


Figure III.1. Operating principle of the ultrasonic cleaner.

The advantages of ultrasonic degreasing are: the possibility of reaching all inaccessible corners or the pipes of the parts to be cleaned, the speed of execution, the use of low temperature and a small quantity of chemical reagents, the absence of Human intervention during cleaning allows you to quickly recoup your investment compared to the cost of labor. Cleaning time between 5 and 20 minutes depending on the condition of the parts.

An ultrasound generator generates high-frequency electrical energy and sends it to the transducers. These transform this energy into vibrations, then transmit it to the cleaning bath. In the cleaning liquid, ultrasonic waves successively trigger complex compression and decompression phases; this is called cavitation. Decompression causes the formation of a multitude of microscopic bubbles which then implode violently during the compression phase. This action causes turbulence comparable to tiny brushes acting on the parts to be cleaned, and causes impurities to come loose even in inaccessible corners. The effect of cavitation is very important since the duration of the implosion is approximately 1µs and very localized (a few μm^2). At the same time, the pulsation of micro-currents generated simultaneously ensures the continuous removal of impurities from the surface of the parts to be cleaned. Ultrasonic cleaning allows the removal of particles larger than 0.15 microns. It was observed that at a frequency of 40 kHz particles from 2 to 100 µm could be removed. The higher the frequency (kHz), the finer the cleaning will be (smaller and more numerous cavitation bubbles). Too low a frequency 25-28 kHz (larger and fewer cavitation bubbles generating a high level of energy) can even damage certain materials.

The ultrasonic cleaning tank works with water in which a detergent is diluted (between 3 and 5%) allowing perfect cleaning. After having selected the temperature ideally between 45° and 55° (above 60° the effectiveness of cavitation decreases), you can place the parts to be cleaned in the basket. All that remains is to select the treatment time using the timer and start the ultrasound operation. The ultrasound stops automatically once the time has elapsed. The parts are then rinsed under running water then dried with a blower or hair dryer.

- **Vacuum degreasing**

Vacuum degreasing guarantees the best environmental quality both in the work area and in the atmosphere. The vacuum ensures the tightness of the installation and the absence of any residue on the parts.

Vacuum treatment allows any part to be perfectly degreased, cleaned and dried, even with complex geometries and deep blind holes, significantly reducing solvent consumption compared to atmospheric cycle washers. In this treatment, the components to be cleaned are placed in a vacuum chamber and heated with radiant heating elements. The treatment temperature and pressure are adjusted to vaporize any contamination present on the components.

III.3. Stripping operation

Pickling and descaling are chemical demetallization techniques used to brighten and/or remove oxides from the degreased metal surface before proceeding with other surface treatments. During pickling treatments, dislocated or adhering layers, such as oxide films, scale and other metal corrosion products, are removed by chemical reaction with an acid-based pickling agent. To effectively remove thick oxide layers, specified acid concentrations, specified temperatures and specified stripping times must be followed. In the field of galvanizing technology, pickling is used as a surface treatment mainly to give metal parts protection against oxidation. An oxide-free surface is created; this also serves as a pretreatment for other surface treatment steps. The chemical solution for stripping, the action time and the temperature are defined according to the material and the characteristics of the workpiece. Very often, the process is assisted by an electric current. Pickling is generally applied to aluminum, stainless steel and cobalt alloys, carbon steels, copper and copper alloys, magnesium, nickel and nickel alloys, titanium, zinc , zircon and special metals.

III.3.1. Mechanical stripping

Mechanical stripping brings together mechanical treatments of very different purposes which have the use of abrasive as a common point. These operations consist of eliminating, among other things, oxides:

- by repeated friction of parts in contact with metal fragments or powdered abrasives, held in (or on) an appropriate system and generally driven by a rotational movement;
- by tearing, thanks to the multiple impacts of small abrasive particles, projected with sufficient kinetic energy.

Friction treatment concerns two disciplines of mechanical surface treatment:

- the first is the work carried out on single parts using hand tools (files or scrapers) or simple machines (buffalo or grinding wheel); the abrasive is then applied to a solid support.
- the second is mechanical stripping by rolling, better known as tumbling or barreling,

which takes advantage of the friction of the pieces mixed dry or with an abrasive load added; the abrasive is here entrained in a fluid flow. This friction machining brings together a very wide range of operations in which the elimination of oxides is not the main function. These operations aim either to remove excess metal left on the surface during the production of the parts (deburring or trimming), or to modify its surface condition in order to satisfy aesthetic needs with a view to obtaining a surface free of traces tools resulting from previous machining (polishing or brightening).

III.3.2. Chemical stripping

It is carried out by immersion or sprinkling, in a mineral acid solution which gradually becomes charged with iron ions and sludge. Common basic reagents are solutions of hydrochloric or sulfuric acids, used respectively at room temperature and above 60°C. Although each process has advantages and disadvantages, hydrochloric pickling is often preferred to sulfuric pickling because of its effectiveness at room temperature and the appearance of the surface of the pickled product: homogeneous appearance of light metallic gray color. Indeed, all things being equal (concentration, temperature, etc.), hydrochloric media have a better stripping power than sulfuric media, a property attributable in part to the difference in solubility between chlorides and sulfates. The aggressiveness of a sulfuric pickling bath can be improved by adding hydrochloric acid. This mixed solution makes it possible to obtain a surface condition comparable to that obtained by hydrochloric acid.

III.3.3. Electrolytic stripping

This type of stripping is generally carried out on stainless steels, treated continuously (strips). The principle is simple and consists of imposing an anodic and/or cathodic polarization on the product to be stripped. The objectives are multiple:

- acceleration of the penetration of the proton into the oxide layer (under the effect of the electric field).
- reduction of “higher” oxides (scale) into iron protoxide.
- action of gas releases (oxygen + hydrogen) at the metal interface, resulting from the alternation of anodic and cathodic polarizations, and promoting the desquamation of the scale layer.
- better control of stripping conditions.
- productivity gain.

The electrolyte used for austenitic steels is generally sulfate-based and can be acidic or neutral. Pickling is done hot to avoid crystallization of metal sulfates.

III.4. Polishing operation

Polishing is a laborious manual operation that takes more time as the surfaces to be treated are complex; Automating this operation makes it possible to reduce its arduousness; it is often also synonymous with productivity gains, with polishing operations on complex surfaces accounting for up to 30% of the total manufacturing time.

In the chain of surface preparation operations, polishing is essentially a finishing operation, which aims to:

- Reduce roughness.
- Reduce the surface topology by eliminating superficial defects highlighted by the stripping operation such as: Microcracks; Porosities; The inclusions.

The different types of polishing are:

Mechanical polishing; Electrolytic polishing; Chemical polishing.

III.4.1. Mechanical polishing

Mechanical polishing by abrasion is carried out in two main stages, under standard metallographic conditions. The first step consists of roughly polishing the surface on rotating sandpaper (SiC), with decreasing abrasive powers and in the presence of water. The second step consists of finishing the polishing by applying the surface to rotating felt mats, on which diamond pastes of decreasing particle size (up to 0.1 μm) have been deposited. The result of this comprehensive treatment is a reduction in surface roughness and its enrichment with iron and chromium oxides. However, the mechanical action of friction by abrasives causes not only surface oxidation phenomena, but also disturbances of the crystal structure. This results in a heterogeneous surface state, physically and chemically poorly defined, whose properties are different from those of the mass of the metal. After mechanical polishing, the surface of the material has three distinct layers: an oxide layer in contact with the external environment, a highly hardened layer called the "Beilby layer", estimated at around 50 Å, and a relatively thick transition zone. (150-200 μm) of deformed metal, between the Beilby layer and the core of the material. In short, mechanical abrasive polishing treatments produce extremely smooth, but deformed surfaces and their applications are restricted to flat surfaces. Another type of polishing is then possible, applying to all types of geometry: electropolishing.

III.4.2. Electrolytic polishing

Electrolytic polishing (also called electrochemical polishing) is one of the material removal processes. In this process, the metal layer is removed by anodic dissolution in an electrolyte bath specially adapted to the material. The objectives of electrolytic polishing are multiple: reduction of surface roughness, i.e. deburring, and obtaining smoothness and shine on the surface. The electrolytes used (chemicals) differ depending on the metals to be machined. We offer electropolishing for aluminum, stainless steel, cobalt alloys, carbon steels, copper and copper alloys, magnesium, nickel and nickel alloys, titanium, zinc, zircon and special metals. Electropolishing is an anodic dissolution process normally used to remove a thin surface layer of a metallic material, through a set of electrochemical reactions in a concentrated acid medium. The principle consists of immersing two metal electrodes in a solution (the electrolyte) between which an electric current is applied. The sample whose surface is to be electropolished is placed as an anode (positive electrode). A reference electrode can be added to the other two in order to measure the voltages at their terminals.

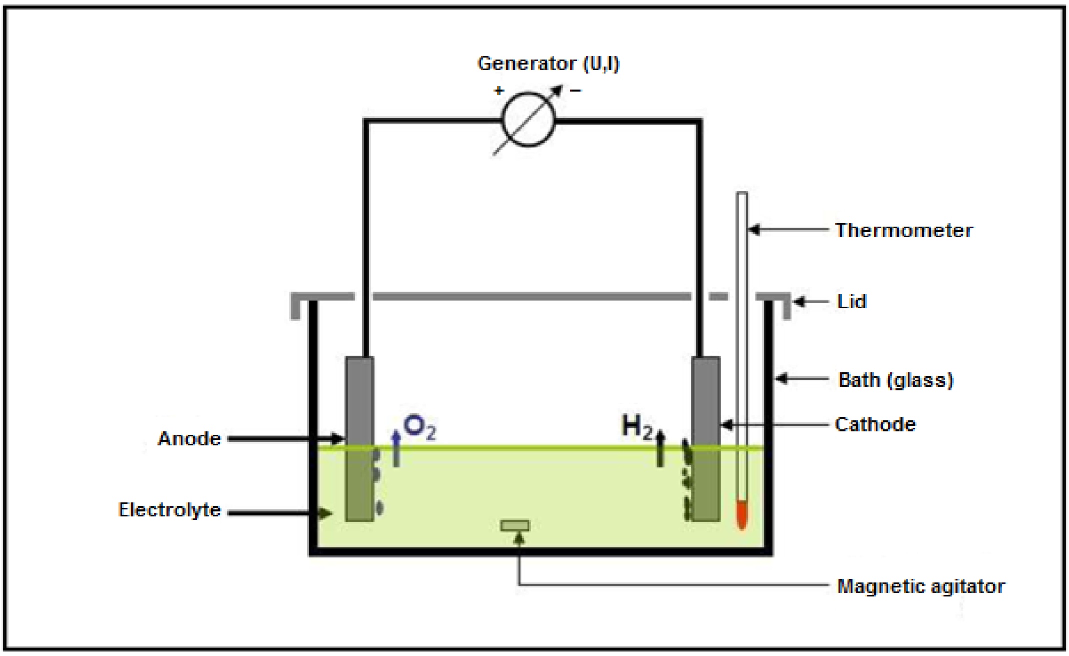


Figure III.2. Schematic of an electrolytic polishing cell.

The advantages of electropolishing are as follows: surfaces with complex geometry can be treated, as well as hard materials. Electropolishing removes metallic inclusions and forms a new thin layer of oxide, homogeneous and uniform, rich in chromium oxide. If the material has previously undergone mechanical polishing, electropolishing allows the removal of the Beilby layer. The consequence of these surface modifications is a clear improvement in resistance to corrosion, local and generalized, which has been demonstrated in particular in the case of 316L stainless steel. Finally, electropolishing reduces the presence of surface defects and reduces roughness.

The disadvantages of electropolishing are: It is sometimes necessary to oversize the samples to be polished, as the amount of material removed during the process can be significant. However, the main disadvantage comes from the fact that many parameters influence the quality of electropolishing, such as current density, electrolyte temperature, treatment duration, etc.

Given that the mechanisms of electropolishing are not yet fully elucidated at present, optimizing the process therefore requires experience, which is often time-consuming and costly. There is therefore no theory on electropolishing, strictly speaking, but rather a set of empirically established principles.

III.4.3. Chemical polishing

With chemical material removal, the part is deburred and smoothed even in hard-to-reach places. The beginnings of cracking are removed. Chemical polishing is a powerless process. It allows the removal of material in places that are inaccessible with mechanical processes. Chemical polishing is suitable for normal steel, carbon steels, titanium, zircon, copper and copper alloys. Chemical polishing of metal surfaces is a well-known technique; it consists of treating the metal surfaces to be polished with oxidizing baths. For chemical polishing of austenitic stainless steels, baths comprising a mixture, in aqueous solution, of hydrochloric, phosphoric and nitric acids are generally used. To improve the quality of polishing, it is usual to incorporate suitable additives into these baths such as surfactants, viscosity regulators and brightening agents. These known polishing baths have the particularity of attacking the metal at very high speed. A polishing treatment of a stainless steel surface with such baths generally cannot exceed a few minutes, otherwise local corrosion may occur. This high speed of action of known polishing baths is a disadvantage, because it makes them unusable for certain applications, in particular for polishing the internal face of the walls of large tanks, such as boilers, autoclaves or crystallizers. . The time required for filling and emptying such tanks being generally much greater than the duration of the optimum chemical polishing treatment, it becomes in fact impossible to obtain a uniform polish of the wall, certain areas of it being insufficiently polished, others being deeply corroded. The high speed of action of known chemical polishing baths also makes the control of chemical polishing very difficult.

Chapter IV

Surface treatments and coatings

IV.1. Introduction

The notion of surface treatment brings together all industrial processes whose objective is to give the treated surface specific physicochemical, mechanical or geometric properties. It may be a simple preparation (rinsing, stripping, degreasing, etc.), a metallic coating or a treatment by diffusion or structural transformation. In recent decades, this sector has experienced great technological change and increasingly broad areas of application.

Surface treatments and coatings of materials have a fundamental role in the preventive and curative maintenance of mechanical parts.

Their economic aspect, both in terms of direct and indirect losses, without forgetting the waste of work and financial resources, is considerable insofar as the two main functions to which they respond: the prevention of corrosion and that of wear, correspond worldwide to a cost that exceeds hundreds of billions of dollars.

IV.2. Classification of surface treatments

There are many ways to classify surface treatments, either by process (electrolytic or chemical, physical deposits, diffusion treatment, conversion or structural transformation, thermal spraying, reloading.), or by function (anticorrosion, decoration, anti-wear, thermal insulation, etc.), or possibly by sector of application (transport, energy, mechanics, building, etc.).

Given the great diversity of techniques used to carry out surface treatments and coatings, any classification approach remains complex.

The most traditional way of classifying surface treatments is to look at the metal substrate side and to differentiate the layers' construction mechanisms according to the metallurgical result. According to these criteria, we distinguish four sectors:

- Surface treatments by structural transformation of mechanical or thermal origin,
- Diffusion treatments,
- Conversion treatments,
- Coatings.

Figure IV.1 schematizes the four surface treatment sectors resulting from the classification according to the layers construction mechanisms.

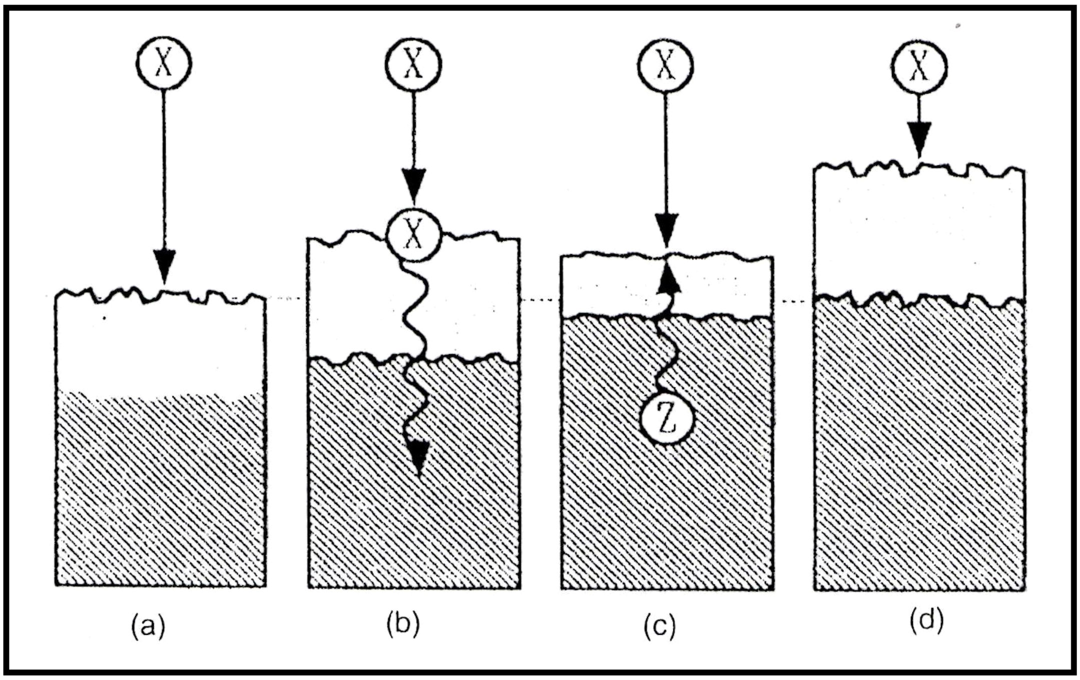


Figure IV.1. The four mechanisms for building a layer on a substrate
(a): treatment by structural transformation, **(b):** diffusion treatments,
(c): conversion treatments, **(d):** coatings.

The current evolution of designations tends to use for these different surface treatment sectors a mixed vocabulary "coatings, surface treatments" symbolized by CST.

Thus, two main classes of operation are distinguished under this vocabulary depending on whether there is a treatment in the mass of the zone underlying the surface (surface treatment) or an addition (deposition) on the surface (coating). The first three sectors belong to all of the surface treatments thus defined and the fourth sector to all of the coatings.

IV.3. Surface treatments by mechanical or thermal structural transformation

In this process, there is no filler material, and only the surface of the part is modified, either by mechanical action or by heat. The aim of this process is to increase the mechanical strength of the surface by introducing residual compressive stresses.

IV.3.1. Structural transformation of mechanical origin

Mechanical surface treatment consists in prestressing surface layers by local plastic deformation, with the aim of introducing residual compressive stresses over thicknesses ranging from a few hundredths of a mm to a few mm, depending on the process used. This treatment can be applied to any type of material exhibiting elastoplastic behavior, i.e. most metallic materials: carbon and stainless steels, titanium and aluminum alloys, superalloys. It can also be applied after certain thermochemical treatments such as carburizing or carbonitriding. The more local and significant the plastic deformation, the more effective the mechanical surface treatment. However, it is essential to avoid damaging the surface layers by over-intensive treatment, which could create internal defects, for example at the interface of inclusions or dispersed phases. Mechanical treatment must also avoid degrading the surface finish, particularly roughness, which could lead to crack initiation due to stress concentration at the bottom of the notch. Figure IV.2 shows schematically the impact of mechanical treatment on the properties of surface layers.

Hardening, in conjunction with changes in roughness, the introduction of residual compressive stresses and the work-hardening effect, will improve a number of surface mechanical properties, in particular:

- fatigue resistance, by substantially delaying the onset of cracks, provided of course that the surface finish is not affected by the treatment,
- resistance to contact and corresponding damage, i.e. the appearance of flaking or the removal of material by delamination,
- resistance to stress corrosion, particularly in the case of austenitic steels and alloys (stainless steels and nickel-based alloys).

The main treatments in this category are shot peening, roller burnishing, deformation knurling, hammering, tribofinishing and laser shock.

Applications are mainly mechanical, notably in the transport industry for highly stressed parts in power transmission (use of roller burnishing and shot peening). There are also applications in the power generation and chemical industries (stainless steels), as well as in aerospace (titanium super alloys).

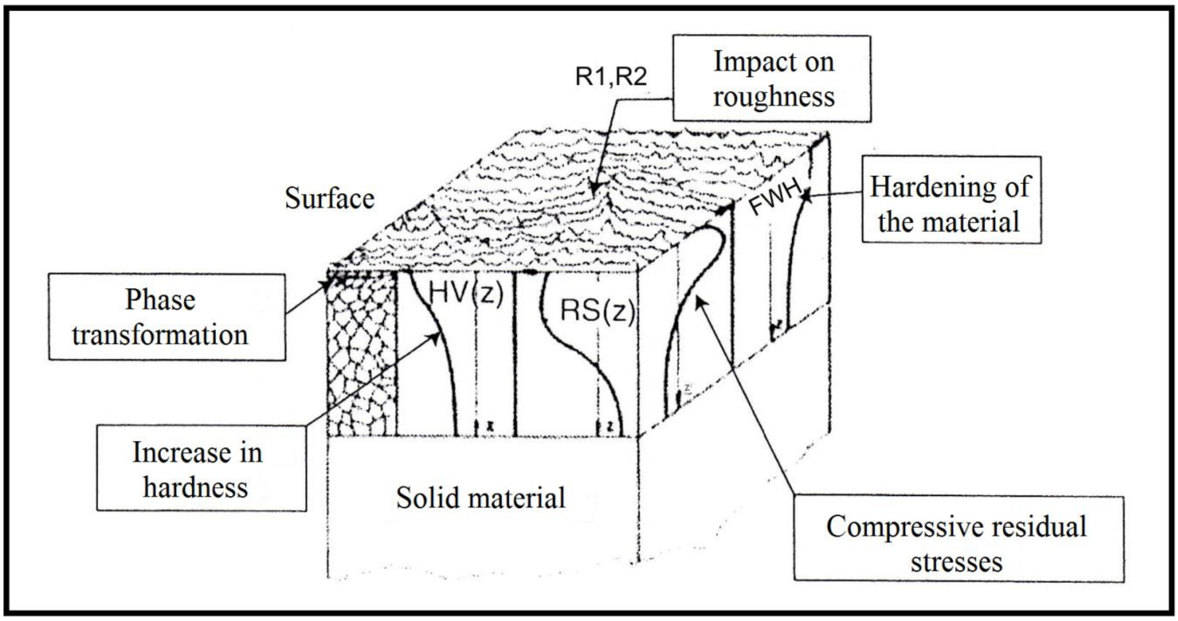


Figure IV.2. Effects of mechanical surface treatments on surface layer properties.

Table IV.1. The various mechanical structural transformation processes.

Process	**Implementation**	**Processed depth [mm]**	**Advantages/disadvantages**
Shooting	Friction	0.01 à 0.03	Long and costly
Shot-blasting	Bead blasting	0.1 à 0.6	Inlays, micro-defects, easy to use
Shingle	Bearing pebble	2 à 3	Dimensional variations, axisymmetric part
Knurling	Work-hardening conditioning with texturing	1 à 2	Simple geometries Surface finish problems
Hammering	Impact of spherical-tipped needles	1 à 2	Surface finish problems, applies to simple geometries
Laser shock	Pulse laser High energy density	Up to 3	Adapts to any geometry, but expensive

- **Shingle**

This treatment is mainly used in the automotive industry to locally improve the fatigue strength of axisymmetric parts, such as cast-iron or steel crankshafts; hardening is achieved by plastic deformation under the action of a high pressure force from a rotating roller.

Residual stresses at the bottom of the groove extend several mm below the surface, and can reach 500 MPa near the surface on both cast-iron and steel crankshafts. As the number of roller revolutions increases, the intensity of the roller burnishing also increases, especially in terms of work hardened depth.

Continuous monitoring of the relaxation of residual stresses by fatigue shows that this phenomenon becomes more pronounced as the service life of the structure approaches.

- **Shot peening**

It is the most widely used process, thanks to its flexibility and high productivity potential. Its field of application has been greatly extended by better control of parameters and the advent of specific variants such as ultrasonic shot blasting.

This treatment is mainly used in the mechanical industry to improve the fatigue life of parts, or in power generation to improve the resistance of stainless steels to stress corrosion. The most commonly used projectiles are hardened carbon steels or ceramics with perfectly spherical shapes to avoid sharp-edged effects and fracture initiation, with turbine propulsion speeds of between 20 and 50 m/sec. Ball dimensions can vary from 0.1 to 2 mm.

There are two types of shot blasting machine, depending on whether the shot is blasted by compressed air or by a turbine. The compressed-air machine is more suited to localized treatments, while the turbine machine is generally used for mass-produced parts. Shot-blasting machines are also very diverse, depending on the system used to present parts under the shot stream. There are drum machines for blasting bulk parts, rotary table machines for blasting small parts, linear conveyor machines for mechanical parts such as coil springs, and overhead conveyor machines. Numerical control enables different zones of the parts to be treated at varying intensities.

- **Laser shock**

Laser-matter interaction over very short timescales (in the nanosecond range) at very high energy densities (in the 108 to 109 W/cm^2 range) generates genuine shockwaves in the material, with a similar effect to shot peening. The pulses generated by a plasma formed on the surface will propagate into the material to depths of between 1 and 3 mm, penetration being facilitated by the quasi-planar shape of the shockwave generated. As a result, compared to shot peening, laser shock results in a much gentler residual compressive stress profile, but with roughly equivalent near-surface values. In addition, laser shocking entails no surface modification of the material, nor any risk of oxide incrustation, since this operation is carried out without thermal modification of the substrate (due to the very short interaction time).

As a result, the results obtained on both steel alloys for mechanical parts and nickel alloys for jet engine blades are extremely promising. In the case of titanium alloys, laser shock allows stresses to be introduced over more than 0.5 mm (0.25 mm in the case of shot peening) without damaging the surface, which is a substantial advantage for these alloys, which are highly sensitive to notching. Double laser impact is also very effective, as it enables high stresses to be introduced without deforming the profile of the treated parts, resulting in a substantial improvement in the fatigue limit of interest for applications in aeronautical fan blades likely to be subjected to in-flight impacts and scratches. In the case of 7075-type aluminum alloys, a triple laser shock is likely to cause work-hardening to a depth of around 1mm. This results in fatigue strength gains of around 40%, with surface compressive stress levels of around 300 MPa. This type of treatment, currently at the pilot stage, should find many niche applications despite its relatively high cost compared with shot peening. It is enjoying renewed interest with the launch of several European industrial programs using high-power lasers.

IV.3.2. Thermal structural transformation

In this processing chain, structural transformations are brought about thermally, using martensitic transformation resulting from rapid heating and vigorous cooling of the part surface. This treatment enables surface hardening without affecting core mechanical properties. Technologies differ essentially in terms of heating mode, power input and rate of temperature rise.

Depending on the process used, structural transformations can involve depths ranging from 0.2 to several tens of millimeters. These transformations are accompanied by an increase in surface hardness, up to 55/60 HRC, and compression of the zone that has undergone the structural transformation. This surface compression is, of course, balanced in the sub-layer by extensional stresses, and the transition zone corresponds, to a first approximation, to the end of the depth concerned by the surface treatment. The resulting structure is generally a fine martensite, and the amorphization threshold can be reached at very high cooling rates, of the order of 5,000°C/sec, particularly in the case of gray cast irons. When the thermal energy density is sufficient, a short time of the order of a few seconds is all that's needed to reach the quenching temperature, and cooling takes place by simple thermal conduction in the substrate. This is the case with electron beam and laser.

Thermal structural transformation treatments are applied mainly to carbon steels, using the hardening capabilities of martensitic tempering. Applications are found in the automotive industry for power transmission, and in metallurgy and mechanical engineering for wear parts (rolling mill rolls, machine tool slides).

Table IV.2. Surface hardening treatment process.

Surface energy supply means	Processing conditions and depths affected [mm].	Application examples
Oxyacetylene flashlight	Power 1.5 to 2 kW/cm^2 Water spray cooling Treated depth 5 to 50	Processing on a conveyor (machine tool slide)
Magnetic induction	Power 2.5 to 25 kW/cm^2 Water spray cooling Treated depth 0.5 to 50	Mill processing (mill rolls, rollers, wear parts)
Laser beam	Power 20 to 60 kW/cm^2 Conduction cooling Treated depth 0.2 to 1.5	Localized reinforcement of complex-shaped parts
Electron beam	Power 100 to 300 kW/cm^2 Conduction cooling Treated depth 0.2 to 1	Vacuum bagging required for processing large series of parts with adapted geometries

- **Surface treatment with blowtorch**

In this process, the surface of the part is heated by the flame of a flashlight or a set of burners judiciously distributed, then quenched more or less violently according to the relative thickness heated by water spraying. The flame obtained with acetylene fuel gas is the one that develops the greatest heating power and consequently gives the highest maximum temperature. The depths treated vary from one to several tens of mm, depending on the thermal power density applied to the surface, the heating time and the hardenability of the steel.

The various flame-hardening processes are either stationary or step-by-step. In the latter case, either the workpiece is moved past a flashlight bar and then sprayed with an appropriate device, or the flashlight bar sweeps the workpiece and the cooling nozzles carry out the quenching in a second sequence. This process is still used, in particular, for the surface treatment of long workpieces, such as machine tool slides.

▪ Superficial induction treatment

Magnetic induction is currently the most widely used energy supply method. Depending on part type and size, hardened thicknesses can vary from 0.5 to 50 mm, depending on the optimum choice of induced current frequency, injected power, power application time and inductor profile.

In practice, the actual heating of the metal is the result of two phenomena:

- direct and rapid heating of the metal by induced currents over a depth of 8, which depends on their frequency and the power injected,
- thermal conductive heating of the metal in the layers underlying the penetration δ, which depends on the metal's thermal diffusivity and the heating time.

▪ Surface treatment with high-energy beams

Surface heat treatment using high-energy beams such as lasers or electron beams offers a number of advantages:

- perfect location of these beams and the ability to move them in space,
- high energy density, with specific powers ranging from around ten $kW.cm^{-2}$ to several hundred $kW.cm^{-2}$, thus limiting the interaction time with the substrate to be treated and ensuring quenching by simple thermal conduction,
- very well-suited to localized reinforcement treatment, especially with lasers.

♦ Laser treatment

Laser surface treatments are carried out for laser-matter interaction durations ranging from 0.1 to a few seconds, and energy densities broadly ranging from 10^3 to 10^5 W/cm^2 . This processing is shown in figure 14.12, which defines the different areas of laser application as a function of specific energy density and laser-matter interaction time.

♦ Electron beam treatment

Typical electron guns can deliver a maximum power of several tens of kW (50 kW or more) at acceleration voltages of several tens of kV (up to 150 kV). Power density can reach 104 $kW.cm^{-2}$. Electron-beam surface treatment conditions are obtained in energy input ranges comparable to those of the laser beam.

IV.4. Diffusion treatment

In this process, the filler material is a metalloid or a metal, in the first case to improve fatigue strength and possibly wear resistance, in the second case to improve resistance to corrosion or oxidation. This sector also includes ion implantation and mixing treatments, which are the result of a physical diffusion process.

IV.4.1. Metalloid diffusion treatment

This includes all thermochemical treatment processes such as carburizing, boriding, nitriding, oxidizing and mixed processes such as carbonitriding and oxynitriding. The latter are currently enjoying a boom, particularly in the mechanical engineering and automotive industries. Thermochemical treatments are widely used in the mechanical engineering industry, particularly in the transport industry for highly stressed parts used in power transmission, as well as in the field of tooling, which is also subject to mechanical stress due to thermal and physicochemical factors. In all cases, the aim is to improve functional properties in terms of fatigue resistance in all its forms (mass fatigue, thermal fatigue and surface fatigue). Certain thermochemical treatments, such as nitriding, can lead to an improvement in functional wear-resistance properties. Some mixed treatments, such as oxynitriding, can lead to a combined improvement in wear resistance and corrosion resistance.

IV.4.1.1. Carburizing

Carburizing is the process of saturating the surface layer of steel with carbon. The main aim of carburizing is to obtain a hard, wear-resistant surface by enriching the surface layer with carbon to a concentration of 0.8 to 1.2% by mass and subsequent quenching followed by low-temperature tempering. This process also increases the fatigue limit.

Carburizing is applied to steels with a low carbon content, ranging from 0.1 to 0.18% C. For larger parts, steels with a higher carbon content are used, ranging from 0.2 to 0.3%. The choice of steels is necessary to ensure that the core of the part, which is not saturated with carbon by carburizing, retains a high level of ductility after hardening.

The parts to be carburized are supplied after machining, which must allow for a grinding allowance of 0.05 to 0.10 mm, or after finishing. In many cases, only part of the part is carburized, the parts that are not to be hardened being protected by an electrolytic copper deposit (0.02 to 0.04 mm thick) or by special coatings consisting of a mixture of fireclay, asbestos sand kneaded with waterglass, etc.

- **Mechanism of formation and structure of the cemented layer**

Carbon diffusion in steel is only possible when the carbon is in its atomic state, obtained, for example, by dissociation of carbon-containing gases (CO, CH_4 , ...). Atomic carbon absorbed by the steel surface diffuses into the metal. The activation energy of carbon diffusion in α-iron reaches 17 to 20 kcal/mol, and in γ-iron, 31 to 32 kcal/mol. This is why in ferrite, diffusion progresses more easily than in austenite. However, at the temperatures at which ferrite exists (below the A1 point), carburization does not take place due to the low solubility of carbon in α-iron.

Carburizing is generally carried out at temperatures above the AC $point_3$ (920 to 950°C), which make the austenite stable, dissolving carbon in quantity. During carburizing, carbon atoms diffuse into the γ-iron lattice. When the carbon saturation limit of the austenite, determined by the SE line of the Fe-Fe_3C diagram (figure IV.3, a) , is reached, conditions favor the formation of a continuous cementite layer on the surface.

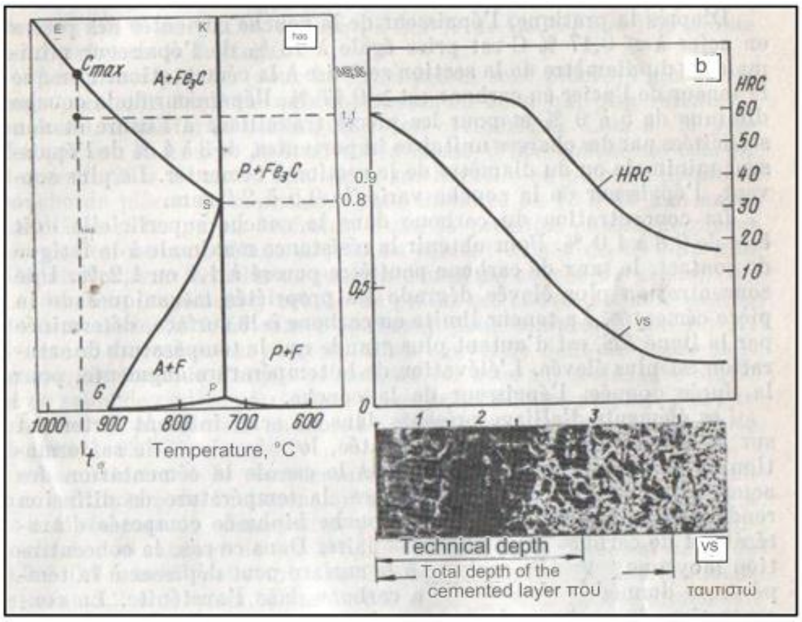


Figure IV.3. Variation in carbon content, microstructure after slow cooling and hardness (after quenching) in the depth of the carburized layer.

Under actual conditions, the formation of a continuous cementite layer on the surface is rare. Under normal conditions, carburizing above the Ac3 point only forms austenite, which decomposes after slow cooling, precipitating ferrite and cementite.

Carbon concentration varies with carburizing depth (Figure IV.3, b), decreasing from the surface in the direction of the work piece core. Slow cooling under these conditions produces three zones in the structure of the carburized layer (figure IV.3, c):

- Hypereutectoid composed of pearlite and secondary cementite, forming a network following the old austenite grain;
- Eutectoid composed of lamellar perlite;
- Hypoeutectoid composed of perlite and ferrite. The amount of ferrite in the latter zone increases steadily as the core is approached.

The thickness of the carburized layer is considered to be equal to the sum of the thicknesses of the hypereutectoid, eutectoid and half of the transition (hypoeutectoid) zones (figure IV.3, c). It is sometimes accepted that the technical thickness of the layer is that whose structure after quenching consists of martensite (95%) + residual austenite. In practice, the thickness of the carburized layer on steel parts (% C $\geq$ 0.17%) is taken to be equal to 15% of the minimum thickness or diameter of the section being case-hardened. When the carbon content of the steel is > 0.17%, the layer thickness decreases by 5 to 9%. For parts subject to wear and not subject to high unit loads, the layer thickness is reduced by 3 to 4%, ranging from 0.5 to 2.0 mm.

The concentration of carbon in the surface layer should be between 0.8 and 1.0%. For maximum resistance to contact fatigue, the carbon content can be increased to 1.1 or 1.2%. A higher concentration degrades the mechanical properties of the cemented part. The limit carbon content at the surface, determined by the SE line in the diagram, is greater the higher the saturation temperature. The higher the temperature, the greater the layer thickness for a given time.

The alloying elements present in a steel strongly influence the structure of the carburized layer, the mechanism of its formation and the rate of diffusion. In the case of carburized steels, the diffusion temperature enables the formation of a two-phase layer composed of austenite and globular carbides. In this case, the average total carbon concentration at the surface may exceed the solubility of carbon in austenite at the given temperature. Carbon concentration in steels containing the elements: Cr, Mn, W, Mo or V can reach 1.8 to 2.0%.

Most alloying elements have different effects on the diffusion coefficient and carbon concentration in the peripheral layer. Their influence on case hardening depth therefore depends on which factor is dominant. Chromium and tungsten reduce the diffusion coefficient of carbon in $D\gamma$ austenite, as they increase the activation energy Q. But by enhancing carbon concentration at the surface, they increase case hardening depth somewhat. Nickel, on the other hand, increases the rate of diffusion, but decreases carbon concentration at the surface, and hence case hardening depth. Manganese has almost no effect on the diffusion coefficient, but increases carbon concentration at the surface and thus somewhat increases case-hardening depth.

- **Carburizing methods**

There are three carburizing processes: solid (carbon-containing), gaseous and liquid.

- **Carburizing by solid cement**

The saturating agent in this operation is a solid cement, most often activated charcoal (birch or oak) in grains 3.5 to 10 mm in diameter, as well as hard coal semi-coke and peat coke.

To accelerate carburizing, activators such as barium carbonate $BaCO_3$ and sodium carbonate $Na_2 CO_3$ are added to the charcoal at a rate of 10 to 40% of the charcoal weight. The solid cement widely used consists of charcoal, 20 to 25% $BaCO_3$ and up to 3.5% $CaCO_3$ added to prevent sintering.

After pickling, the parts to be cemented are placed in welded rectangular or cylindrical steel or, more rarely, cast-iron cases. When the parts are placed, the bottom of the box is covered with a 20 to 30 mm thick layer of rammed cement, on which the first layer of parts is placed, maintaining a distance of 10 to 15 mm between the parts and the side walls. The first layer of parts is then covered by a further layer of 10 to 15 mm thick rammed cement, onto which the second layer of parts is placed, and so on. The last (top) layer of parts is covered with a 35 to 40 mm thick layer of cement to compensate for any shrinkage. The box is covered with a lid, the edges of which are filled with fireclay or a mixture of clay and river sand kneaded in water to form a paste. The body is then placed in a furnace. Carburizing temperatures range from 910 to 930°C.

Holding time at carburizing temperature is 7 to 9 min per centimeter of minimum case size. For a case with a minimum dimension of 150 mm, the carburizing time is 5.5 to 6.5 h, resulting in a layer thickness of 0.7 to 0.9 mm. With a dwell time of 9 to 11 h, the thickness reaches 1.2 to 1.5 mm. In the case of a large box (minimum dimension 250 mm), to obtain a case-hardened layer 0.7 to 0.9 mm thick, the dwell time must be 7.5 to 8.5 h, and for a thickness of 1.2 to 1.5 mm, 11 to 14 h.

After carburizing, the cases are not opened until they have cooled in air to 400 or 500°C.

We have already indicated that steel is carburized with carbon in its atomic state. In solid cement, atomic carbon is obtained in the following way. The case contains air, including oxygen, which reacts at high temperature with the carbon in the cement to produce carbon oxide. In the presence of iron, the carbon oxide dissociates:

$$\mathbf{2CO \rightarrow CO_2 + C_{at}}$$

The carbon thus obtained is atomic at the moment of its formation, and diffuses into the austenite. The addition of carbonates makes the cement much more active and enriches the carburizing atmosphere with carbon monoxide:

$$\mathbf{BaCO_3 + C \rightarrow BaO} + 2CO$$

- **Gas carburizing**

Gas carburizing involves heating parts in a carbon-containing gas medium. It offers several advantages over carburizing in a solid medium, which has led to its widespread use in high-volume production plants.

This form of treatment enables the exact concentration of carbon in the layer to be achieved, reduces process times by eliminating the need to pre-heat cement-filled cases with low thermal conductivity, makes it possible to fully mechanize and automate the manufacturing process by significantly simplifying the subsequent heat treatment of the parts, and allows templating to be carried out directly out of the furnace.

The best carburized layer is obtained by using natural gas (CH_4), composed entirely of methane, as the case-hardening agent, as well as specially treated mixtures of propane and butane.

Liquid hydrocarbons (benzene, kerosene, synthol) are often used for carburizing. The main carburizing reaction is the dissociation of methane and carbon monoxide:

$$\mathbf{2CO \rightarrow CO_2 + C_{at}} \text{ or } \mathbf{CH_4 \rightarrow 2H_2 + C_{at}} ; \mathbf{C_{at} \rightarrow Fe\gamma = austenite\ Fe\gamma\ (C)}$$

Gas carburizing is usually carried out in continuously operating muffle and muffle less furnaces, as well as in discontinuously operating shaft furnaces. In the case of shaft furnaces, kerosene, synthol, alcohols, etc. are used for carburizing, and are fed into the furnace in drop form. The high thermal stability and good vaporization of liquid hydrocarbons (kerosene, synthol, etc.) mean that the gas production and carburizing processes can be carried out in the same usable space.

In continuous furnaces, natural gas is the main fuel used. To obtain the required carbon concentration (usually 0.8%), an endothermic controlled atmosphere is usually used, consisting of 92-95% endogas and 5-8% natural gas. An endothermic atmosphere (20% CO, 40% H_2 and 40% N_2) is obtained by partial combustion of natural gas or another hydrocarbon at 1000 or 1200°C in a special endothermic generator in the presence of a catalyst. The reaction is as follows: $\mathbf{CH_4 + 0.5\ (O_2 + 3.8\ N_2) \rightarrow CO + 2H_2 + 1.9\ N_2}$

To shorten the process time, the industry generally uses gas carburizing, in which the carbon potential of the endothermic atmosphere (by carbon potential of the atmosphere we mean its carburizing power, which ensures a defined concentration of carbon on the surface of the carburized layer) is first maintained at a high level to ensure 1.3 to 1.4 % C in the steel surface zone, then reduced to 0.8 % C. The carbon potential of the atmosphere is determined by the dew point (the dew point is the temperature at which condensation of water vapors in the atmosphere begins. It is measured by special equipment) or by its CO_2 content, since the concentrations of water vapors and CO_2 are linked. To achieve a concentration of 0.8% C at the steel surface, the dew point must be 8 to 10°C, and for 1.3 to 1.4% C, 12 to 16°C (at 930°C).

Continuous furnaces have two zones along the length of the furnace. In the first zone, which covers approximately 2/3 of the furnace length, gas is fed, consisting of natural gas (10 to 15%) and endothermic gas (90 to 85%) (atmospheric carbon potential: 1.3 to 1.4% C); the second zone receives only the endothermic gas in equilibrium with the carbon concentration to be obtained at the surface (usually 0.8%). When applying this carburizing method, it should be borne in mind that the reduction in carbon content of the layer from 1.3 or 1.4 to 0.8% is achieved solely at the expense of the carbon dissolved in the austenite.

Nitrogen, by dissolving in the austenite, partially compensates for chromium and manganese losses, thus increasing its stability. However, it should be borne in mind that a high ammonia content in the atmosphere can lead to the formation of a so-called "dark component" (probably pores) in the diffusion layer, which adversely affects the steel's mechanical properties (the nature and mechanism of this "dark component" are to be determined by further study). To eliminate internal oxidation, we recommend the use of steels with additional nickel and molybdenum.

Case hardening is carried out at a temperature of 930 to 950°C. The operation takes 6 to 12 hours to produce a layer 0.7 to 1.5 mm thick at 930°C in continuous muffle (or muffleless) furnaces, and 3 to 10 hours in shaft furnaces.

To speed up the process, gases are circulated and, in some cases, the gas carburizing temperature is raised to (1000 - 1050) °C, provided the steels used are hereditarily fine-grained. Case hardening is also accelerated if the parts are manufactured using cold plastic forming methods.

- **Carburizing with liquid cement :**

Carburizing baths are made up of sodium cyanide NaCN, barium chloride $BaCl_2$ (activator) and alkaline chlorides (moderators), enabling suitable fluidity to be achieved. Powdered graphite floats to the surface of the bath, preventing the action of air. The predominant cementation reaction can be expressed as follows:

$$\mathbf{2\ CN^- + Ba_2 + \rightarrow Ba\ (CN)_2 + C}$$

There are two types of bath:

- One contains 20% NaCN and can be heated to (870-900)°C,
- The other contains 8% NaCN and can be heated up to 950°C, enabling faster carburizing.

The parts are immersed in a salt bath containing mainly sodium cyanide NaCN (contains C, N and Na). The bath is heated to between 850°C and 950°C. The parts are suspended by a mild steel wire (at around 500°C) (cyanidation), to a depth of 0.5 mm after one hour's treatment. After quenching, the cyanized layer is much harder than that produced by solid carburizing. However, it is very brittle due to the iron nitride content. The carbon content of the carburized layer reaches 0.7%, and the hardening quench must be carried out at 775°C. As the operation is rapid (1 hour), the metal is not overheated, so no regeneration treatment is required. Water quenching for Cr-Ni steels is followed by tempering at 175°C to increase impact strength. The use of cyaniding is limited to small parts that are not subject to shocks or high stresses (sewing or writing machine parts, axles, gears, etc.).

IV.4.1.2. Boriding

Boriding is a thermochemical surface treatment that has been known since 1895, based on the work of Moisson, and was first used industrially in the 1970s in several countries. The boriding process involves placing the parts to be treated in a boron-rich medium, then placing them in high-temperature furnaces to facilitate boron diffusion and promote the formation of borides with the base material.

Boriding treatment can be applied to a wide variety of materials (ferrous alloys, non-ferrous alloys based on Ni, Ti, Co, and cermets) because of the good mechanical and chemical properties it brings to treated materials. Indeed, boride-treated steels have a high surface hardness that is maintained at high temperatures, good resistance to adhesive and abrasive wear, and good chemical stability to attack by acids and molten metals (in particular, zinc and aluminum).

Depending on the medium containing the boron source, boriding treatments can be carried out in a gaseous, liquid or solid medium.

Before discussing the properties of boride layers and the processes used to obtain them, we thought it would be useful to talk about the Iron-Boron binary equilibrium system and the phases that make up this system.

- **Study of the Fe-B binary equilibrium system**

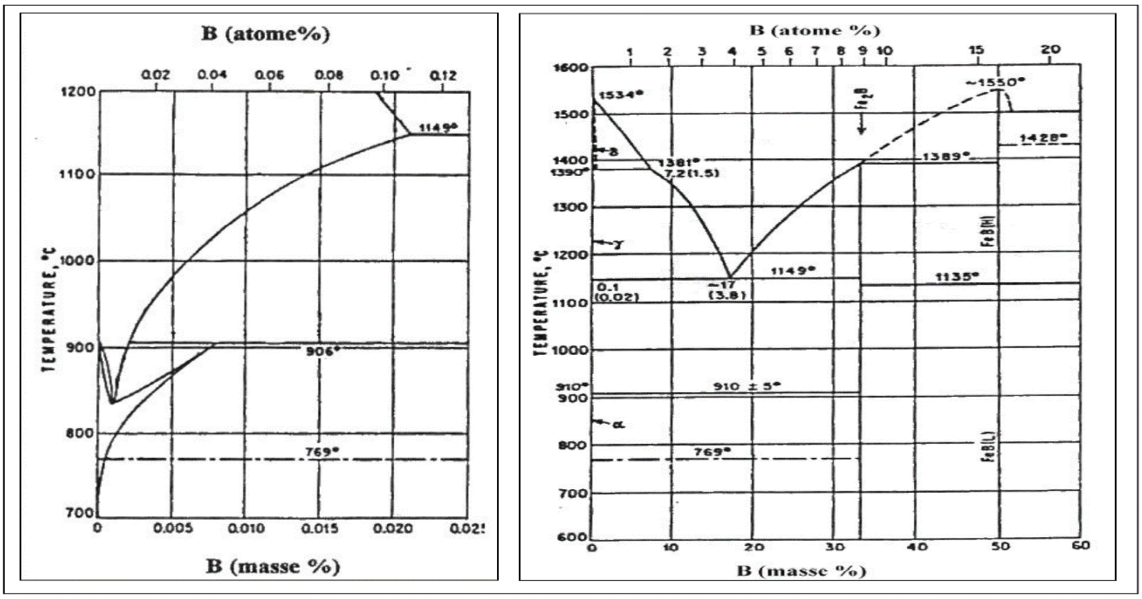


Figure IV.4. Equilibrium diagram of the Fe-B binary system.

Figure IV.4 shows that the solubility of boron in iron is very low, ranging from a minimum of 2 ppm in ferrite at 720°C to a maximum of 210 ppm in austenite at 1149°C. Table IV.3 shows the solubility of boron in iron as a function of temperature.

Table IV.3. Boron solubility in iron at different temperatures.

Temperature (°C)	Boron in solution ppm (by mass)
710 ( )	2
906 ( )	82
906 ( )	21
1149 ( )	210

Beyond the solubility limits of boron in iron, boron and iron together form the borides Fe_2 B and FeB:

- Boride Fe_2 B: This is a chemical compound formed between iron and boron with a boron atomic concentration of 33.33%. The same boride, Fe_2 B, forms a eutectic with iron at 1149°C.

- Boride FeB: This chemical compound has an atomic boron concentration of 50%. This second FeB boride is stable only over an extremely narrow range of chemical composition (Figure IV.4).

- **Boride layer formation**

The transformations taking place in the steel as a result of the gradual diffusion of boron into the substrate, leading to the formation of boride layers, are shown in figure IV.5.

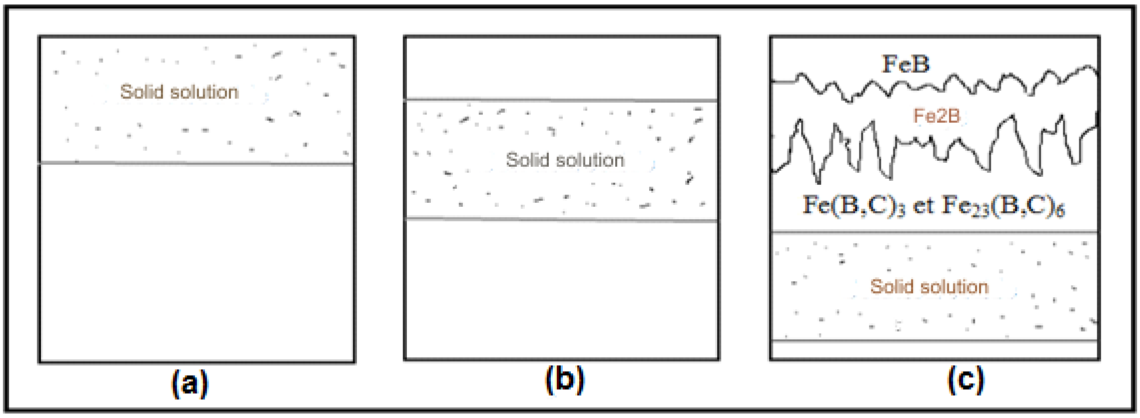


Figure IV.5. Schematic representation of the transformations taking place in steel as a result of progressive diffusion of boron into the substrate.

Figure 3.5 shows that there are four stages in the formation of boride layers on steels:

- Step 1: Boron atoms released by the boriding medium are adsorbed onto the substrate surface and then dissolved in the steel (figure IV.5a).

- Step 2: When maximum boron solubility in the substrate is reached, the borocarbides $(Fe, M)_3$ (B, C) and $(Fe, M)_{23}$ $(B,C)_6$ * precipitate (figure IV.5b).

- Stage 3: Above a certain boron concentration, the first Fe_2 B seeds appear on the most reactive points of the treated part surface (scratches, grain boundaries, dislocation, etc.).

- Step 4: When the boron concentration at the boriding medium/Fe_2 B interface reaches a critical value, boride FeB seeds begin to appear on the substrate surface (Fig. IV.5c), and the borided layers continue to develop with the presence of two interfaces (FeB/Fe_2 B and Fe_2 B/substrate).

- **Growth kinetics of boride layers**

Depending on the boriding technique or process adopted, borided layer growth can be governed by atomic boron deposition on the substrate surface and/or boron diffusion into the substrate.

According to the literature, some authors have found that the growth of FeB and Fe_2 B do not obey the same laws. Indeed, following work carried out on electrochemically boronized layers, they have shown that Fe_2 B grows according to a parabolic law of boriding time, whereas FeB follows a linear time law. This difference was interpreted by the fact that boron diffusion controls the growth of the Fe_2 B layer, whereas cathodic boron discharge controls the growth of the FeB layer.

The growth of electrochemically boronized layers is initially governed by the deposition of atomic boron on the substrate surface, but once a certain critical concentration of boron is reached on the surface, control reverts to diffusion.

▪ Boride layer thickness

Theoretically, there is no limit to the thickness of a boride layer. Simply increase the treatment time and/or temperature to obtain thicker and thicker boride layers.

Due to the great fragility of boride layers, the thickness of the latter is often limited to depths appropriate to working conditions:

- Thicknesses of the order of 10 to 20 µm are limited for mechanical parts working under shock conditions, to avoid cracking and spalling of boride layers.
- We can go up to 400 µm for parts subjected to abrasive wear without impact.

However, it should be pointed out that during boriding treatments, an excess thickness of around 20-25% of the boride layer thickness is recorded on the treated parts. Consequently, this phenomenon must be taken into account during boriding treatments, by undersizing the parts to be treated from the outset.

▪ Steel boriding processes

The boron diffusing through the surface of treated materials can be supplied by a chemical or electrochemical reaction between a boron-containing medium and the material. These different boriding methods have been the subject of much research, and each has its own advantages and disadvantages. In this section, we present the main methods used for boriding steels.

♦ Boriding in gaseous media

Gaseous boronation involves the decomposition or thermal dissociation of volatile boron compounds. The compounds most commonly used in this process are diborane (B_2H_6), boron halides (BF_3, BCl_3, BBr_3,...) and organic boron compounds ($(CH_3)_3$ B, $(C_2H_5)_3B$,...).

a- Diborane

Generally, diborane is used in the form of a "diborane-hydrogen" mixture to obtain boride layers of satisfactory quality. The efficiency of boron transfer from the gaseous medium to the substrate can be improved by incorporating an ion bombardment device in the boriding chamber. However, diborane is not widely used, due to its toxicity and flammability.

b- Boron halides

Boriding with boron trichloride (BCl_3) or boron tribromide (BBr_3) is accompanied by severe corrosion of the treated steel, generally resulting in non-compact layers.

c- Organic boron compounds

The most commonly used organic compounds are boron tri-methyl (CH)$_{33}$ B and boron tri-ethyl (C H)$_{253}$ B. As these compounds are rich in carbon, their use concomitantly causes carburizing of the treated steels, which has the effect of reducing the quality of the surface layers obtained.

In general, the boride coatings produced are uniform and have a very good surface finish, making it unnecessary to clean the treated parts.

♦ Boriding in liquid media

The release of boron from the surface of the treated part requires chemical reduction of the boron-bearing compound. This can be done either electrochemically under an applied voltage, or chemically by adding a reducing agent to the boriding bath. Several researchers have extensively described the salts used in boriding treatments, with or without electrolysis.

a - Electrochemical boriding in molten salts

The electrolytes most commonly used in this process are generally based on sodium tetra borate (known as borax: $Na_2B_4O_7$) or potassium tetra fluoroborate (KBF_4). Pure borax ($Na_2B_4O_7$) and pure potassium tetra fluoroborate (KBF_4) have been used successfully. However, fluorides and alkali chlorides are generally added to the base compounds, in order to improve the physico-chemical properties of the boriding baths (liquidus temperature, viscosity, electrical conductivity, etc.). The chemical composition of the boriding bath is chosen according to the operating temperature:

- KBF_4-based electrolytes are used for temperatures between 600 and 850°C.
- Electrolytes based on $Na_2B_4O_7$ are used for temperatures ranging from 800 to 1050°C.

In all cases recorded, electrolytic boriding resulted in two-phase boride layers.

b - Thermochemical boriding in molten salts

The boriding mechanism in molten salts presupposes the formation of a galvanic cell in which the substrate acts as cathode and the fine particles of reducing agent suspended in the bath act as microanodes.

According to this mechanism, studied in detail by Lyakhovich, boriding takes place if and only if the surface potential of the treated part is higher than that of the reducing agent.

Several metals and chemical substances can play the role of reducing agent to obtain the atomic boron required in all boriding treatments. The most commonly used reducing agents are :

- Aluminum: Aluminum's high affinity for oxygen makes it suitable for reducing boron, which is present in the form of boric anhydride (B_2O_3), formed after the thermal dissociation of borax.

This type of reducer generally leads to two-phase boride layers (Fe_2B+FeB) of fairly satisfactory thickness. However, it should be pointed out that all borax-aluminum baths are characterized by very high viscosity, which remarkably hampers the boriding process to the point of blocking it in some cases.

Sometimes cryolite (Na_3 AlF_6) or certain neutral salts are added to the boriding bath to reduce viscosity and restart the process.

- Boron carbide: Boron carbide is the most widely used reducing agent in boriding treatments in borax-based molten salts. The proportion of boron carbide in the borax should not exceed 40% by mass, to avoid the bath becoming pasty and leading to non-uniform boriding of the treated surface.

- Silicon carbide: Silicon carbide (SiC) is used to produce a single-phase boride layer (Fe_2B). The reaction of boric anhydride resulting from thermal dissociation clearly shows that sufficient oxygen is required for the release of atomic boron.

$$2B_2O_3 + 3SiC + 3O_2 \rightarrow 4B + 3SiO_2 + 3CO_2$$

The proportion of silicon carbide in the boriding bath is also limited to 35% by mass to keep its viscosity at an acceptable level.

Other reducing agents other than those mentioned in the previous paragraph, based on ferroalloys or several researchers have also used carbides (silicon, calcium-silicon, ferrosilicon, ferromanganese, calcium carbide and boron powder). Calcium carbide in particular has given more than satisfactory results, but its explosiveness has limited its use.

♦ Boriding in solid media

a- Powder technology

Because of its simplicity and the cleanliness of the parts it produces, powder boriding is the technique most widely used in most industrialized countries today. This technique involves packing the parts to be treated in steel boxes filled with boriding powder, then heating these boxes in muffle furnaces. As boriding, powders generally have poor thermal conductivity, relatively long times are required for temperature homogenization.

b- Pasta technique

This technique is mainly used for partial boriding and for boriding large parts that are difficult to process using the powder technique. The parts to be borided are covered with boriding paste, then heated by induction or Joule effect, or fired in conventional furnaces.

In the case of partial boriding, the areas not to be borided are protected by electrolytic deposits of copper or other products that prevent boron diffusion and inhibit high-temperature corrosion.

Boriding pastes are made up of two components:

- A solid component containing a boron-rich source (boron carbide, ferroboron, amorphous boron), an activator (cryolite or fluoroborates) and an inert diluent (alumina or silicon carbide).
- An organic liquid binder (methylcellulose or nitrocellulose dissolved in butyl acetate).

Table IV.4. Boriding using the paste technique.

Boriding medium	**Boriding temperature (°C)**	**Boriding time (h)**	**Boride layer thickness (μm)**	**Borides obtained**
50% B_4C + 50% Na_3AlF_6 + binder	1200	2-3	35-125	$FeB+Fe_2B$
45% B_4C + 55 % Na_3AlF_6 +binder	950	4	120	$FeB+Fe_2B$
80% (50% Al_2O_3 + 50% B_4C) + 20% Na_3AlF_6	800-1050	2-4	30-250	$FeB+Fe_2B$
80% B_4C + 20 % Na_3AlF_6	800-1050	2-4	30-250	$FeB+Fe_2B$
40-60% B_4C + 60-40% NaF	1100	0,15	90-120	$FeB+Fe_2B$
95% B + 5% MgF	950	1,5	85	Fe_2B
60% B + 40% $Na_2B_4O_7$ + binder	750-950	0,5-2	15-200	$FeB+Fe_2B$

Boriding processes other than those already described are also used to produce borided layers on steels or other substrates. These include:

- Boriding in a fluidized bed;
- Boriding by physical vapor deposition (PVD);
- Boriding by chemical vapor deposition (CVD);
- Boride spraying by plasma torch;
- Multi-component boriding;
- Boriding by ion bombardment.

IV.4.1.3. Nitriding

Nitriding has been gaining in technical importance for over fifty years. After carburizing, it is the most widely used thermochemical process in industry. Nitriding is a nitrogen diffusion treatment, mainly for iron-based alloys (steels and cast irons), but also for titanium alloys. For ferrous alloys, this treatment is carried out in the ferritic phase, i.e. below 600°C, which avoids the need for a subsequent quenching operation and limits the risk of deformation.

- **Structure of nitrided layers**

Nitriding temperatures for ferrous alloys are generally between 459 and 580°C. These treatment conditions can be easily explained by considering the iron-nitrogen equilibrium diagram (figure IV.6), in which different ranges can be distinguished:

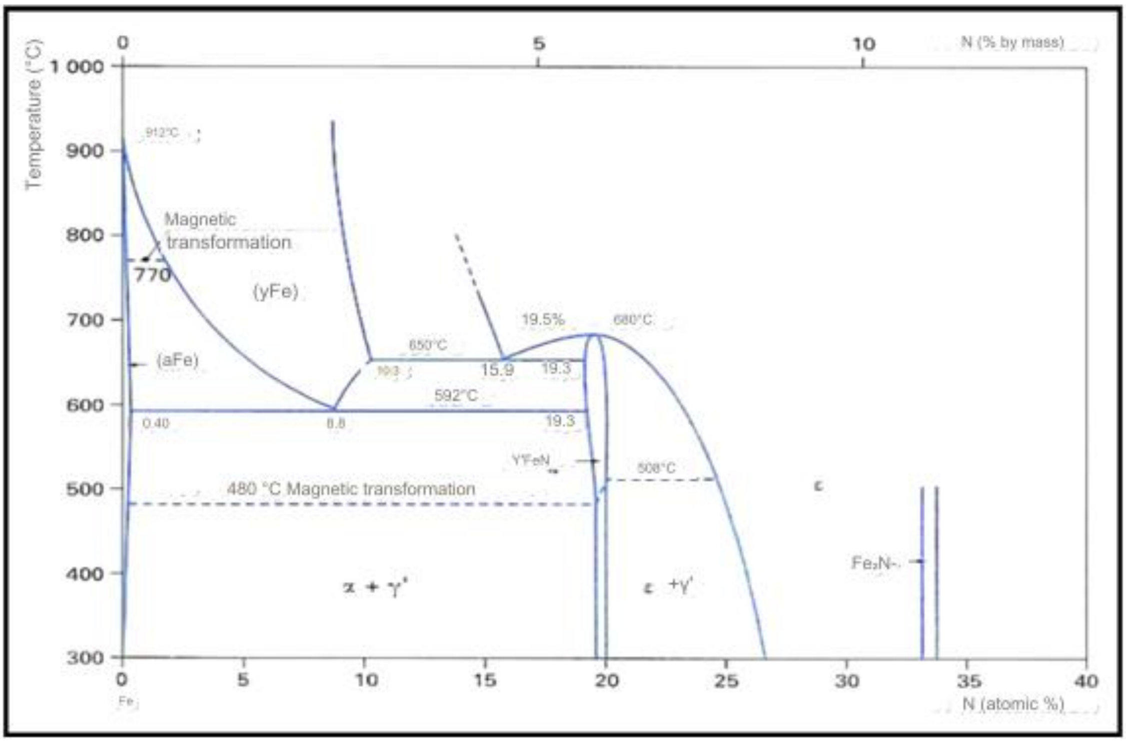


Figure IV.6. Iron-nitrogen equilibrium diagram

- **α:** interstitial solid solution of nitrogen in iron,

- **$\alpha + \gamma'$:** iron nitride Fe_4 N, face-centered cubic structure, high hardness (approx. 800 HV), range below the eutectoid temperature of 590°C,

- **$\gamma' + \varepsilon$:** iron nitride with a compact hexagonal structure and a composition covering a wide range between Fe_3N and Fe_2N, corresponding to nitrogen contents of 6 to 11%.

In the presence of a reactive atmosphere containing nitrogen, the ferrous alloy undergoes nitriding with the following elements in succession:

- a layer of defined ε and γ' nitride compounds, up to 30µm thick,
- a nitrogen diffusion layer, between 0.05 and 1 mm thick.

The increase in hardness results from modifications to the crystal lattice through nitrogen insertion and nitride precipitation of the alloying elements (Cr, Al, V, Ti). The richer the steel is in these elements, the greater the surface hardness, but with a reduction in diffusion layer thickness due to nitrogen fixation by precipitates. Surface hardness, which can reach 1,600 HV, gradually decreases in line with the nitrogen diffusion profile. An increase in treatment temperature results in a decrease in maximum hardness and an increase in the depth of the nitrided layer. Another treatment parameter is the nitriding potential, which is related to the amount of nitrogen input: an increase in this parameter results in an increase in nitriding depth and profile stiffness, without any change in the maximum hardness achieved.

As with case-hardening, there is a conventional nitriding depth for assessing the thickness of the layer formed during treatment. This is the depth at which the hardness is equal to the required core hardness plus 100 HV.

- **The different nitriding processes**

There are three types of nitriding: gas nitriding and reduced-pressure nitriding, ion bombardment nitriding (which is actually plasma-assisted gas nitriding) and salt bath nitriding. In all cases, only nitrogen in its nascent state, i.e. atomic nitrogen, is active.

- **Gas nitriding**

The most commonly used nitriding agent is a mixture of ammonia gas and nitrogen, or ammonia gas and endothermic gas. When ammonia comes into contact with work pieces at treatment temperature, it is cracked into nascent nitrogen and hydrogen. The presence of endothermic gas also provides carbon, which stabilizes the ε phase and increases its growth kinetics (nitrocarburizing treatment). This is a time-consuming process for temperatures up to 550°C, in which case a brittle two-phase combination layer is obtained, but it can be used on parts with very different geometries. Nitriding under reduced pressure (300 to 500 mbar) in an NH_3/N_2O atmosphere reduces treatment times and enables very small bores to be machined. This type of treatment also reduces the volumes of gas used and the risks associated with rejects.

- **Ion nitriding**

Developed in the 1930s-1940s, ion nitriding has only really taken off since the early 1970s. This treatment is based on the physicochemical phenomena of a glow discharge in a rarefied atmosphere of nitrogen and hydrogen at pressures of the order of a few mbar. Nitrocarburizing is also possible at 570°C in an atmosphere of nitrogen, hydrogen and methane. Other treatments can be carried out, with other diffusing elements such as oxygen or sulfur, to modify the surface structure of the nitride layer and consequently its functional properties.

There are therefore a large number of ionic nitridations available, and this type of treatment is extremely flexible in use, with the possibility of producing single-phase combination layers (γ'ou ε) or diffusion layers alone in a temperature range from 450°C (stainless steels) to 800°C (titanium alloys). In fact, the various treatment parameters (gas mixture composition, temperature, pressure) can be set independently of each other, which is not the case with other types of treatment. Dimensional capacities are significant: up to over 6m in length and 1.8m in diameter. However, this process has a number of drawbacks, including the difficulty of nitriding the inside of small bores, in order to avoid the hollow cathode phenomenon, and temperature homogeneity problems for parts with different geometries. This results in the need to arrange parts of a homogeneous nature in a rotationally symmetrical manner in the reactors, in order to obtain a good temperature uniformity, which penalizes the filling rate and makes the treatment relatively costly.

- **Nitriding in salt baths**

This treatment is carried out in mixtures of cyanates, cyanides and carbonates at temperatures close to 570°C. The nitrogen input is due to the thermal decomposition of cyanates into carbonates, the latter being reduced to cyanates by the urea and cyanides present (to a level of around 3%).

$$4\ NaOCN \rightarrow Na_2CO_3 + 2\ NaCN + CO + 2\ N$$

$$2\ NH_2\text{-}CO\text{-}NH_2 + Na_2CO_3 - \rightarrow 2\ NaOCN + 2\ NH_3 + CO_2 + H_2O$$

The simultaneous presence of nitrogen, carbon and oxygen accelerates nitriding kinetics, and combination layers 20 µm thick can be obtained in less than 2 h at 570°C.

In the 1980s, cyanide substitutes were developed for carbonate reduction, using sulfur compounds (K_2S) and lithium salts to catalyze the reaction. These less polluting baths contain traces of cyanides, and the presence of sulfur on the surface of the combination layer improves the tribological properties of the nitrided layer, especially in the presence of lubricants.

This process is highly flexible and inexpensive, but it requires parts to be washed and the effluent treated an operation that is increasingly penalizing in economic terms as environmental constraints become more stringent.

- **Carbonitriding**

This treatment is derived from case-hardening by incorporating ammonia into the reactive atmosphere. The result is a simultaneous addition of carbon and nitrogen, with the consequent increase in layer growth kinetics, lowering treatment temperatures below 900°C and enabling hardness levels of 900 HV to be achieved on thicknesses of less than 0.6 mm.

For many years, the interpretation given to this increase in diffusion layer growth kinetics was that nitrogen increased the value of the diffusion coefficient of carbon in iron. Studies carried out some ten years ago showed that the increase in carbon penetration rate during carbonitriding was due rather to a change in physicochemical processes at the gas-solid interface. Indeed, the atomic hydrogen released by ammonia decomposition on the steel surface facilitates the elimination of oxygen adsorbed on the same surface by CO decomposition, thus reducing solid gas transfer resistance.

- **Conventional gas carbonitriding**

There are a number of differences between carbonitriding and gas carburizing that can be summarized as follows:

- the steel grades used have higher carbon contents during carbonitriding (0.25 to 0.30% instead of 0.15 to 0.20%);
- lower surface carbon contents, from 0.20 to 0.25%, due to partial substitution of carbon by nitrogen;
- limiting treatment temperatures to 850/890°C, instead of 950/1000°C for carburizing;

- hot oil quenching instead of cold oil quenching for carburizing, thus avoiding the stress-relieving tempering that is systematically carried out after quenching for carburizing;
- treatment thicknesses limited to 0.6 mm (for carburizing, generally at least 1 mm).

The steels most commonly used for carbonitriding are chromium 38 to 42CrMo4, manganese chromium 16 to 27MnCr5, nickel 20NiCrMo2 and C38. Boron steels cannot be carbonitrided, as the effects of nitrogen and boron are neutralized by the precipitation of boron nitrides.

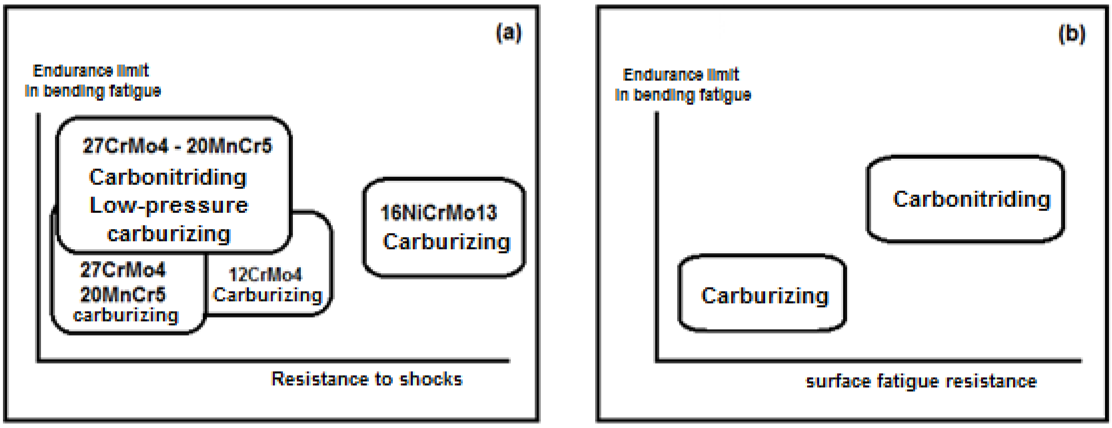


Figure IV.7: (a) Diagram giving the position of the different treatments in a graph resistance to fatigue / resistance to shocks.
(b) Diagram giving the position of the different treatments in a graph resistance to fatigue /surface fatigue resistance

This treatment is widely used in the automotive industry (gearbox gears and control parts, engine tappets). Figure IV.7 shows a number of comparisons between carburizing and carbonitriding, demonstrating the benefits of the latter technique, particularly in terms of surface fatigue resistance.

Figure IV.7.(a) shows the technical advantage of using alloy steels for impact resistance, as well as the advantage of low-pressure carburizing over conventional gas carburizing due to the absence of surface oxidation. Figure IV.7.(b) shows the advantage of carbonitriding over conventional carburizing, particularly with regard to surface fatigue resistance, due to the presence of a greater quantity of residual austenite (nearly 30% in carbonitriding compared with less than 20% in carburizing). This component mechanically transforms into martensite during surface fatigue stresses, thereby delaying crack initiation through structural reinforcement.

- **Low-pressure carbonitriding**

The reactive gases used in this case are acetylene and ammonia. A low-pressure carbonitriding cycle is a combination of carburizing under a reactive atmosphere of acetylene and diffusion phases, during which ammonia is injected, causing nitrogen to be inserted into the carbon diffusion layer. The advantage of acetylene is that it provides a large quantity of carbon, making it possible to reduce the duration of enrichment phases in favor of diffusion phases.

Depending on the desired property gradient, in most cases it is sufficient to inject ammonia into the last diffusion phase. The best results are obtained by lowering the temperature in the last diffusion phase, and injecting ammonia into this treatment sequence before the final quench. The advantage of incorporating nitrogen into the property gradient layer is to improve its hardenability, which is favorable for gas quenching under conditions where the risk of deformation is minimized (quenching under a pressure of 6 bar).

IV.4.1.4. Oxidation

Like nitriding, thermochemical oxidation treatment has a relatively long history, particularly in the tooling and mechanical engineering sectors. The aim of this treatment is to create an oxide layer on the surface of the material, which can modify the functional properties of the surface to make it more resistant to corrosion, friction or wear. Two variants are distinguished: oxidation only and oxynitriding.

- **Oxidation only**

Oxides formed on the surface of metallic materials by thermochemical oxidation treatment depend on two factors: partial oxygen pressure and temperature. These films, which do not exceed a few µm in thickness, are used to improve functional properties such as resistance to friction and wear, or resistance to corrosion in aqueous or gaseous media. This treatment is used in machining on high-speed steel, in the chemical industry and energy production on zirconium alloys, and in mechanical engineering on titanium alloys.

- **Oxidation on ferrous alloys**

The diagram in Figure IV.8 shows the existence domains of the different iron oxides as a function of temperature and oxygen partial pressure. It shows that at temperatures below 570°C and for low partial pressures of O_2 , iron will be in the presence first of the Fe_3O_4 oxide alone, then of the Fe_3O_4 , Fe_2O_3 oxides.

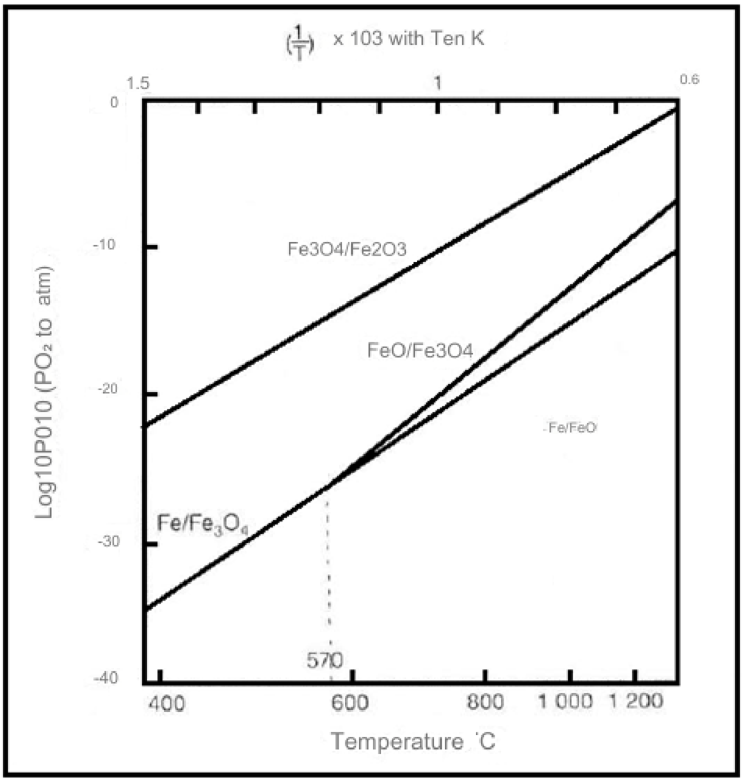


Figure IV.8. Equilibrium of iron and its oxides as a function of oxygen partial pressure and temperature

For treatments carried out at temperatures below 570°C, the growth mechanism of the oxide layer is governed by the diffusion of iron into Fe_3O_4 magnetite and by the diffusion of oxygen into Fe_2O_3 hematite. If the partial pressure of O_2 is sufficiently low, or if there are oxidation and diffusion sequences, the oxide layer will consist of Fe_3O_4 oxide alone, which is what is sought in oxidation treatments of steels because of the improved toughness of the layers due to the presence of a single constituent. These treatments are relatively old and rarely used today. Only steam oxidation treatment of high-speed steels will be discussed.

This treatment, carried out for 30 minutes in an atmosphere containing steam at 550°C, is relatively well-known. The aim is to obtain a surface film of Fe_3O_4 which lowers the coefficient of friction between the chip and the tool. The susceptibility of the oxide layer to chipping is reduced if the substrate is strengthened by a preliminary nitriding treatment.

- **Oxidation on zirconium and titanium alloys**

On the other hand, oxidation treatment of zirconium alloys under reduced pressure (1 to 10 mbar) in an argon-oxygen mixture is much more recent. Temperatures used are between 500 and 900°C, in a relatively wide range where either a thin zirconia layer (a few µm thick) is preferred at low temperatures (between 500 and 600°C), or a zirconia layer 10 to 20 µm thick on an oxygen diffusion layer 50 to 100 µm thick at higher temperatures (800°C). There are numerous applications for this treatment in power generation (nuclear) and the chemical industry, and emerging applications in the biomedical sector for zirconia-coated orthopedic prostheses.

Oxidation treatment of titanium alloys is also carried out under reduced pressure (1 to 10 mbar), as for zirconium alloys, but at a lower temperature (between 500 and 600°C) because the TiO_2 oxide formed is brittle, hence the low thicknesses required. This treatment has numerous applications in the chemical and automotive industries.

- **Oxynitriding**

The main purpose of this treatment is to improve the friction and corrosion resistance of nitrided layers. There are two main types of treatment: nitriding followed by oxidation, and oxynitriding, which consists of diffusing nitrogen and oxygen together. These treatments are carried out in the gas phase, with or without plasma assistance. The same separation also exists in the case of oxynitrocarburizing treatments. In this case, treatments can be carried out in the liquid or gaseous phase, with or without plasma assistance.

Following nitriding treatment in a salt bath, liquid oxidation can be carried out in baths based on nitrates and alkali hydroxides, buffered with carbonates and oxidation activators such as bichromates, permanganates or metal halophosphates. Oxidation treatment temperatures in this case are between 350 and 450°C. By the gaseous route, it is possible to use ammonia atmospheres with nitrogen and oxidizing mixtures containing O_2, CO_2, or even N_2O. A variant of this treatment is to use reduced pressures (1 to 5 mbar) of N_2/O_2 or Ar/O_2 atmospheres with plasma assistance. In all cases, the oxynitrided structure consists of a nitrogen diffusion layer and a nitride combination layer ε $Fe_{23}N$ (sometimes $\gamma' Fe_4N$) with a surface layer of Fe_3O_4 oxide offering both anti-seize properties and suitable corrosion resistance (3-fold increase in salt spray resistance compared with nitriding alone). With a subsequent passivation or impregnation treatment, it is even possible to further improve the corrosion resistance of the oxidized layer and achieve salt spray resistance of 800 hours.

These treatments are now widely used in the mechanical engineering industry for parts subjected to friction, wear, fatigue and corrosion. Examples include:

- cylinder and shock absorber rods, connecting and lifting axles, in which case the treatment can replace the hard chrome coating;
- valves nitrided to resist seawater corrosion, replacing electrolytic zinc coating;
- brake pistons, joint bolts and hydraulic excavator trunnions, also as an alternative to electrolytic chromium plating.

IV.4.2. Metal diffusion treatment

These include diffusion treatments for metals such as chromium or aluminum, to improve the corrosion and oxidation resistance of steels and nickel-based alloys (in the case of aluminum), or resistance to the combined action of corrosion and wear (in the case of chromium plating). Mixed chromaluminizing treatments are also available to further improve oxidation resistance, particularly for nickel-based alloys. These treatments, which are already relatively old because they use solid metal additives, are now widely used in the aeronautics and mechanical engineering industries.

IV.4.3. Ion implantation treatment

The process originated in the electronics industry in the 1960s, and has been widely used since then to dope silicon and other semiconductors. Research into the effects of ion implantation on the surface mechanical properties of metals began in Great Britain in the 1970s, with rapidly encouraging results, notably in the field of carbide forming tools with nitrogen implantation.

- **Process principle**

This purely physical treatment involves selecting ions and accelerating them under very low residual pressure (a few 10-5 mbar) to energies ranging from a few dozen to a few hundred kilo electron volts, in order to introduce them into the surface layers of a material. By affecting the chemical composition and physical parameters over a maximum thickness of 200 nm, the surface properties of the material are significantly modified. There are two types of ion implanter, depending on the nature of the species implanted: the simplest, used for nitrogen in particular, comprises only a source, an acceleration device and a chamber where the ion beam is focused and scanned over the substrate surface; the most sophisticated, used for metallic species (Cr, Si, Ti, B...), also includes a device for sorting the ionized species by mass spectrometry, before final acceleration.

- **Implanted layer structure**

The concentration profile of the implanted ions obeys a Gaussian curve, linked to the sequence of collisions with the atoms of the structure, which is absolutely random. As previously mentioned the implantation depth does not exceed 200 nm and depends on the incident energy of the ions. Indeed, an increase in energy results in a lowering of the maximum concentration and an increase in the implanted depth, as shown by the curves in figure IV.9. An increase in dose, at the same energy level, results in an increase in maximum concentration, up to a saturation value corresponding, for most metallic materials, to 2.10^{17} ions/cm^2, at energy levels between 40 and 100 keV.

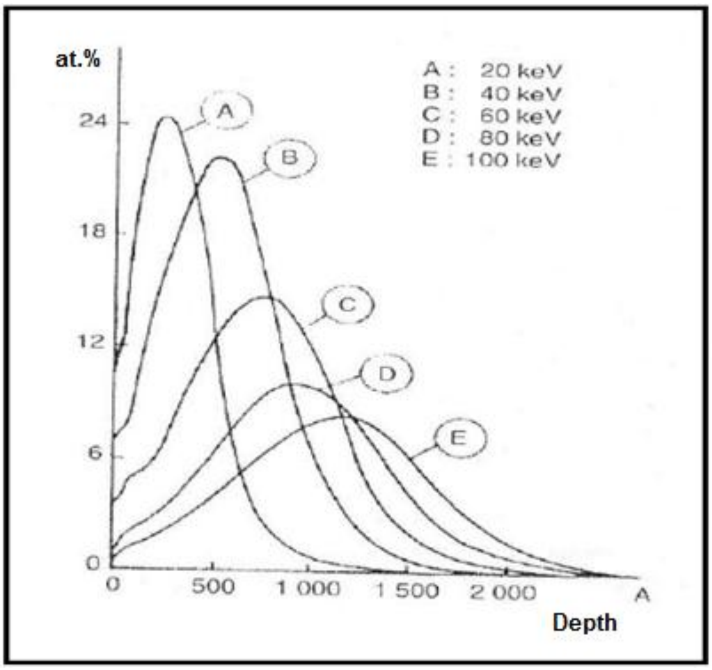


Figure IV.9. Influence of incident ion energy on the concentration profile of the implanted species. Case of nitrogen in X steel$_{20}$ Cr$_{13}$

Microstructurally, high-energy implantation results in changes that have been the subject of a large number of studies in the case of nitrogen, and which can be described by the diagram in figure IV.10.

- on the surface, the higher the dose, a layer where the disorder brought about by the implanted species is such that amorphization occurs;
- deeper down, a layer of very fine precipitates (nitrides in this case) just a few nm in size, linked to two phenomena: very high local temperatures caused by atomic collisions and accelerated diffusion by irradiation;
- a final layer characterized by the sole insertion of the implanted species.

The amorphous surface structure is characterized by good functional properties in terms of friction and wears resistance, as well as good corrosion resistance, provided that the precipitation of fine nitrides in the sub-layer is not too high. The implanted layer is also subject to high compressive stresses, which delay the onset of cracks and delamination associated with the wear process.

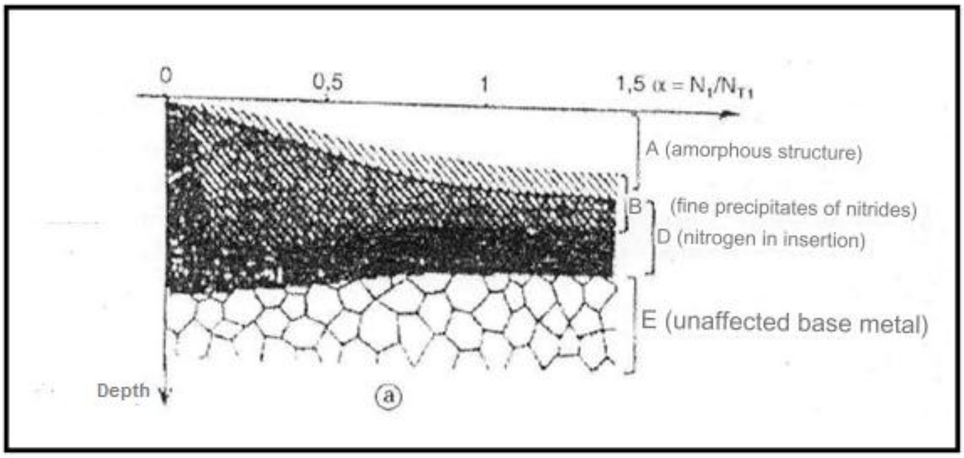


Figure IV.10. Microstructure of an implanted layer (case of nitrogen).

Ion implantation is used in two fields: microelectronics and mechanical engineering. In **microelectronics,** the implantation of impurity elements in silicon wafers, after an annealing operation, makes it possible to produce the reduced-size semiconductors that have led to the miniaturization of printed circuits. In **mechanics,** nitrogen ion implantation can improve the friction and wear resistance properties of finished machined parts, provided the entire surface of the substrates is reached by the incident ion beam. This treatment has been used successfully in several fields:

- joint surfaces of orthopedic prostheses made of titanium alloy or Co-Cr alloy, and surfaces of HDPE (high-density polyethylene) antagonists,
- taps and drills in high-speed steel,
- hard chromium coatings on plastic tools (one-fold improvement in coating life due to increased resistance to crack initiation).

However, operating temperatures of up to 250°C limit the effect of nitrogen implantation, and a gain of around 100 degrees in the operating range can be achieved with joint implantation of carbon and titanium instead of nitrogen.

Ion implantation can also improve the wear and corrosion behavior of mechanical parts likely to work in aggressive environments, through joint implantation of chromium and nitrogen (improved passive layer formation kinetics).

IV.5. Conversion treatments

This is a treatment process in which the filler metal reacts superficially with the substrate to produce a structural improvement. These treatments are the result of chemical etching, electrolytic or dry oxidation, or electrochemical or cold plasma functionalization.

The conversion treatment process is traditionally used to provide the surface with a suitable physico-chemistry to improve the adhesion of a poly-material or ceramic to facilitate bonding operations or to give a good appearance, or even to ensure bio-integration. This die is widely used in a large number of fields, including the aerospace, automotive, architectural construction, jewelry and biomaterials industries. This process is by far the most widely used for aluminum alloys, with the emphasis on other functional properties such as wear and corrosion resistance.

IV.5.1. Chemical conversion treatments

This type of treatment is widely used, as it involves processes that are both inexpensive and easy to implement. The main treatments include phosphating and chromating on steels and aluminum alloys, oxalating on stainless steels, burnishing on steels and etching on magnesium alloys. This sector also includes "sol-gel" treatments, which involve quenching in solutions with subsequent gelation of the surface.

- **Phosphating treatment**

Phosphating is the result of attacking the metal surface with a solution of phosphoric acid and phosphates of various metals: Zn, Mn, Ca, Fe, with various additives that accelerate and catalyze the attack reaction. It is used to protect steels against atmospheric corrosion or to facilitate the bonding of varnishes and paints; it also facilitates metal deformation by wire drawing or cold heading, with less wear and tear on tools. There are light posphating, 1 to 2 µm thick, known as bonderization, and thicker posphating, 10 to 30 µm thick, known as parkerization.

The phosphating treatment is carried out in a dilute medium of phosphoric acid PO_4H_3 with primary metal phosphates $(PO_4H_2)_2Me$, Me being Zn, Ni, Mn, Ca, and gas pedals, organic or inorganic oxidizing products, at a temperature of between 60 and 95°C, at a pH of between 2.5 and 5. Under these conditions, a phosphate layer develops on the metal surface following the overall reaction:

$$Me + H_3O^+ \rightarrow Me\ x^+\ x/2\ H_2\uparrow + xH_2O$$

This overall reaction is the result of oxidation-reduction phenomena, with dissolution of the metal substrate in the anodic zones and hydrogen release in the cathodic zones (see figure IV.11). The role of gas pedals (a mixture of nitrates and nitrites) is, in the anodic zones, to limit the chemical attack, and in the cathodic zones, to limit the release of hydrogen and depolarize the reaction to allow the attack to continue. In solution, these gas pedals oxidize Me $^{x+}$ ions to Me$^{(x+1)+}$, resulting in the formation of insoluble phosphates which precipitate as sludge.

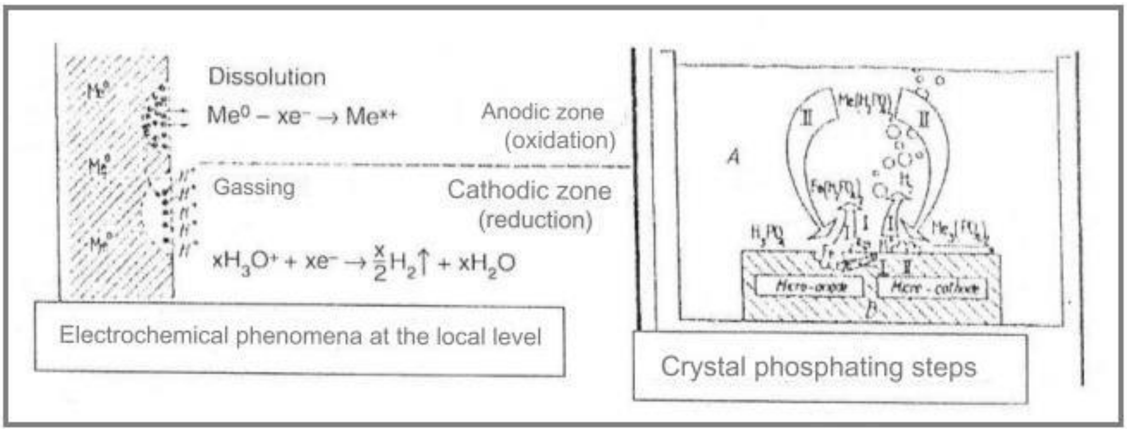


Figure IV.11. Phosphating principle with redox reactions

Steels suitable for phosphating are those for general use, steel construction and mechanical engineering. The most troublesome element is chromium, and steels containing more than 4% of this element are difficult to phosphate. This is the case for nitriding steels of the 30CrMoV$_{12}$ type or mold and tool steels containing 5% Cr and, of course, martensitic stainless steels. On the other hand, some steels containing more than 5% alloying elements are suitable for phosphating, such as Maraging steels containing 18% Ni with cobalt and molybdenum, or Hadfield steels containing 11 to 14% Mn.

Phosphating is mainly applied to uncoated steels to facilitate cold forming operations, and to zinc-coated steels to facilitate paint adhesion. The structure of the phosphate layer depends on the nature of the cations present in the baths. On zinc-coated steel, the layer is $Zn_3(PO_4)_2, 4H_2O$, with a rather acicular orthorhombic structure; on uncoated steel, it is $Zn_2Fe(PO_4)_2, 4H_2O$, with a monoclinic cobblestone structure. The phosphating treatment can also be applied to FGL and FGS cast irons. Surface preparation (degreasing, pickling, possibly sandblasting) has a major influence on the germination and structure of the phosphate layer.

There are several types of phosphating on steels, depending on the functionality required. The thickenss of the layer is assessed by weighing it after chemical dissolution in a 200 g/l chromic acid solution at 80°C. The thickness in µm is equal to the weight in g/m2 up to thicknesses in the µm range, then 1.2 to 3 µm for weights between 1.5 and 4 g/m^2. Beyond that, given the porosity of phosphate layers, the correspondence is more random, and the layer weight/thickness ratio can vary between 1 and 3, depending on the surface condition of the steel, the type of surface preparation (nature of the degreaser and pH of the solution) and the balance of the phosphating bath.

- **Chromating treatment**

Chromating consists in forming a protective layer of complex chromates on a metal surface by attacking it with an acid solution containing dichromates and mineral activators. This treatment can be applied to steels, aluminum alloys and zinc; it significantly improves the atmospheric corrosion resistance of treated parts and enhances paint adhesion.

Chromating is the conversion of hexavalent chromium (sodium or potassium dichromate) in an acid bath. It is a redox process in which the chromate ion participates directly as an oxidizing agent:

$$Cr_2O_7^{2-} + 14\ H^+ + 6^{e-} \rightarrow 2Cr^{3+} + 7\ H_2O$$

Alkalinization transforms dichromates into chromates and precipitates gelatinous hydroxides:

$$Cr_2O_7^{2-} + H_2O \rightarrow 2CrO_4^{2-} + 2\ H^+$$

$$CrO_4^{2-} + 2\ Cr^{3+} + 4\ OH^- \rightarrow Cr(OH)_3 + Cr(OH)CrO_4$$

This treatment is carried out using organic or inorganic activators (sulfates, fluorides, acetates, formates). The operation is carried out at a temperature of between 20 and 60°C, at a pH optimized to avoid both attack on the layer being formed (pH too low) and attack on the substrate by reducing the rate of layer formation (pH too high). Chromate coatings have the character of a gel with good absorption power on the metal, hence good adhesion and the ability to close in the event of scratching. In addition, the pores in the layer facilitate absorption for impregnation.

Drying the conversion layer at 60°C leads to slow hardening. Drying above this temperature (80°C) causes dehydration of the film and the development of a large network of cracks, an operation facilitated by the presence of extensional stresses whose intensity ranges from 15 to 100 MPa and depends on treatment time and bath composition. An excessively hardened and cracked layer becomes practically hydrophobic, making it more difficult to apply an organic finish.

This treatment provides good corrosion protection and, thanks to the presence of hydrated chromium oxides, is an excellent adhesion primer for paints. It can be applied to a wide range of metals: zinc-coated steel, aluminum, cadmium, magnesium, copper and silver. Coat thicknesses range from 0.2 to 1 µm, depending on the substrate.

- **Oxalation treatment**

Oxalating is used on stainless steels and refractory steels to improve the wettability of liquids and thus the adhesion of lubricants, to facilitate cold forming of these materials (like conventional phosphating on carbon steels).

This treatment is an alternative to phosphating for special steels where the sum of alloying elements exceeds 5%, notably the stainless steel and heat-resistant steel families.

The treatment consists of immersing the parts (after nitrofluoric pickling and rinsing with water) in an aqueous solution of oxalic acid for around ten minutes, at a temperature of between 60 and 65°C, at a pH close to 1.7. The reaction is activated by adding hydrofluoric acid and hydrochloric acid in the presence of gas pedals such as thiosulfates and thiocyanates.

Ferrous oxalate, consisting essentially of $Fe(COO)_2$, $2H_2O$ is a porous layer around ten microns thick, which enables lubricants to bind to it and facilitates the processing of stainless steel without the formation of vermiculures for drawing, tube and section drawing, and cold heading operations. The optimum coating weight varies according to the type of operation to be carried out: 8 to 10 g/m^2 for wire drawing, 10 to 15 g/m^2 for tube and section drawing, or cold heading. The tribological properties of machine components (slides, keys, joints) are improved by applying a MoS_2 varnish after oxalating 10 g/m^2. This conversion treatment must comply with current legislation on waste treatment, and is now in competition with other processes such as electrolytic copper plating, whose performance is more advantageous.

- **Burnishing treatment**

Burnishing is mainly applied to steels, and in addition to its aesthetic appeal, it protects treated parts against atmospheric corrosion.

This relatively old treatment is applied to steel both to give it an aesthetic appearance and to provide protection against atmospheric corrosion, possibly in a marine atmosphere. There are two types of formulations for this treatment, an alkaline formulation used at 140°C and an acid formulation used at room temperature.

The alkaline formulation consists of a mixture of soda ash (580 g/l) with sodium nitrite and sodium nitrate (145 g/l for both), with a complexing agent (EDTA) to limit the entrainment of alkaline vapors. Black coloration is obtained after 15 minutes in the bath, by the formation of a 1µm-thick film of Fe_3O_4 oxide, sufficient to absorb protective oil. A better coloring effect can be obtained with a two-bath process, the first at a temperature of 120°C, the second at 140°C. Under these conditions, the corrosion resistance evaluated by the standardized salt spray test corresponds to duration of 15 to 20 hours.

The acid formulation is based on selenious acid and copper sulfate, with pH set at 3 and controlled by measuring free acidity. The black color is obtained after 5 minutes of holding, and is duller than that obtained by treatment in an alkaline bath. It probably consists of CuSe copper selenide, and permanent filtration of the bath is necessary to avoid powdery coatings. The layer thickness is also around 1 µm, and its resistance to corrosion after oiling is comparable to that obtained after treatment in an alkaline medium.

- **The sol-gel technique**

These techniques are more recent than their predecessors, and can be likened to chemical conversion treatments. Indeed, the specificity of sol-gel techniques is that the starting state of the material is a stable dispersion of colloidal particles, which is then transformed into a gel. Generally, these techniques are based on systems composed of an organometallic polymer that first ensures the sol-gel transition, then hardening by subsequent heat treatment.

The molecular precursors used in sol-gel processes are generally metal alkoxides with the general formula $M(OR)_n$ where M is a metal and R is an organic group. These precursors, in solution at room temperature in the form of finely dispersed particles of between 1 and 100 nm in size, give rise to polymerization reactions, resulting in the formation of increasingly condensed species that lead to a colloidal suspension of solid particles in a liquid that forms the "sol". The polymerization process is initiated by hydrolysis, leading to the formation of reactive functions with hydroxide bridges, as follows:

$$M\text{-}(OR)_n + nH_2O \rightarrow M\text{-}(OH)_n + nR\text{-}OH$$

Condensation continues by transforming the $M\text{-}(OR)_n$ groups into oxygen bridges to give a "gel" according to the reaction:

$$M\text{-}(OR)_n \rightarrow M\text{-}O_{n/2} + n/2\ H_2O$$

Sol-gel transformation results in a three-dimensional mesh of nanoparticles in solution, and several factors, including pH and synthesis temperature, nature and concentration of reagents, solvent type and product ageing, can influence the characteristics of sols and gels. Acid or base catalysis can influence either hydrolysis and condensation rates, or the structure of condensed products.

Heat treatment at moderate temperatures (< 120°C) completes the condensation and drying of the film. The resulting layer has mechanical, physical and chemical properties that can be adjusted to provide the protection system with adhesion to the substrate, adhesion of organic films and a barrier effect against corrosive agents.

Ceramic barriers can also be produced using this technique; in this case, the final heat treatment is carried out in open air at temperatures above 500°C. The organic compounds in the deposit decompose into CO_2 and H_2O at temperatures below 400°C to form an amorphous, nanoporous film, which begins to crystallographically arrange itself from 500°C onwards. The structure of the film becomes denser, and its characteristics depend on the processing parameters: temperature, holding time and cooling conditions. Heating conditions vary: furnace, infrared or UV exposure. Film thicknesses of the order of µm are limited by the stresses induced during drying.

IV.5.2. Electrochemical conversion treatments

This treatment process is also widely used for highly oxidizable metals such as aluminum, titanium and magnesium alloys, and to lesser extent stainless steels. This is the anodic oxidation process, which can be combined with sulfurization in molten salts and functionalization by grafting various types of molecules, particularly organic molecules, to form an "adhesion primer".

- **Anodic oxidation**

Anodic oxidation consists in creating an oxide (or hydroxide) layer on the surface of aluminum, titanium, magnesium and stainless steel alloys by electrolysis in a solution rendered conductive by the addition of an acid, with the part connected to the anode. Aluminum and magnesium alloys can be "anodized" to improve corrosion resistance, titanium alloys can be "anodized" to improve corrosion resistance, titanium alloys can be "anodized" to improve varnish adhesion or to impart a specific color. Aluminum alloys can be anodized to improve surface hardness under specific electrolysis conditions, to obtain layers with good compactness, or to improve bonding properties under other conditions, to create porous layers. Finally, stainless steels can be anodized to improve varnish adhesion or bondability.

♦ Anodic oxidation of aluminum alloys

This is the most common surface treatment used on this type of alloy. The formation of the alumina layer is the result of oxidation-reduction reactions, with dissolution and hydrolysis on the anodic side, and hydrogen evolution on the cathodic side, according to the following reactions:

- anodic dissolution $2Al \rightarrow 2A1^{3+} + 6^{e-}$ and hydrolysis $2\ Al^{3+} + 3\ H_2O \rightarrow Al_2O_3 + 6H^+$;
- at the cathode: $6\ H^+ + 6^{e-} \rightarrow 3\ H_2$;

The overall reaction balance is as follows:

$$2Al + 3\ H_2O \rightarrow Al_2O_3 + 3\ H_2$$

The minimum electrolysis voltage is 1.68 V (difference between the H^+/H_2 and $A1^{3+}/Al$ pairs). After a certain electrolysis time, an insulating barrier layer is formed, which must be partially etched away by the solution to allow the oxide layer to grow. Several processes are available, depending on the dissolving action of the electrolyte on the alumina:

- electrolytes with a weak dissolving action,
- electrolytes with a moderate dissolving action,
- electrolytes with a strong dissolving action.

♦ Anodic oxidation of titanium alloys

Compared with anodic oxidation processes on aluminum alloys, the structure of the oxide film obtained on titanium alloys is different, as the TiO_2 oxide is not attacked by electrolytes containing sulfuric, phosphoric or chromic acid. In all cases, a thin, compact, insulating barrier film is formed.

The evolution of the thickness of this film as a function of the applied voltage is of the form: **E (nm) = a . V** (volts) **+ b (**a = 1.5 to 3 nm/V and b = 2 nm, residue after etching)

Treatment conditions are as follows for all electrolytes: temperature: 15 to 30°C, current density: 0.2 to 0.5 A/dm^2, voltage: 20 to 100 V, duration: 5 to 30 minutes, layer thickness: 20 to 300 nm.

Sulfuric anodizing (concentration 150 to 300 g/l) is designed to improve rub resistance after impregnation with organic compounds or varnishes. This treatment is also designed to reduce the hygroscopic nature of the oxide film and marking effects during handling. It has numerous applications in the aerospace and defense industries, particularly for fasteners.

Anodizing in **chromic media** ensures good conversion with surface enrichment of hydrated chromium oxides to facilitate bonding, or to bond dry lubricants and varnishes. Industrial applications of this technique are found in armaments, aeronautics, construction and sporting goods, with film thicknesses ranging from 40 to 60 nm.

Anodizing in **sulfuric and phosphoric media** (0,35 M H_2SO_4 and 0,35 M H_3PO_4) is widely used in medical technology for marking dental and orthopedic implants, plates and instruments. Interference colors range from silver to gold, blue and even pink, depending on the thickness of the oxide film (between 20 and 250 nm). This point will be taken up in the following chapter on metal coloring.

- **Anodic oxidation of stainless steels**

The passive layer thickness of stainless steels can be increased by anodizing in a nitric medium 50% by volume at room temperature, or in a sulfochromic medium (concentrated solution of commercial sulfuric acid with 400 g/l of $K_2Cr_2O_7$ at 70°C). In both cases, current densities are around 0.5 A/cm^2 and treatment times between 30 min and 1 h. Oxide thicknesses are of the order of 20 nm for nitric anodizing and 70 nm for sulfochromic anodizing. These oxides are characterized by a marked increase in chromium concentration, which results in a significant improvement in the bondability of stainless steel after such surface preparation. This improvement is correlated with the increased chromium content in the oxides and hydroxides of the passive layer, resulting in a higher proportion of strong chemical bonds with the adhesives.

- **Anodic oxidation of magnesium alloys**

In magnesium alloys, this treatment produces a film of complex oxides and salts, including fluorides, fluosilicates and phosphates and, in some cases, chromates, depending on the process used. The aim of this treatment is to provide good corrosion protection for the substrate, which is extremely reactive (- 1.8 V compared with the hydrogen electrode). It also provides a bonding base for varnishes and paints, and improves friction and wear resistance for thicker oxides. Two types of anodic oxidation have been developed, the first in a phosphoric acid medium and the second in a basic medium after an initial chemical conversion in a low-acid medium.

- **Low-temperature sulfurization**

Low-temperature sulfurization is a low-temperature electrochemical conversion treatment which consists in creating a layer of solid lubricant in situ on the surface of parts. This treatment is applied to high-performance mechanisms where there is a risk of seizure at the start of operation, when the oil film has not yet formed, or of film breakage due to accidental overloads.

This is an electrochemical sulfurization treatment in a molten bath at a temperature of around 190°C at a current density of between 2 and 3 A/dm^2 .

The metal substrate (usually steel) is in the anodic phase, and the treatment lasts around ten minutes. The layer is formed in two stages:

- S^{2-} species from the reactive medium accumulate on the positively-charged substrate surface, forming a thin film of insulating sulfur,
- the formation of electrical micro-discharges, combined with the treatment temperature and high current density, provides the energy needed to form an iron sulfide film.

The resulting layer is perfectly embedded in the steel substrate, and its thickness ranges from 4 to 7 µm, depending on the processing parameters and the nature of the substrate. It is essentially iron sulfide FeS, with a hexagonal structure and a particularly pronounced solid lubricant character.

- **Electrochemical grafting**

This is a process based on electrolysis in an organic liquid medium, which enables a polymerization reaction to be initiated and grow on the surface of the metal substrate. The result is a polymeric organic layer covalently bonded to the surface that gave rise to it. This is an electrochemical conversion treatment.

Polymer films are obtained on a conductive surface by electro-initiating the polymerization reaction from the surface, followed by purely chemical chain growth, monomer by monomer. The main electropolymerizable monomers are vinyl monomers such as acrylonitrile (AN), methacrylonitrile (MAN), N-vinylpyrrolidone (NVP), methyl methacrylate (MMA) and hydroxyethylmethacrylate (HEMA).

This technique enables surface functionalization to be achieved in a single step, with an organic layer firmly attached to the metal surface.

This layer can, in turn, serve as an anchoring point for conventional post-functionalization reactions. For example, an electrografted PMAN film can be used as a precursor for amide ($R\text{-}CN + H_2SO_4 \rightarrow R\text{-}CONH_2$) and carboxylic acid ($R\text{-}CONH_2 + NaOH \rightarrow R\text{-}COOH$) groups on metal surfaces. This transformation then enables hydrophilic surfaces to be obtained quite simply from hydrophobic electrograft films.

The electrografted organic layer, which is in the low to very low thickness range (< 1µm), acts as a kind of "molecular velcro", enabling the surface to be functionalized as required, making it adherent or non-adherent, biocompatible, conductive or insulating. All kinds of molecules with high specificity potential can be attached to this surface: proteins, polyelectrolytes...

IV.5.3. Dry conversion treatments

This sector includes coloring treatments for stainless steels and titanium alloys, as well as plasma-assisted conversion treatments.

- **Plasma conversion**

Cold plasmas, resulting from electrical discharges in gases at pressures ranging from 10^{-3}mbar to atmospheric pressure, were described in previous chapters on surface preparation. It should be remembered that their properties derive from the activation of the gas in which the electrical discharge takes place by electrons, resulting in the formation of highly reactive species: excited neutrals, radicals and ions.

These chemically highly active species can therefore be used to modify the metal structure at thicknesses of just a few nm. These include the breaking of chemical bonds or the grafting of new radicals, the adsorption of excited neutrals, surface chemical reactions, not forgetting the thermal effect of ion bombardment, which can facilitate the diffusion of certain species deposited on the extreme surface. The result is the modification of certain physico-chemical properties to provide new functions: electrical insulation, adhesion of a polymer or ceramic partner, improved mechanical properties or corrosion resistance. Plasma conversion of a metal substrate begins with a cleaning operation, followed by the actual conversion.

- **Metal coloring**

Coloring gives metallic materials two functions: an aesthetically pleasing appearance, and a convenient means of facilitating sorting and assembly operations, or of marking as a safety feature in certain installations. Coloring is a sought-after process for three classes of metallic materials: stainless steels, aluminum alloys and titanium alloys.

IV.6. Coatings

This is by far the most important sector, accounting for over 60% of sales of surface treatments and coatings (excluding paint). The various techniques can be classified either by medium (liquid or gaseous), or by temperature (which may or may not involve diffusion, or even dilution, between deposit and substrate).

Table IV.5. Schematic representation of the various metal coating processes.

Coating sector	Conditioning	Interface structure	Processes
Low thermal effect	Aqueous medium	No interface displacement	Galvanoplasty, chemistry, chemical reduction
Low thermal effect	Gaseous medium	No interface displacement	PVD deposits, PACVD
Low thermal effect	Pulverulent in metal contribution form	No interface displacement	Thermal projection
Strong thermal effect	Gaseous medium	Diffusion displacement	CVD deposition (static, dynamic)
Strong thermal effect	Liquid process, coating	Diffusion displacement	Salt bath deposits, molten metal, slurries, enameling
Strong thermal effect	Metal contribution in wire or powder form	dilution displacement	Recharge TIG, MIG, plasma, laser

IV.6.1. Coatings with low thermal effect

These include coatings obtained in aqueous media (electroplating, displacement, chemical reduction), in gaseous media (PVD, PACVD), and thermal spraying techniques.

- **Aqueous coatings**

This includes electroplating, displacement and chemical reduction deposits.

- **Electroplated deposits**

This sector is of major economic importance, accounting for around 25% of all coatings and surface treatments. It enables new performances to be achieved on metallic materials, such as corrosion resistance, resistance to friction and wear, appearance and conductivity. Metals that can be deposited include nickel, chromium, cadmium, copper, zinc and tin, as well as noble metals (Au and Ag).

Deposits of alloys or co-deposits are currently booming, as is the production of composite deposits by incorporating hard particles (SiC) into the coating or facilitating sliding.

The electrolytic process can be used for localized pad coating of large parts, or for the hardfacing of worn parts. It can also be used for continuous treatment of steel sheet in the steel industry (electro-galvanizing lines). The use of forced circulation (high electrolyte flow) or pulsed current systems increases deposit speeds and quality.

This process is used in a wide variety of fields, including mechanical engineering, the food industry, plastics and chemicals, energy production and the steel industry, as well as the transport and aeronautics industries. This sector comprises two families of deposits, depending on the thickness achieved:

- Mining layers, 10 µm thick or less,
- Medium layers, between 10 and 200µm thick.

♦ **Deposits produced by chemical reduction**

These are deposits obtained by autocatalytic chemical reduction, essentially in the case of nickel. These coatings are obtained by reducing nickel sulfates using hypophosphites or borohydrides, with phosphorus or boron incorporated into the nickel deposit. Significant levels of hardness can be obtained by heat treatment. Either at around 200°C in the case of aluminum alloys, or at around 400°C in the case of steels, to ensure the metal substrate's resistance to corrosion, friction and wear. Composite deposits can be produced by incorporating hard (SiC) or friction-reducing particles.

The thickness of deposits produced by chemical reduction is at most a few tens of µm. This process is mainly used in the mechanical, chemical, plastics and power generation industries, mainly on steels (carbon and stainless) and aluminum alloys.

♦ **Deposits by displacement**

This die is used to produce deposits that are more noble than the substrate, through an exchange reaction between the ions of the metal to be deposited and those of the etching substrate. The thicknesses achieved in this case are only a few µm, to facilitate the subsequent electroplating of other metals. This is the case for nickel deposits on steel prior to enameling, or zinc and tin deposits on aluminum alloy prior to electroplating.

▪ **Coatings produced in a gaseous environment**

These include physical vapor deposition (PVD), plasma-assisted chemical vapor deposition (PACVD) and sputtering.

♦ **Physical Vapor Deposition (PVD)**

The techniques used to produce these deposits are either simple thermal evaporation, plasma-assisted thermal evaporation (ionic deposition), sputtering or arc evaporation. The deposits obtained by these different techniques are thin (3 to 20µm). These are metals if the residual atmosphere in the equipment is neutral (Ar), and defined compounds if the residual atmosphere is reactive (carbides, nitrides, oxides).

Deposits can be made either statically in appropriate chambers, or continuously on equipment with airlocks, enabling the transition from atmospheric pressure to working pressure in just a few units, at speeds compatible with industrial productivity. This process is used in a wide variety of fields, including mechanical engineering, forging and sheet metal working, plastics processing, power generation, metallurgy and steelmaking, as well as the transport and aeronautics industries.

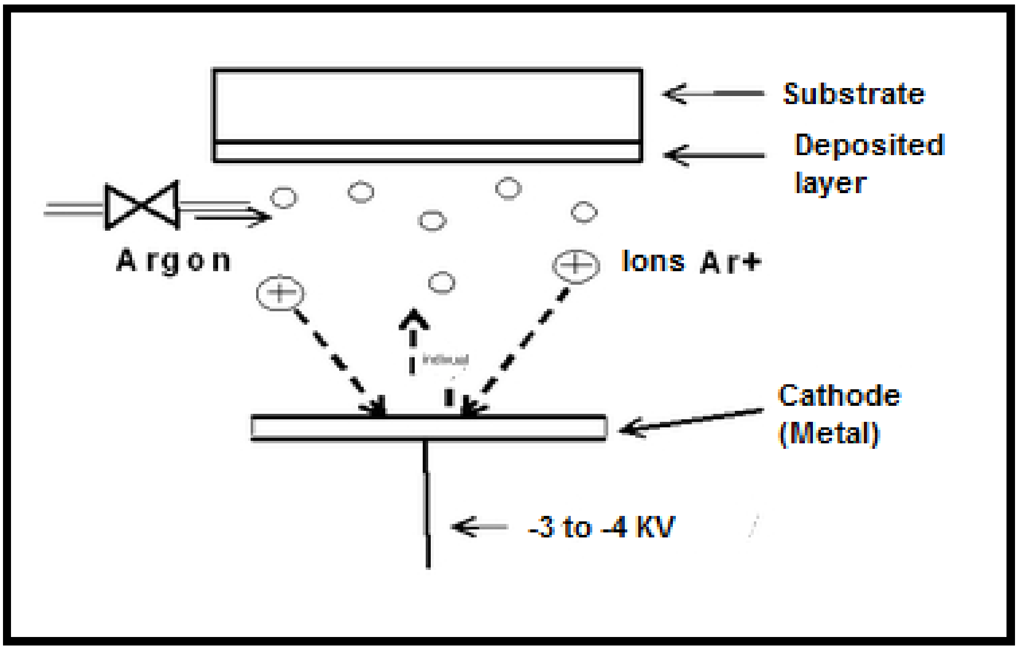


Figure IV.12. Schematic diagram of the spraying process.

- **Plasma-Assisted Chemical Vapor Deposition (PACVD)**

The use of cold plasmas facilitates the decomposition of a vapor phase and lowers processing temperatures to levels compatible with most metal substrates used for mechanical applications (treated steels, even aluminum alloys).this technique enables the synthesis of defined compounds (oxides, carbides, nitrides, adamantine carbon, etc.) at low thicknesses, generally less than 10 µm. It is used in a wide range of fields, including mechanical engineering, forging and sheet metal working, machining, biomaterials and the automotive industry. Multilayer coatings can be used to provide multifunctional properties, such as resistance to wear and oxidation.

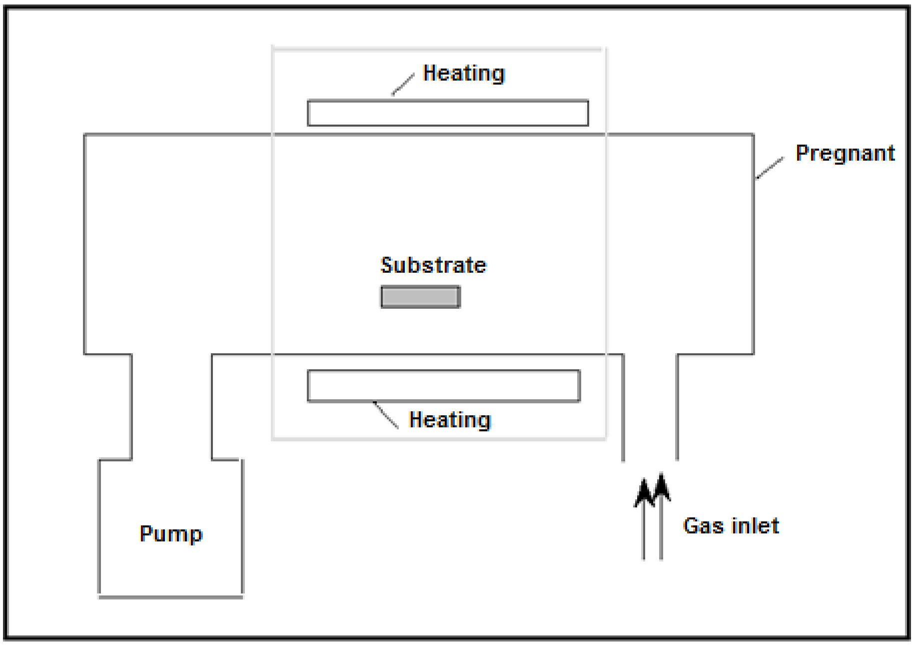


Figure IV.13. Schematic diagram of chemical vapor deposition (CVD

- **Spray coatings**

This type of treatment combines a number of techniques for applying thermal energy to the metal deposited in powder form to bring it to a paste-like state on the metal substrate: oxyacetylene flashlight, plasma torch, detonation gun and continuous-fire device (HVOF or High Velocity Oxygen Fuel). These "metallization" processes can deposit metals (molybdenum, MCrAlY alloys), cermets (ZC-Co mixtures, for example) or ceramics (yttrium-stabilized zirconia or alumina) at thicknesses of up to several hundred µm. The application properties targeted are corrosion resistance in molten metals (zinc, tin and aluminum in particular).

This process is used in a wide variety of fields, including mechanical engineering, power generation, glassmaking, metallurgy and steelmaking, transport and aeronautics. In the latter field in particular, work is currently underway in the USA to substitute this type of coating for electrolytic chromium deposits. Hydroxyapatite (HAP) is also sprayed onto metal alloys (stainless steels, titanium alloys) to facilitate their osseointegration into bone tissue.

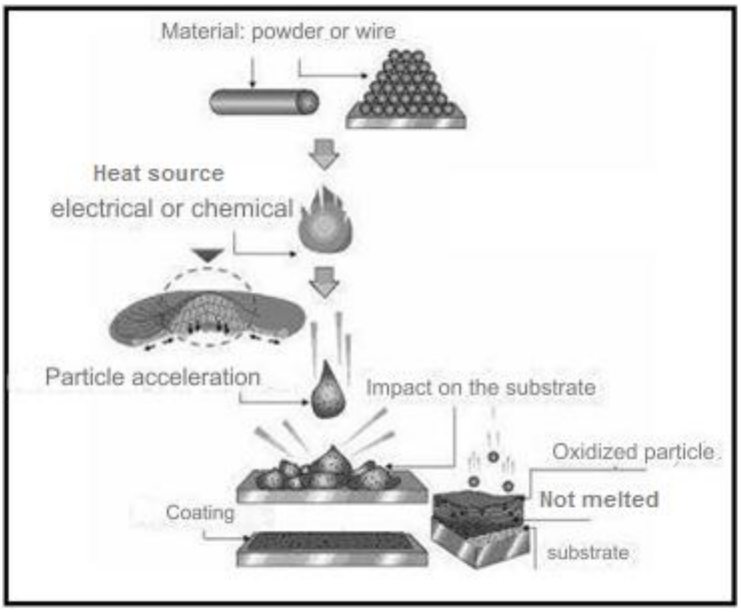


Figure IV.14. Basic principle of thermal spraying.

IV.6.2. Coatings with high thermal effect

This category covers coatings produced at high temperatures (above 800°C), either in liquid media (molten baths) or in gaseous media (chemical vapor deposition, slurry diffusion deposition), and so as to achieve interdiffusion between coating and substrate. Also classified in this group are coatings with interface displacement by dilution, such as solder overlay.

- **Coatings in liquid media**

These are coatings produced by immersion in liquid metals (tin, zinc, aluminum) on small parts, large series or continuous processing (galvanizing, tinning, aluminizing of steel strips). Interdiffusion between the coating and substrate produces layers with filler metal and substrate surfaces, and compounds defined by the equilibrium diagram between filler metal and substrate. Diffusion treatments carried out after deposition allows these intermetallic compounds to be given preference, with the aim of improving certain properties such as adhesion or, in some cases, corrosion resistance. This process is widely used in power generation and transmission, metallurgy and the steel industry. Carbide hard coatings in particular can be obtained by immersing carbon steel metal parts in molten salt baths (e.g. chlorides) at between 900 and 1000°C. The back-diffusion of carbon from the substrate to the coating makes it possible to achieve a high degree of hardness in certain applications, such as die-casting molds for aluminum alloys or tooling for sheet metal working. In this category of treatments carried out in liquid media, we might mention coating processes, in particular the slurry method, and enameling techniques.

- **The slurry method**

Consists in depositing a suspension of powder and organic binder mixture on a metal surface, then, during a thermal cycle, first removing the binder, then diffusing the deposited element. This method is mainly applied to metals with low vision points (Sn, Zn, Al and boron-containing elements with low-melting eutectics). Applications can be found in the chemical industry (Sn on stainless steels) and in mechanical engineering to combat static seizure.

- **Glazing or vitrification**

Generally applied to steels, this involves depositing a mineral coating based on alkaline or alkaline-earth oxides, with a thickness of around 1 mm. Subsequent vitrification of the coating at high temperature gives the steel excellent resistance to corrosion in most aggressive media (with the exception of FH and alkaline media). Enameling is mainly used in the chemical industry.

- **Coatings produced in a gaseous environment**

This category includes coatings where the interface with the substrate is displaced by solid-state diffusion (CVD). These coatings are produced by thermal decomposition of a vapor phase (halides) in contact with the metal surface in the temperature range from 800 to 1100°C. The adhesion of the deposit is very good, all the more so as the carrier gas is often hydrogen, which eliminates all residual oxides. Numerous defined compounds can thus be deposited on materials that can withstand such high temperature ranges: ferrous steels and alloys, cermets, etc. Layer thicknesses range from 3 to 20 μm to improve resistance to friction, wear and oxidation. The fields of application for this die are quite numerous, in the mechanical industry, forging and stamping, plastics and chemicals, aluminum and magnesium alloy casting, machining, the transport industry and aeronautics.

- **Reloading deposits**

This sector encompasses processes involving the addition of material in thicknesses of several mm, with displacement of the interface by dilution. The techniques used are those of welding: MIG, MAG, TIG, plasma and laser processes. Material is added by coated wire or electrode in the first three cases, and in powder form in the last two cases. Coatings are applied in thicknesses of up to ten mm, to produce genuine multimaterials designed to withstand high thermomechanical loads in sometimes aggressive environments.

In parallel with this weld cladding technique, powder metallurgy can be used to create complex, multi-functional assemblies using high-speed compounding, hot isostatic compaction and plasma resistance sintering techniques.

There are numerous applications in the forging and stamping industry, in the plastics industry and in mechanical engineering for wear parts.

The alloys brought to the surface by the techniques defined above are iron-based alloys (e.g. chromium cast irons) and cobalt- and nickel-based alloys.

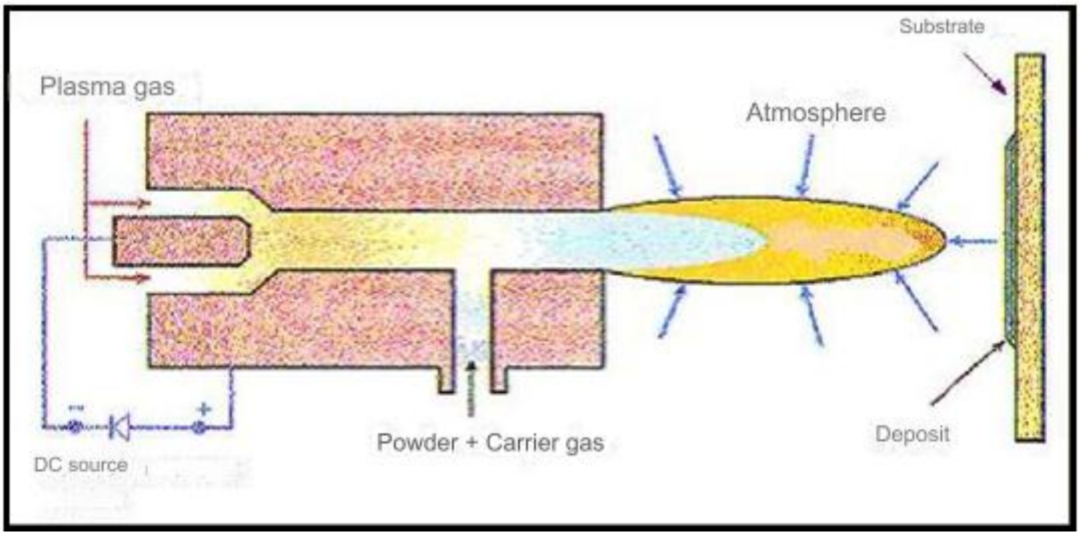


Figure IV.15. Schematic diagram of a plasma arc torch.

Chapter V

Control of surface treatments and coatings

V.1. Introduction

The inspection of coatings and surface treatments is one of the quality assurance actions that take place at the final stage of product development. It certifies compliance with specifications and the suitability of the material for a given function. It is an absolutely essential operation, and the aim of this chapter is to provide the user with elements to guide him in his choice of the most appropriate checks to carry out.

V.2. Objectives of the control operation

One of the main objectives of the control procedure for a coating or surface treatment is to ensure that the properties targeted by this operation are guaranteed. As a reminder, the various material functionalities likely to be satisfied after surface treatment or coating are as follows:

- resistance to mechanical stress,
- chemical resistance,
- suitability for gluing or paint coating,
- appearance, color, reflectivity,
- physical surface properties (conductivity or insulation).

V.2.1. Resistance to mechanical stress

The aim is to assess the material's ability to withstand mechanical stresses such as friction and wear, and to withstand impacts and cyclic stresses in all their forms: mechanical fatigue, surface fatigue, thermal fatigue. This resistance is highly dependent on directly measurable properties, such as..:

- surface hardness and the hardness gradient at depth,
- mechanically or thermally reinforced metal depth,
- the depth of the hardness gradient in the case of thermochemical treatment,
- the thickness of a hard coating obtained by various liquid or vapor-phase methods, and its adhesion to the substrate,
- the state of residual stresses on the surface and at depth (e.g. risk of bursting in the case of heavily loaded coatings already under compressive stress, in connection with the process),
- the chemical composition of the surface and the gradient of properties (absence of surface oxidation in the case of thermochemical treatments).

V.2.2. Chemical resistance

The aim is to assess the material's resistance to corrosion in an electrolytic environment, or to oxidation by gases, or to changes in appearance by simple atmospheric corrosion, particularly in industrial environments. These properties naturally depend on the degree of protection provided by the coating, and in particular:

- the chemical composition of the surface exposed to the reaction medium,
- the internal health of the coating and the state of residual stresses, especially when the material is more noble than the substrate,
- the thickness of the coating, particularly in the case of sacrificial protection.

V.2.3. Suitability for gluing or paint coating

In this case, it's a question of evaluating the most appropriate surface physicochemistry to ensure good metal-polymer bonding, and the results will depend on a number of parameters:

- surface roughness,
- the chemical composition of the surface and, if possible, the state of bonding,
- the thickness of the coating obtained by chemical, electrochemical or plasma conversion,
- absence of organic or mineral pollution.

V.2.4. Appearance and reflectivity

These functionalities are of particular importance for applications such as biomedical, architecture, jewelry, urban or domestic furniture, the automotive industry and aeronautics. They are dependent on a number of parameters, including the following:

- surface roughness,
- the chemical composition and homogeneity of the coating,
- absence of defects and good adhesion, to ensure protection against any risk of corrosion, as these are generally noble coatings which in some cases even have insulating properties,
- coating thickness,
- good surface hardness for certain applications such as biomedical.

V.2.5. Special physical properties

In this case, the aim is to ensure certain physical properties such as electrical conductivity or thermal insulation (thermal barriers). These properties depend on a number of parameters, such as:

- the thickness of the coating when thermal barriers are used, as well as the state of residual stresses, since these stresses will add to the thermomechanical stresses in service and contribute to the risk of galling,

- the internal structure of the coating when surface electrical conductivity is required,

- adhesion of the coating to the substrate in both cases.

V.3. The various control methods

As mentioned above, the characterization and control of coatings and surface treatments depend on the intended field of application. They will focus on their various characteristic properties: appearance, roughness, adhesion, thickness, corrosion resistance, surface hardness, residual stress state, etc. The methods available are many and varied, some being specific to external surfaces, others more specific to volume and the study of a gradient of composition or mechanical properties. Some testing procedures are destructive, others non-destructive. As a first approximation, testing procedures can be classified into four different groups:

- analytical control: identify the nature of the chemical elements, their concentration and sometimes their chemical bonds, assess homogeneity of distribution;

- topographic or geometric control: identify the roughness profile and determine certain physical and statistical criteria associated with it, including appearance and reflectivity;

- mechanical control: assessing surface hardness and residual stress levels, as well as the mechanical property gradient;

- control of coating **thickness and adhesion**, and potential for protection against corrosion or oxidation.

There are other more specific control modes for certain applications, such as electrical conductivity or thermal insulation, magnetic susceptibility, as well as microstructure (crystallized or amorphous state) and possible textural effects. This last parameter is particularly important in the case of coatings with thicknesses in excess of ten µm.

V.3.1. Analytical control

Advances in surface treatments require ever greater knowledge of the surfaces of the materials being treated. Many functional properties, such as friction and wear resistance, corrosion resistance and adhesion of polymer coatings or ceramics, are directly linked to the chemical composition of surfaces. When developing or testing treated parts, it is therefore essential to characterize surfaces analytically in order to identify and understand the phenomena involved. Surface analysis techniques can be veritable measurement, control and diagnostic tools for determining the nature of surface layers, identifying potential oxides or contaminants, studying the migration of elements on the surface or at the coating-substrate interface, or understanding the surface modifications brought about by conversion treatment.

There are a large number of physical analysis methods that can provide information on the chemical composition of the surface and underlying layers. These techniques operate on two different principles:

- sending X-rays, electrons or ions onto the surface. The primary beam interacts with the surface, emitting a secondary beam which is then analyzed to provide the information required. The most common of these techniques are as follows: ESCA (Photoelectron Spectrometry), AES (Auger Electron Spectrometry), SIMS (Secondary Ion Mass Spectrometry), LEEIXS (Low Energy Electron Induced X-Ray Spectrometry) and SDL (Glow Discharge Spectroscopy); all these techniques are performed under vacuum or ultra-high vacuum; the use of vibrational spectroscopy, whose particularity is to be sensitive to chemical bonding without providing direct elemental analysis. These techniques include FTIR (Fourier Transform Infrared Spectrometry) and Raman spectroscopy, and are performed at atmospheric pressure.

- **Vacuum techniques**

A distinction must be made between analysis techniques performed under ultra-high vacuum, such as AES (Auger electron spectrometry), ESCA or XPS (photoelectron spectrometry) and SIMS (secondary ion mass spectrometry), and those performed under primary vacuum, such as SDL and LEEIXS spectrometry.

Ultra-high vacuum techniques are generally limited to the study of the first atomic layers. They are therefore of interest for the identification of elements present at the surface, even in trace amounts, or for the analysis of very thin layers with a thickness of less than or equal to one micron. These techniques can also be used to analyze local concentration changes (heterogeneities, segregation at grain boundaries), and to produce concentration profiles on a continuous basis by SIMS analysis, or discontinuously by XPS or AES analysis. In the case of XPS and AES techniques, the connection of a preparation chamber to the equipment frame enables in situ studies, for example of adhesion, interfacial brittleness and plasma-surface interaction problems. The most effective technique for determining chemical bonds is XPS analysis. It enables measurements to be carried out on very small quantities of the product analyzed, on both conductive and non-conductive surfaces. This technique is probably of greatest interest in the field of conversion layers, passive layers and functionalization treatments. However, the three analytical methods XPS, AES and SIMS have a number of limitations, not least the ultra-high vacuum, which makes them somewhat cumbersome to use. On the other hand, they are excellent complements to scanning electron microscopy (SEM).

Although less well-known than the ultra-high vacuum techniques mentioned above, Low Energy Electron Induced X-ray Spectrometry (LEEIXS) uses an excitation source consisting of a discharge tube operating in a primary vacuum. The area analyzed is of the order of a cm^2 over a depth of 0.1 μm. The method is sensitive to light elements and offers the possibility of carrying out analyses when the fine structure of certain X-ray emission bands undergoes modifications as a function of the chemical environment of the atoms considered. LEEIXS spectrometry is ideal for providing information on surface pollution of mineral or organic origin, as well as for carrying out quantitative analyses on thin coatings or conversion treatments.

Glow discharge spectrometry (GDS), which is performed in a primary vacuum and, like LEEIXS spectrometry, uses a discharge tube as an excitation source, is the only technique that can produce multi-element concentration profiles from 0.5 nm down to 150 microns with satisfactory depth resolution. With this technique, it is therefore possible to analyze concentration profiles at depths of less than a micron (ion implantation), coatings of a few μm to a few tens of μm and concentration gradients in carbon or nitrogen over more than 100 μm obtained by thermochemical treatment.

The surface under analysis is eroded by Ar^+ ions and is therefore analyzed globally over the entire eroded surface, on the order of cm^2. The spectral intensities of around ten elements can be measured simultaneously. This technique is also useful for highlighting interfacial phenomena between coatings and substrates, or between layers of different natures. However, it has two main limitations:

- the impossibility of carrying out local analyses due to low lateral resolution,
- the absence of direct information on the nature of chemical bonds for the elements analyzed.

Analysis can be carried out by direct current discharge on conductive materials, or by radiofrequency discharge on insulating materials. In the latter case, proper calibration enables quantitative analysis.

- **Vibrational techniques**

Infrared spectrometry and Raman spectrometry belong to the family of vibrational spectrometers, whose distinctive feature is that they do not provide a direct elemental analysis, but are sensitive to chemical bonds. In infrared spectrometry, absorption wavelengths in the mid-infrared range are directly linked to the vibrational modes of a molecule: they therefore represent a precise fingerprint of the bonds between atoms. Infrared spectrometry has developed considerably over the last twenty years, with the advent of the Fourier Transform (FTIR) technique. This technique has increased the sensitivity and integration time of the method. Analysis is carried out mainly in reflection-absorption mode, through superficial films on a surface that acts as a reflecting mirror. Layers with thicknesses ranging from a few nm to tens of µm can be analyzed non-destructively.

In Raman spectrometry, the light scattered by excitation of the surface with a laser beam is analyzed spectrally to provide the vibrational bands. Whether or not these bands are observed depends on the molecular symmetry of the compound to be analyzed, and on selection rules that are different from those implemented in infrared spectrometry. Lateral resolution of around 1 µm (compared with 10 µm in infrared spectrometry) can be achieved using an associated microscope. The technique is non-destructive, provided that laser power is controlled. It can be applied to a wide variety of sample configurations, such as surfaces immersed in a liquid or massive parts. One limitation is the low signal intensity, which often requires long accumulation times.

V.3.2.Topographic and geometric control

This control mainly concerns metal coatings and conversion treatments, and to a lesser extent surface hardening or thermochemical treatments, when a surface finish is required for specific conditions of use, such as appearance and reflectivity for decoration, or simple appearance for applications in the building, automotive or aeronautical industries.

- **Roughness control**

A surface profile is made up of different geometric deviations defined as follows:

- order 1: shape deviation, origin: heat or thermochemical treatment,
- order 2: corrugation deviation, origin: tool machining, e.g. turning,
- order 3: roughness deviation, e.g. grinding strike,
- higher orders: very short wavelength deviations, e.g. due to conversion treatments

(anodic oxidation, phosphating, chromating).

For measurement processing, current standards lead to the introduction of two families of parameters: those obtained by filtering and calculating the mean line of the profile, and those resulting from the decomposition of the profile into a succession of elementary patterns. Parameters from the first family are those most commonly used in current practice. From a roughness profile traced over a length L, three criteria can be determined:

- the maximum roughness Rt, corresponding to the peak-to-valley amplitude (Zmax - Zmin) ;

- mean square roughness Ra, corresponding to the amplitude of the mean profile:

$R = {}^{1}/_{L} \int |Z| \, dx$;

- Rz roughness, calculated on the average of 5 successive corrugations.

Two other parameters can be added to these three criteria:

- the standard deviation σ of the distribution defined by : $\sigma^2 = {}^{1}/_{L} \int Z^2 \, dx$;

- the bearing capacity, expressed as a percentage of the profile's bearing capacity at depth Z.

This last parameter is of interest for assessing the loading of a surface during mechanical contact, based on knowledge of the roughness profile of the two opposing surfaces. This involves transforming the contact between two rough surfaces into that of an ideally smooth surface and a rough surface that integrates the roughness parameters of both surfaces. The technique used consists in describing the size of the asperities by means of two parameters, vertex altitude z and mean radius R, and in dimensioning their distribution functions using the roughness and waviness parameters defined above. This makes it possible to add the roughness of the two opposing surfaces to obtain the roughness of the sum surface.

The Rt, Ra and Rz criteria are determined directly from a two-dimensional profile using an online calculator. It may be useful to visualize the roughness of a surface by drawing a series of curves to obtain a three-dimensional sheet.

There are currently two types of roughness characterization techniques: the more traditional contact methods and the more recent non-contact methods.

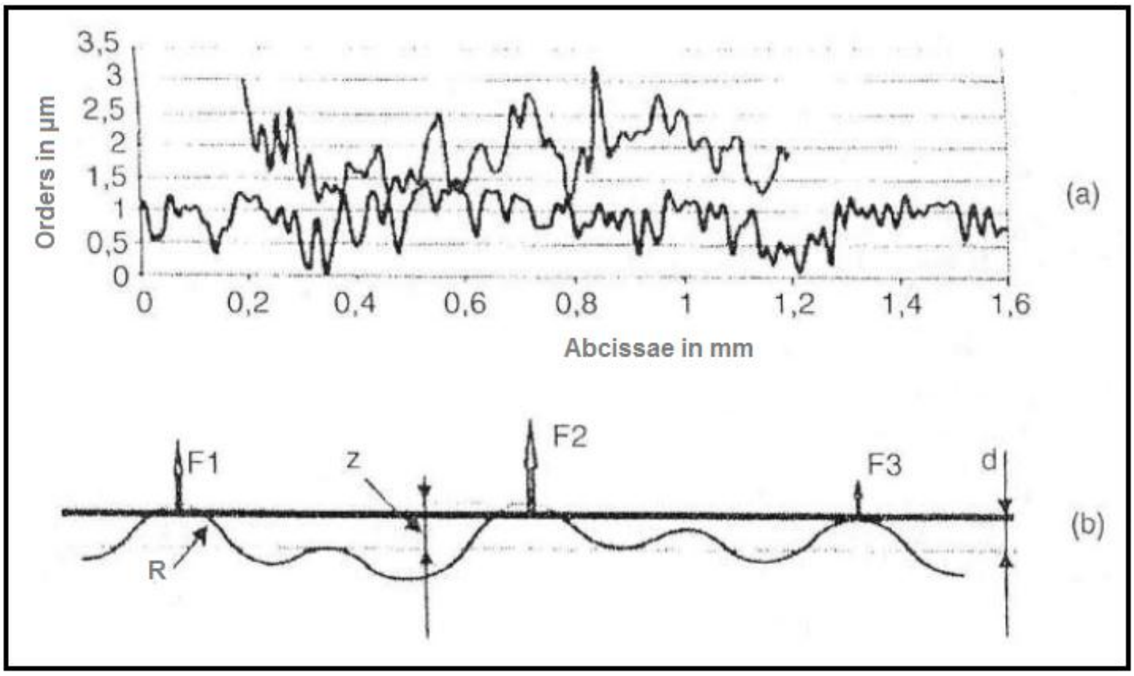


Figure V.1. (a): contact between two rough surfaces, **(b):** use of the sum surface integrating the roughness of the two antagonistic surfaces facing an ideally smooth surface.

- **Contact methods**

Contact devices are equipped with a probe, essentially a diamond tip with a tip radius of between 1 and 5 µm in contact with the surface. Diamond displacements are converted into electrical signals and, after amplification, recorded graphically. This type of mechanical probe is best suited to characterizing high-hardness surfaces. For more malleable surfaces (zinc and tin, for example), the equipment features inductive electronic comparators with a much larger top radius (250 to 500 µm).

- **Non-contact methods**

Non-contact devices are equipped with optical micropipers, which use laser beams permanently focused on the surface under examination by a servo-control system. It is the displacement of the optics, to maintain focus that is transformed into an electrical signal. The diameter of the focal spot is only 1 µm, and the measurement can be carried out on any type of coating or substrate. Recently, systems have been developed using axial chromatism in white light, the principle of which is to transform a point source of natural light into a continuum of small monochromatic image points distributed along the optical axis. Scanning frequencies of 1, 4 and 30 kHz from a spot of 2 µm in diameter enable three-dimensional images of the surface condition to be obtained with a resolution of 10 nm vertically and 0.5 µm laterally, with insensitivity to variations in the object's reflectivity. There are already various types of device on the market using this principle for optical profilometry, some of which are portable and suitable for in-line metrology, both on a flat surface and inside tubular elements.

- **Appearance and gloss control**

Visual inspection is essential at the end of the manufacturing process, when parts are received. Quick and easy to implement, this inspection enables us to check various characteristics required of coatings and surface treatments, such as appearance or color, gloss and absence of defects. This inspection covers all coating and conversion processes.

- **Appearance control**

Appearance control is very important in many fields of industry, as it is the indicator of a drift in operating conditions. Defects can have several origins:

- irregularities both in liquid electrolysis conditions and in the vapor phase of dry deposits,
- pits and craters that disrupt the crystallographic structure of the coating by locally modifying its roughness.

The means used to assess appearance defects are as follows:

- visual inspection at the end of the operation or on receipt of the parts: quick and easy to use, it allows you to check color and its homogeneity, as well as the presence of veils, pitting and craters;
- binocular magnifying glass examination: this examination is also carried out when the parts are received, to determine the nature of any defects detected during visual inspection;
- scanning microscope examination: this additional observation is necessary when binocular examination proves insufficient to detect the nature of the defect observed; this examination also makes it possible to determine the nature of any foreign bodies that may have altered the deposit's crystallization state.

- **Gloss control**

Gloss (also known as reflectivity) can be checked by simple visual examination in well-defined light conditions, by comparison with control samples. However, the need to avoid the subjectivity associated with operator perception has led to the preferential use of equipment known as "glossmeters" or "reflectometers", whose principle is as follows: a beam of light is sent onto the surface at a given angle of incidence, and a sensor measures the quantity of light reflected in the specular direction (angle of reflection equal to the angle of incidence). Gloss is then defined as the ratio of reflected intensity to incident intensity. The value given by the device lies on a scale arbitrarily set by the manufacturer, the maximum of which corresponds to a totally reflective, polished surface. The angle of incidence at which the measurement is taken depends on the product's gloss level. In general, four angles are recommended: 20, 45, 60 and 85°. Large angles are used for matt surfaces, and small angles for high-gloss surfaces.

Surface gloss can be measured at various stages of the coating process, particularly for decorative applications: after polishing (mechanical, chemical or electrolytic), after liquid or dry coating, after zinc coating and conversion treatment for automotive body sheet metal. This method can only be applied to flat surfaces of sufficient size. However, with good calibration, it can be used to monitor corrosion degradation after exposure to aggressive natural or synthetic media.

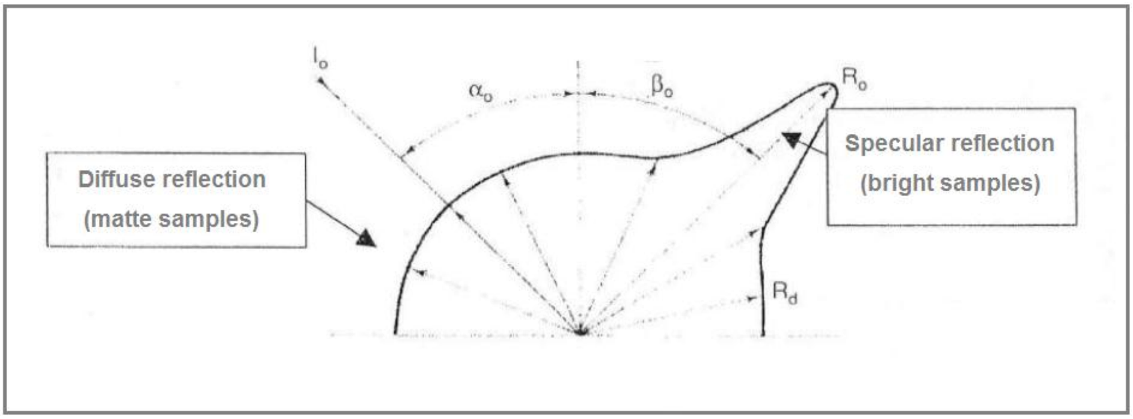


Figure V.2. Light intensity reflected by a matte or glossy sample. Gloss is actually the combination of specular reflected light and diffuse reflected light.

V.3.3. Mechanical control

This involves assessing the mechanical properties of the surface, i.e. the surface hardness of a coating or the hardness gradient obtained after surface treatment, as well as the corresponding state of residual stresses. Knowledge of these properties and their possible drift is extremely important for all mechanical applications: resistance to friction and wear, resistance to fatigue, surface fatigue or thermal fatigue.

- **Hardness control**

This is an essential property in mechanical applications, particularly in the fields of surface heat treatment, thermo-chemical treatment, wet and dry hard deposition, hot spray deposition and hardfacing. It is a complex mechanical characteristic, often difficult to interpret, which depends on the nature and shape of the indenter, as well as on the method of application. Hardness tests are generally simple to perform, fast and, in most cases, non-destructive, as they are carried out either on a control or on the non-active part of the treated parts.

A large number of measuring methods are available, generally adapted to the shape and thickness of the coated or surface-reinforced zones. The most common methods involve measuring the dimensions of an indentation made by an indentor under an imposed load. This indentor may be shaped like a ball, cone or pyramid.

- **Brinell hardness**

In this test, the indenter is a polished ball made of hardened steel or tungsten carbide. Its diameter D is normally 10 mm, and the load P applied to the surface is 29400 N or 3000 kgf (the standard requires the ratio P/D^2 to be equal to 30 for P expressed in kgf). After the load has been removed, the ball leaves a permanent circular imprint obtained by elastoplastic deformation of the surface, the diameter d of which is measured to be greater the less resistant the material is to penetration.

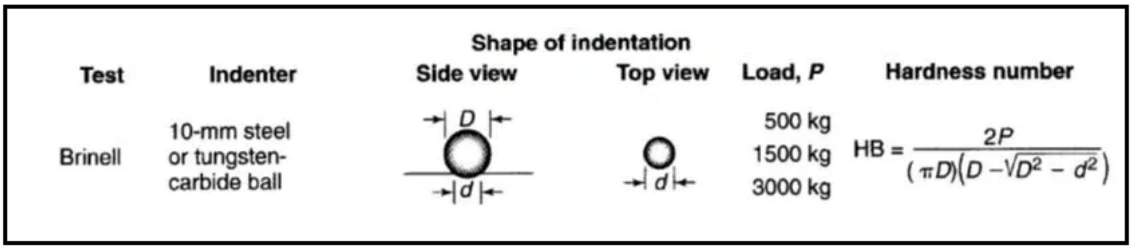
Hardness is expressed as the ratio of the load P to the surface area S of the spherical cap imprinted in steel. Tables give Brinell hardness directly as a function of the diameter d of the impression obtained under given conditions of load and ball diameter. This is in fact a hardness index expressed by the symbol followed by the indication of the ball diameter (in mm), the application load (in kgf) and the holding time (in sec): HB 10/3000/10.

The Brinell test requires a flat, machined or ground surface. The surface must be in such a condition that the diameter of the indentation can be easily read, especially if the indentation is small. The load is applied normally to the surface, without impact, so as to reach the load in 15 sec. The load is maintained for 10 to 15 sec. only, to avoid any risk of creep. The diameter of the impression must be measured in two perpendicular directions.

The possibility of ball deformation during the test must also be taken into account. It is not to be feared with a steel ball for HB < 450, nor with a tungsten carbide ball for hardnesses HB < 600. Above 600, diamond indenters should be used (Rockwell or Vickers test).

Precautions must also be taken to avoid deformation of the treated or coated part during measurement: the distance from the center of the indentation to the edge of the part must not be less than 2,5d, and the distance between two adjacent indentations must exceed four times the diameter. The thickness of the part or overlay must be at least eight times the cavity depth, so that no deformation is visible on the opposite side or at the coating-substrate interface.

Under these conditions, the Brinell hardness test is particularly well suited to assessing the hardness of cast structures such as cast irons, steels (rolling mill rolls or, more generally, bimetallic tools) or certain ferrous alloys used for hardfacing. On the other hand, this test is not at all suitable for assessing the hardness gradient obtained, for example, by a surface heat treatment or a thermochemical treatment such as carburizing, carbonitriding or nitriding. The most common measurement is obtained with a 10 mm diameter ball under a load of 29400 N (3000 kgf).



Test	Indenter	Shape of indentation Side view	Shape of indentation Top view	Load, P	Hardness number
Brinell	10-mm steel or tungsten-carbide ball			500 kg 1500 kg 3000 kg	$HB = \frac{2P}{(\pi D)\left(D - \sqrt{D^2 - d^2}\right)}$

Figure V.3. Brinell hardness test

- **Rockwell hardness**

The test consists in measuring the residual indentation of a penetrator, pressed under light load on the surface to be assessed, after application of an overload under specific conditions. The indenter used is:

- a diamond cone (Rockwell C test) with circular cross-section, 120° vertex angle, spherical rounded tip (0.2 mm radius);

- a 1.59 mm (1/16 inch) diameter hardened steel ball (Rockwell B test).

In the Rockwell C (HRC) scale, used for very hard materials (cast irons, tool steels, hardfacing alloys), the overall load is 1470 N, and in the Rockwell B (HRB) scale, used for medium-hard materials (mechanical strength level below 750 MPa, steels in the annealed state, for example), it is 980 N. The measurement involves three steps:

a): contact between indenter and surface, under preload F (98 N), with zero setting of the indentation indicator,

b): imposition of overload F, enabling test load to be reached,

c): return to preload and read the press-in indicator.

The indentation indicator is a comparator that measures indentation depth to the nearest μm after removal of load F. The lower the indentation, the greater the hardness, and the reading on the dial is made directly in Rockwell units; one unit corresponds to an indentation of 0.002 mm.

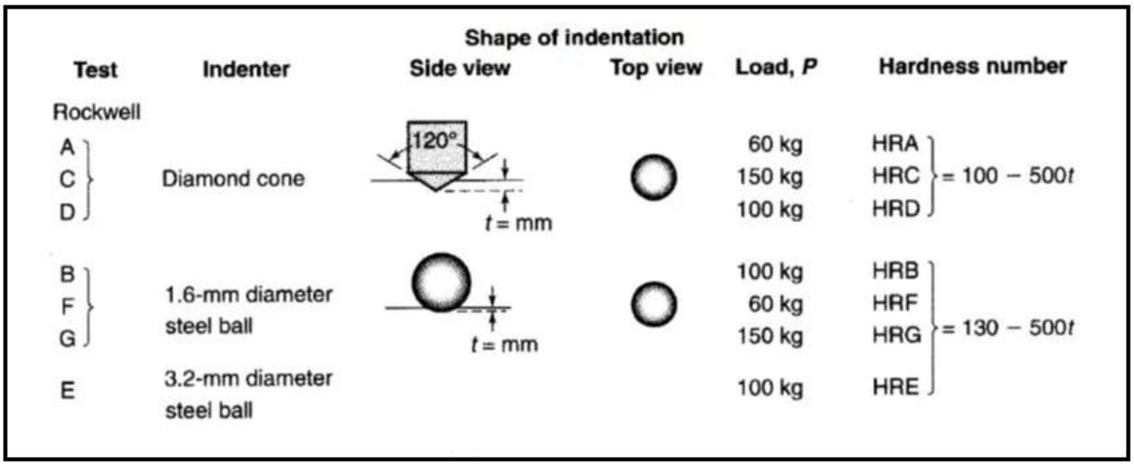
Rockwell hardness measurement requires a number of operating precautions:

- the surface condition of the part must be satisfactory, for example with 00 grade paper polishing. Indeed, the presence of scratches can lead to dispersions due to the ridge or valley effect, which reduces or increases the penetration rate;

- the part must rest firmly on its support when the load is applied;

- the thickness of the part or coating must not be less than 8 times the penetration depth. Under no circumstances should any deformation be visible on the opposite side to that of the measurement, or at the interface between the coating and the substrate.

Rockwell C hardness is sometimes used to assess the hardness gradient over large depths, e.g. after surface heat treatment on carbon steels (machine tool slides, rolling mill rolls) or roller burnishing on mechanical parts (crankshafts). It is necessary to respect the rule that the thickness of the hardened zone must be greater than 10 times the depth of the indentor's residual indentation.



Test	Indenter	Shape of indentation		Load, *P*	Hardness number
		Side view	Top view		
Rockwell					
A	Diamond cone	120° *t* = mm		60 kg	HRA = 100 − 500*t*
C				150 kg	HRC
D				100 kg	HRD
B	1.6-mm diameter steel ball	*t* = mm		100 kg	HRB = 130 − 500*t*
F				60 kg	HRF
G				150 kg	HRG
E	3.2-mm diameter steel ball			100 kg	HRE

Figure V.4. Rockwell hardness test

- **Vickers hardness**

The principle of the test is the same as that of the Brinell test, but in this case the indenter is a diamond pyramid with a square base: the angle between two opposite faces is 136°, chosen to match the Brinell test. The advantage of diamond is the absence of indenter deformation when measuring high hardnesses.

The diamond leaves a square indentation, and the length of the diagonal of the indentation (or the average of the two diagonals) is measured to within 0.002 mm using a 120 magnification microscope linked to the machine and automatically positioned above the indentation. Vickers hardness is the quotient of the test load and the area of the indent of diagonal d, and is therefore homogeneous to the average pressure exerted on the material. With current units (i.e. P expressed in N, d in mm), $HV = 1.854 \times 0.102\ P/d^2$, which with old units (P in kgf and d in mm) corresponds to $HV = 1.844 \times P/d^2$.

The tables supplied by the various manufacturers give HV directly as a function of P and d.

The most frequently used load is 294 N (30 kgf), however, the range of usable loads, 49 to 980 N (5 to 100 kgf), enables this method to be applied across the entire hardness scale and with all sample dimensions, by choosing the load giving a footprint such that the diagonal d is greater than 0.4 mm, but less than two-thirds of the thickness. In these conditions, the symbol HV is followed by the load used (in kgf) and the holding time (in sec): example HV30/20. In most cases, however, we simply indicate the load used (e.g. HV30).

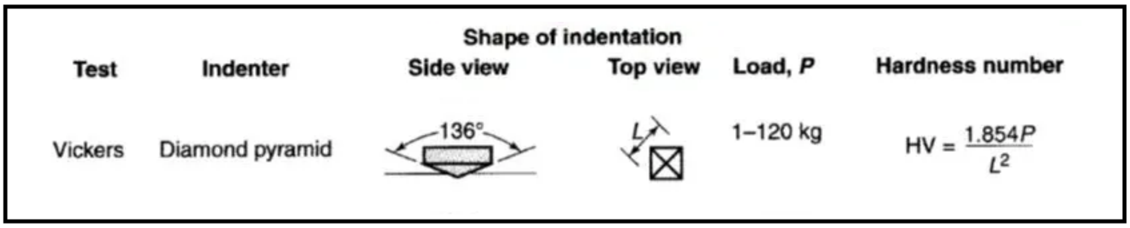
As far as operating precautions are concerned, it is necessary to polish the surface as perfectly as possible to make the impressions visible, especially for high hardness and low loadings. It is advisable to start with a ground surface polished with 00 paper and finish with micrographic alumina polishing. Furthermore, the distance between the center of a cavity and the edge of the part or the sides of another cavity must not be less than 2.5 times the diagonal. The thickness of the treated part, the hardness gradient zone or the deposit must be greater than 1.5 times the diagonal of the indentation. The condition of the diamond must also be checked frequently, as there is a risk of pyramid tip wear when measurements are taken on high-hardness surfaces.

The best-known of these is the "Hanemann" system, which comprises both indenter and objective lens, and is mounted on a conventional metallographic microscope. The indenter is set into the front lens of the objective used to examine the sample and locate the measuring point. The most common range of variation for the application load is between 0.049 and 0.98 N (5 to 100 g), obtained by means of two flat annular springs.

Vickers hardness is by far the most widely used method for assessing the performance of a surface treatment or coating, particularly for mechanical applications, combining the possibilities offered by conventional hardness indentations under loads ranging from 49 to 980 N (5 to 100 kgf) or microhardness indentations under loads ranging from 0.049 to 0.98 N (5 to 100 g). Vickers microhardness, in particular, provides extremely interesting results in the following situations:

- surface layers (hard deposits such as PVD, PACVD, coatings of hard chromium, chemical nickel, a few μm thick),
- hardness gradients obtained, for example, after thermochemical treatment (nitriding, carbonitriding, carburizing) or surface heat treatment,
- oxide coatings (hard anodizing on aluminum alloys, thermochemical oxidation

treatment on titanium or zirconium alloys).

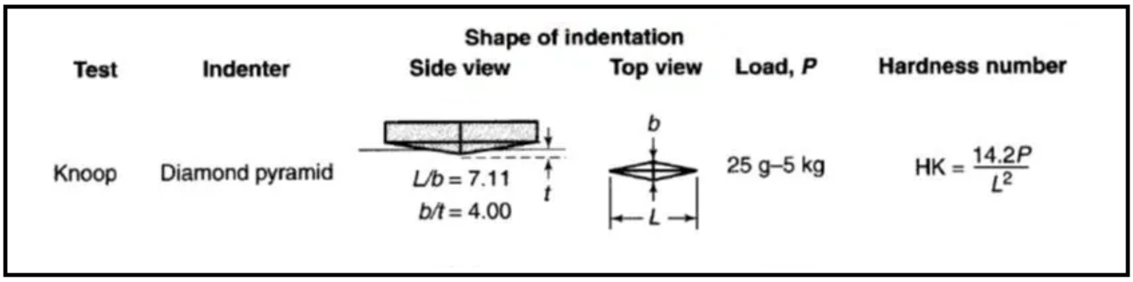


Test	Indenter	Shape of indentation		Load, P	Hardness number
		Side view	Top view		
Vickers	Diamond pyramid	136°	L	1–120 kg	$HV = \frac{1.854P}{L^2}$

Figure V.5. Vickers hardness test

♦ Knoop hardness

The indenter used is a diamond pyramid with a diamond base, the diagonals of which are roughly in the ratio 1 to 7 (see figure 20.1d). The advantage of this system is that it gives a sufficiently large indentation for a very low load, while soliciting a very small volume of material. Applied loads range from 0.049 to 19.6 N (5 g to 2 kgf). Knoop hardness is expressed as the ratio of the applied load F to the projected area A of the indentation, and can be assessed by measuring the largest diagonal of the indentation with a microscope whose magnification can exceed 650. This method can be used, for example, to evaluate the hardness of deposits obtained by liquid or dry processes, with fairly high sensitivity.



Test	Indenter	Shape of indentation		Load, P	Hardness number
		Side view	Top view		
Knoop	Diamond pyramid	t $L/b = 7.11$ $b/t = 4.00$	b L	25 g–5 kg	$HK = \frac{14.2P}{L^2}$

Figure V.6. Knoop hardness test.

▪ Residual stress evaluation

There are two types of stress in coatings or areas with gradients in mechanical properties:

- internal stresses, essentially corresponding to residual stresses resulting from the material's history during surface treatment, possibly supplemented by heat treatment;
- applied stresses, divided into surface stresses and volume stresses, which are added locally to the internal stresses.

Internal constraints are obviously of most interest in terms of control, and can be defined on two levels:

- level 1, which corresponds specifically to residual stresses: in the absence of applied forces, they balance out in the volume of the material; on the other hand, they are superimposed on applied stresses;

- level 2, which corresponds to stresses occurring at grain level; these stresses do not cause macroscopic deformation, but they can influence certain properties such as corrosion resistance or mechanical properties such as hardness and ductility.

Level 1 residual stresses have been the subject of much methodological development. A distinction is made between destructive, semi-destructive and non-destructive methods.

- **Destructive methods**

Destructive methods involve monitoring the return to equilibrium of a part that has been progressively destroyed using a gentle layer removal method that does not generate new stresses. These are the Le Luan method on a flat surface and the Sachs method on a cylindrical surface, which make no assumptions about the distribution of the stress field, but do require knowledge of the elastic constants of the analysis components. This method has been successfully used to evaluate residual stresses in relatively thick deposits obtained by reloading.

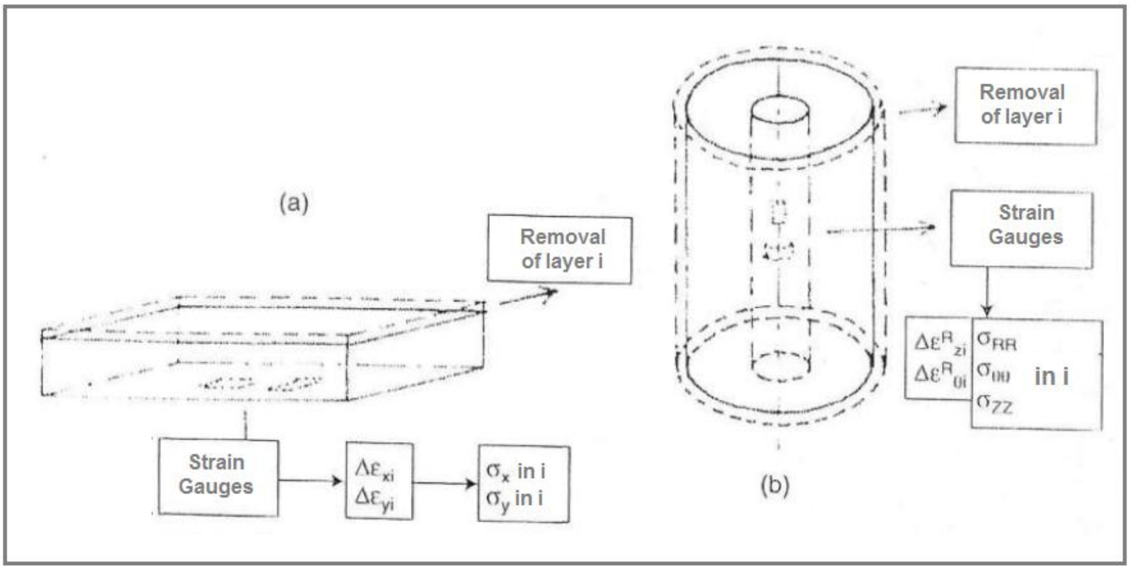


Figure V.7. Schematic representation of the methods of: Le Luan (a) and Sachs (b) for determining residual stresses in hardfacing on flat or cylindrical surfaces.

- **Semi-destructive methods**

Semi-destructive methods consist, after local removal of material, in measuring relaxation using strain gauges. This is the incremental hole by successive passes method, where gauges are arranged in a rosette around the drilled zone and the drill bit for gauges located inside a circular groove.

In both cases, residual stresses are deduced from continuum mechanics. These local measurement methods are well suited to assessing residual stresses down to depths of around ten mm. Beyond that, it is necessary to apply the destructive methods previously described with complete removal of successive layers.

- **Non-destructive methods**

Non-destructive methods use either the inter-reticular distances of crystallographic planes, ferromagnetic noise (Barkhausen effect) or the curvature of a flat specimen as a strain gauge. In the first case, the method used is X-ray diffraction (possibly neutron diffraction), in the second the ferromagnetic noise method and in the third the deflection method.

- **X-rays**

X-ray stress analysis is based on the measurement of strains in the crystal lattice of a sample in different directions. Stresses are then calculated from these deformations using stress-strain relationships obtained from the mechanical approach to a polycrystalline assembly. In the case of an elastic, homogeneous and isotropic continuous material, the strain & measured in a direction o, relative to a reference frame attached to the part, is directly linked to the stresses by the relationship:

$\varepsilon_{\varphi\psi}= (1/2)S_{2(hkl)}\ \sigma_{\varphi}\ \sin^2\psi + S_{1(hkl)}\ (\sigma_1+\sigma_2)$ avec $(1/2)S_{2(hkl)} = (1 +\nu)/E$, $S_{1(hkl)} = -\nu/E$, σ_1 and σ_2 being the principal constraints.

$S_{1(hkl)}$ and $S_{2(hkl)}$ are the radiocrystallographic elastic constants. They depend on the choice of diffracting plane family and the material studied. Strictly speaking, this method is limited to cases where the following assumptions are met:

- the measurement is superficial, as the penetration of the X-ray beam is only a few µm, the σ_3 component is considered to be zero,
- deformations and stresses are homogeneous throughout the irradiated volume.

The complete stress tensor can be derived from different measurement directions, provided that the material's laws of behavior in the elastic domain are well understood.

X-rays use diffraction peak displacement and broadening to evaluate both Level 1 and Level 2 residual stresses. In the first case, residual stresses are assessed using the $\sin^2\psi$ method described above. In the second case, the state of microstrain is qualitatively assessed using the width of the diffraction peak at half-height. This method is easy to use, and there are a number of portable devices that can be used on large industrial parts. Non-destructively, the state of residual stresses and micro-deformations on the surface can be determined. It is also possible to produce profiles of these same values, but in conjunction with a gentle means of material removal (electrolytic polishing), in which case the method becomes destructive.

The limitations of the X-ray method are directly linked to the above-mentioned assumptions. Textural effects and coarse grain sizes run counter to the isotropy of the material, and high stress gradients run counter to stress homogeneity in the irradiated volume.

As far as texture effects are concerned, analyses have taken into account stress variations as a function of orientation and to enable the calculation of the biaxial stress state. The problem only really arises for very pronounced textural effects, such as columnar coatings obtained by liquid or dry processes.

As far as stress gradients are concerned, X-ray penetration is not the same depending on the angle of incidence ψ, but this is only noticeable for gradients greater than 50 $MPa.\mu m^{-1}$, which is rarely the case in practice with the exception of ion implantation.

- **Ferromagnetic noise**

In the case of magnetic materials, the Weiss domains corresponding to well-defined magnetizing material elements evolve as a function of applied magnetic fields. These changes are reflected in the hysteresis cycle by a "characteristic noise" or Barkhausen effect.

The displacement of the domains in the direction of the imposed magnetic field depends on the state of residual stress, as the latter can lead to the multiplication of elementary jumps. The amplitude and average level of the noise are therefore directly correlated with the state of stress. With reference to the relaxed state, the Barkhausen noise is modified as follows:

- compressive stresses and a magnetic field applied in the same direction will favour the same domains, resulting in a Barkhausen signal shifted towards weaker fields, with a narrower and higher peak;

- compressive stresses and a magnetic field applied in the same direction will favor different domains, resulting in a Barkhausen signal shifted towards stronger fields, with a wider, lower peak and more or less pronounced bulges corresponding to 90° wall movement.

This effect is widely used to determine applied, residual or internal surface stresses. This is particularly true of mechanical surface treatments (shot-peening, peening, laser shocking). In the field of surface treatment by thermal structural transformation, the Barkhausen signal is also sensitive to metallurgical transformations.

Indeed, the thickness of the material layer involved in the measurement is of the order of a few tenths of a mm, and changes with the cycling frequency of the imposed magnetic field. As the size of the magnetic domains is of the order of a few µm, the signals measured are also highly dependent on the material's microstructure (precipitation, residual austenite content, etc.).

The dual sensitivity to microstructure and stress often results in trends in the same direction in the case of surface hardening treatments. The result is greater complexity in interpreting the observed trends.

- **Arrow method**

This simple and relatively sensitive method can be used for a number of applications: monitoring processes such as shot peening to assess changes in treatment parameters, or evaluating stresses when the depth affected by the treatment is very small and difficult to measure using other techniques (e.g. ion implantation). This method can also be used to determine stresses in a thin, single-sided deposit.

In the case of shot peening, the models developed at CETIM have made it possible to establish simple relationships giving the value of maximum stress and surface stress with a very good approximation. Based on these relationships, abacuses were drawn up to obtain these values directly from the measurement of the only parameters: deflection of the specimen after shot peening and depth of plasticized metal.

Residual stress profiles can also be established by removing successive layers using chemical reagents adapted to the substrate (25-50% nitric acid for steels, 20 g/l soda ash at 30/40°C for aluminum alloys and aqua regia at 40°C for steels and stainless alloys). This is a semi-destructive method analogous to X-rays. In the same way, it is possible to evaluate stresses in thin coatings applied to only one side of the blade. For a curvature r of the blade of thickness t, the average value σ of the stress in the coating of thickness d (especially when $d > t/2$) is expressed by the relationship:

$$\boldsymbol{\sigma = R \cdot t \cdot E_{sub} / 6.r.f\,(R, d, t)}$$

R being the ratio E_{dep} / E_{sub}, and f a function of the parameters R, d and t. Approximate expressions for σ can be used when the deposit thickness is small and less than t/2.

However, the sag method applied to galvanic deposition control has two drawbacks: the evolution of distances between electrodes per curvature, which modifies deposition parameters, and stress relaxation, which results in default values. Nevertheless, this method is interesting for monitoring stress evolution as a function of the process parameters used.

- **Thickness control**

The thickness of coatings is an essential feature when the aim is to protect against corrosion or reduce wear.

There are destructive methods (metallography, electrolytic dissolution and calotest) and non-destructive methods (eddy currents, magnetic measurements, ultrasonic backscatter, X-ray fluorescence, ß rays and optical reflection).

- **Destructive methods**

- **Metallography**

Metallography is the only method that provides an absolute measurement of thickness on the cut surface, serving as a standard for other methods and allowing arbitration in the event of a dispute. A number of metallographic reagents adapted to different types of deposition are available to facilitate observation of the coating-substrate interface.

This method is only valid for layer thicknesses of 5 µm. For lower layer thicknesses, and provided that surface roughness is not too high, it is possible to make a "skew" metallographic cut, provided that the cutting angle is well known.

- **Electrolytic dissolution**

Electrolytic dissolution is performed in a DC cell on a sample placed in anodic condition with a stainless steel cathode. By applying Faraday's law, the thickness e of the coating can be measured using the equation :

$$\mathbf{e = AIt/nF\rho S}$$, in which:

- A: is the atomic mass of the deposit metal (in kg/mol),
- I: is the electrolysis current,
- t : is the duration of electrolysis,
- n: is the oxidation state of the dissolved element,
- S: is the surface area in contact with the electrolyte,
- ρ : is the specific mass of the deposit component,
- F: is Faraday's constant (96,490 C/mol).

Commercially available equipment allows the value of the electrolysis current to be fixed, and under these conditions the thickness to be measured is proportional to the dissolution time. This method is well suited to measuring the thickness of deposits a few µm thick, and to assessing multilayer deposits. Thicknesses measurable by this method are in the fractional range of µm to 50 µm. Care must be taken with baths to avoid the impact of bath aging on electrolysis efficiency, which must be as high as possible. To overcome these problems, a preliminary calibration on a sample of known thickness is necessary.

This electrolytic method is ideal for homogeneous or multilayer metal coatings, such as copper, nickel and chromium coatings on steel.

- **Calotest**

The calotest consists of creating a calotte in the deposit by wear until the substrate appears, using a WC-Co cermet ball impregnated with diamond powder and driven by a rotational movement. This relatively simple test is widely used to assess the thickness of high-hardness coatings obtained by the dry process (PVD, PACVD), with the added difficulty of limiting wear to just the metal-deposit interface. In the case of multilayer or nanostructured coatings, it enables the different layers to be clearly distinguished and the thickness of each to be evaluated.

If R is the radius of the carbide ball, D the diameter of the ball's total footprint, d the diameter of the ball's footprint on the substrate, the thickness e of the coating is given by:

$$e = 1/2 - (\sqrt{4R^2 - d^2} - \sqrt{4R^2 - D^2})$$

This calotest method is best suited to measuring deposit thickness on high-hardness substrates and for flat geometries with good surface finish.

- **Non-destructive methods**

Non-destructive methods for assessing the thickness of a coating or a gradient of mechanical properties have in common the fact that they are sensitive to physical parameters (elastic behavior, electrical properties, refractive index, absorbency of ionizing radiation, etc.). The choice of method depends on the nature of the surface treatment or coating to be tested, and whether absolute or relative information is required.

- **Eddy currents**

One of the most important is the electromagnetic eddy current method. It uses the influence of variations in the material's physical properties (conductivity σ and permeability μ) on the distribution of currents induced near the surface by an electromagnetic sensor. Induced currents or eddy currents depend on the structural characteristics encountered. The principle of the method is a measurement of impedance variation of the transmitting coil or an auxiliary coil. This imbalance is translated into amplitude and phase on a control screen. The method is well suited to checking structural modifications to axisymmetric parts (bars, tubes), as well as to flat surfaces.

These measures are of two types:

- differential measurements used to highlight small-scale discontinuities (cracks, lack of material),
- absolute measurements to analyze slow variations in a parameter, such as conductivity or permeability, or changes in thickness.

The conventional penetration depth of eddy currents is equal to $1/\pi f\mu\sigma$, an expression in which f is the current frequency (Hz), μ is the permeability and σ the electrical conductivity. This value is very useful for knowing the limit of correct measurements. As the eddy current method is sensitive to variations in chemical composition and microstructure, it is a global measurement technique that can be applied both for assessing the thickness of coatings and for measuring depths treated by surface hardening, or assessing a gradient of mechanical properties obtained by thermochemical treatment.

In the first case, the devices on the market operate on the principle of measuring high-frequency induced eddy currents. To achieve this, the coating and its substrate must exhibit a sufficient difference in electrical conductivity. Under these conditions, the method enables the thickness of:

- conductive coatings on conductive substrates (e.g. Cu, Ni, Zn, Cd on steel),
- insulating coatings on conductive substrates: anodized coatings, for example,
- conductive coatings on insulating substrates (e.g. copper on epoxy resin).

Measured thicknesses range from 2 µm to several tens of µm, depending on the frequency used to excite the sensor. A calibration curve adapted to each frequency is used to correlate the measurement result with the coating thickness.

In other cases, the aim is to evaluate a gradient of mechanical properties and microstructures over greater thicknesses. The use of low-frequency eddy currents with harmonic analysis is sensitive to microstructural evolution and gradients in chemical composition. It has been possible to establish correlations between the relevant measurement parameters and the treated depths assessed by destructive testing and hardness filiations. As a result, sensors adapted to certain part geometries such as gear teeth or bearing seats have been developed to assess carbonitriding depths. We have also developed a method for measuring nitrided depths on stainless steel tubular cladding elements for remote control applications in nuclear power plants.

- **Magnetic measurements**

Magnetic measurements are applicable to non-magnetic and non-conductive coatings on ferromagnetic substrates, magnetic coatings on ferromagnetic substrates and magnetic coatings on non-ferromagnetic substrates. They are based on two types of measurement:

- the force of attraction of a magnet: this method is of interest for non-magnetic coatings and deposit thicknesses of less than 50 µm, such as oxide layers; this method is relatively imprecise, as it is sensitive to substrate curvature and the position of the measuring probe;
- the reluctance of a magnetic circuit formed by the part to be measured and a permanent magnet (or electromagnet): the reluctance R of the magnetic circuit thus formed is the quotient of the magnetomotive force F and the associated induction flux φ (which varies with the thickness of the coating, considered as an air gap); this method can be used to measure the thickness of non-ferromagnetic coatings on ferromagnetic substrates.

- **Ultrasonic backscattering**

The ultrasonic method applicable to layers hardened by surface heat treatment or thermochemical treatment is based on the scattering of ultrasonic waves by the crystalline structure of the substrate. Rayleigh waves, or surface waves, are preferred for the study of hardening structures. These so-called guided waves predominate over volume waves in the frequency range from 1 to 15 MHz. For steels, their scattering is much weaker in the case of a ferrito-perlitic structure than in the case of a martensitic structure. Measurement of the thickness of the hardened layer is therefore obtained by evaluating the wave propagation time in this zone.

The transition between the martensitic structure of the surface layer and the intermediate structure of the sub-layer (bainite, martensite revenue or ferrito-perlitic assembly) requires appropriate instrumentation. The transceiver is positioned at an angle to the surface to be inspected, so as to maximize surface wave scattering and recover maximum information at the end of the hardened layer.

The coupling between the part to be inspected and the ultrasonic transducer can be achieved by total immersion of the assembly, or more generally, in most applications, by means of a column of water held between the part and the transducer with specific devices. Generally speaking, the use of this device is satisfactory for evaluating hardened depths of between 1,5 and 13 mm. Measurement accuracy depends on a number of parameters, in particular the surface finish and geometry of the part. A high degree of roughness increases the width of the interface echo, making it impossible to isolate diffusion echoes that are too close together, corresponding to low hardened depths. Furthermore, excessive curvature, such as at the bottom of a groove, is unfavorable for wave propagation conditions. Finally, from a metallurgical point of view, this method will give good results if the microstructural transition between the hardened zone and the substrate is fairly abrupt.

- **X-ray fluorescence**

The principle of the method is to send X-rays from various sources (radioactive sources, electromagnetic radiation sources) onto a metal surface, causing it to emit fluorescent radiation identified by dispersive spectrometry. The control equipment comprises an X-ray generator, with goniometer and scintillator, a detector probe and measurement electronics, with computer storage of the results obtained.

In the case of a coated metal surface, we measure either the absorption by the coating of the fluorescence radiation emitted by the base metal, or the X-ray fluorescence emission of the coating alone. The lower detection limit corresponds to atomic number 20 (Ca).

The application of X-ray fluorescence to thickness measurement is described in standard NF EN ISO 3497, two cases must be considered:

- the element making up the deposit is present in a thin layer and its atomic number is greater than 20. We then measure the fluorescence intensity of the layer (emission measurement), and compare it with standard curves to deduce its thickness;
- the element making up the coating has an atomic number below 20, but the substrate has an atomic number above 20. In this case, the attenuation of the substrate's fluorescence by the deposit must be measured (absorption measurement) and the coating thickness deduced by comparison with standard curves.

Calibration must be carried out in a geometry strictly identical to that of the measurement. The most accurate method is to plot the variation of the signal as a function of the thickness measured micrographically. The measurement range extends over relatively small thicknesses, from d to 50 µm, with an accuracy that is currently 5%. This method can also be applied to multi-coatings after evaluating the thickness of the outermost layer.

- **Grip control**

Most coatings are applied for a specific purpose, such as decoration or corrosion protection. For this purpose to be achieved, the coating must adhere well to the substrate. Adhesion is a measure of both the quality of the preparation of the surfaces to be coated and the quality of the coating operation.

Perfect adhesion exists insofar as the bonding force between the coating and the substrate is greater than the inherent resistance (tensile strength, for example) of each of them. The aim of the adhesion test is therefore to identify cases of imperfect adhesion.

- **Folding**

The bending test is performed on a cylindrical or conical mandrel (variable bending radius). In the case of a cylindrical mandrel, its diameter is correlated to the thickness of the sample. Standard NF EN ISO 2819 suggests a diameter four times the thickness. This type of test is obviously applicable to coated sheet metal. The deformed area is then examined for signs of flaking or blistering of the deposit; it is very important to note that the appearance of cracks is not an indication of poor adhesion. The coating must then be able to be peeled off or lifted on either side of the crack with a blade.

- **Punching and stamping test**

According to NF EN ISO 2819, the deep-drawing test carried out on coated flat products consists in forming a cone in a 60 mm-diameter disc until it breaks. In this case, deposits with good adhesion must not flake off.

For solid parts, the punching test consists of driving a hemispherical punch to a depth of 0.5 mm and observing the edges of the impression under the microscope. Adhesion is good when the periphery of the indentation is free of cracks and poor when delamination and flaking are observed.

These tests are sensitive to substrate and coating ductility. The greater the hardness of the coating (e.g. chromium and nickel coatings), the greater their sensitivity to the detection of adhesion defects.

- **Thermal or mechanical shock tests**

The impact test consists in dropping a steel ball of known mass from a measured height and observing the deformation and any cracks around the crater formed by the ball. The hammering test consists in striking the surface repeatedly with tools of various shapes, and observing the impressions made. All these simple application tests are essentially qualitative in nature, enabling us to control a process and any deviations from it. They are ill-suited to highly ductile coatings. The thermal shock test uses the differences in expansion coefficients between the coating and the substrate to generate thermal stresses which are made more severe by sudden cooling after the heating cycle. The coated sample is heated to a temperature set by standard NF EN ISO 2819, depending on the nature of the substrate and coating. In particular, any parasitic phenomena of diffusion or recrystallization of the coating which could influence the results must be avoided.

To avoid surface degradation due to oxidation, the test is limited to a holding time of 15 min, after which the sample is quenched in water. Adhesion defects are classified according to their decreasing severity as exfoliations or the presence of blisters that detach from the coating. Interpretation of the results is sometimes tricky, as the presence of blisters on a coating obtained by the liquid route may reflect the fact that liquid has remained trapped in the pores, without the adhesion of the deposit being called into question.

- **Scratch test**

Coatings for mechanical applications are currently mainly assessed using the "scratch test" method. This involves scratching the surface of the sample with a Vickers-type diamond-tipped indenter under increasing load (from 0 to 100 N), and examining the indentation trace under a scanning microscope. The evolution of the tangential force is recorded in conjunction with the acoustic emission signal, which is representative of coating degradation. The adhesion limit is defined by the normal critical load Fn corresponding to the sudden increase in the acoustic emission signal. This is correlated with the appearance of the first cracks and flakes along the scratch. Scanning microscope examination of the indentor trace provides a qualitative assessment of the deposit's adhesion:

- if adhesion is good, there is only cracking of the coating perpendicular to the direction of movement of the indentor, in the middle of the indentor's track;
- if adhesion is poor, the coating will decohesive in the form of large flakes.

Results depend on coating thickness, substrate hardness and any gradient in the latter's mechanical properties. Like its predecessors, this test is by no means a quantitative evaluation of adhesion; it can only be an indicator of a potential drift in the manufacture of the deposit, which is why it is currently widely used to check the adhesion of a coating for mechanical applications.

- **Photothermal thermography**

The general principle of this test is to send a luminous flux (low-power laser source) onto the surface of the material to be studied, in order to induce thermal effects through interaction with the deposit. This flux, generally of near-infrared wavelength, is modulated by reflection from a rotating mirror. Part of the energy is absorbed by the coating, while the rest is radiated. An infrared optical measurement chain is used to detect the radiated part.

The aim of the test is to detect discontinuities in the coating/substrate interface, which will result in local temperature increases ("heat sinks"). The temperature variations induced by these discontinuities are detected by the measurement chain and the result is provided in the form of a thermogram, a true map of the flux distribution.

- **Control of ductility and porosity**

These two properties are essential for coatings designed to withstand mechanical stresses, and which may be immersed in aggressive media. For some applications, particularly in lubricated conditions, however, surface porosity is required to achieve a lubricant retention effect, provided ductility is not excessively affected.

- **Ductility control**

The notion of brittleness in the case of coatings is relatively complex to define, since it involves both the properties of the deposit and those of the substrate. Tests designed to define coating ductility are described in ISO 8401. They include bending tests, flexure tests and fracture tests.

- **Bending tests**

The purpose of these tests is to determine the stress the coating can withstand during mechanical deformation. There are several bending procedures, all of which can be applied to coated flat products: U-bend, vice bend and mandrel bend.

- U-bend

The flat product is manually bent into a U-shape. The resulting specimen is placed between the jaws of a micrometer device. The micrometer is closed until cracks appear. The ductility δ is a function of the value 2 r read on the micrometer and the thickness d of the specimen, according to the expression:

$$\delta \text{ (in \%)} = 100\, d/(2\, r - d)$$

This test is applicable to coatings with a thickness of between 20 and 40 µm.

- Vise bending

The 10 x 50 mm substrate, held in a vice, is manually bent 90° to either side of its initial position, repeatedly, until the first cracks appear. The ductility of the deposit is assessed by the number of bends. This test is, of course, relatively coarse and not well suited to highly ductile coatings.

- Mandrel bending

Several procedures are available, depending on the shape of the mandrel (spherical, cylindrical or conical) and the load application mode (3 or 4 points). One of the simplest tests consists in bending strips of metal coated on one side at 180° around mandrels of decreasing diameter until cracking of the coating is detected at a magnification of 10. The mandrel diameters can be spaced evenly, for example from 3 mm to 3 mm. The ductility of the coating is given by:

$$\boldsymbol{\delta = 100\ d/(d + e)}$$, where :

δ: coating ductility, d: smallest mandrel diameter allowing 180° bending without apparent cracking and e: total thickness of coating and substrate.

This method is widely used to assess the ductility of glossy deposits, particularly for decorative applications.

For coatings produced by the liquid process (galvanic or chemical deposits), there is a less severe ductility test described in ISO 4524/5, which involves bending flat samples on a mandrel of larger diameter, by a given angle θ, and assessing the amount of cracking. This test gives a qualitative estimate of the deposit's behavior and enables us to assess any drift in the process.

- **Bending tests**

This test is particularly well suited to assessing the ductility of hard coatings produced on substrates with high mechanical properties. There are two types of test, performed on prismatic bars of cross-section B x H: the 3-point bending test and the 4-point bending test.

During bending, the fibers are subjected to different stresses: compression above the neutral fiber and extension below. An acoustic measuring device detects the appearance of the first cracks when the outer fiber is extended. The deflection is recorded as a function of load, and the critical load at which the first cracks are detected by acoustic detection is noted. The selection criterion chosen is the elongation of the outer fiber corresponding to the critical cracking load.

The main applications of this bending test are thermochemical treatments, surface heat treatments and dry-process hard coatings for mechanical applications. As an indication, the critical elongation levels measured on various dry-process coatings on tool steel substrates for sheet metal working operations are as follows:

- 0.1 to 0.2% for DLC coatings,
- of the order of 1% for TiN coatings,
- between 0.6 and 1% for CrN coatings,

- between 0.2 and 1% for a coating of (Ti, Al)N and TiCN,
- of the order of 3% for a nitrided layer with no defined surface compound.

- **Fracture testing**

The absorption of hydrogen by the metal during surface preparation prior to treatment (e.g. acid pickling) and during galvanic deposition (e.g. chromium plating, cadmium plating, zinc plating) can lead to fracture at a loading level below the substrate's yield strength. This is the phenomenon of deferred fracture, an effect that is all the more pronounced the higher the substrate's mechanical strength. Standards recommend a post-deposition hydrogen diffusion treatment to mitigate this phenomenon. This treatment is carried out at a temperature of between 180 and 200°C.

Testing can be carried out using either slow bending tests or slow tensile tests on smooth or notched specimens. By measuring breaking load and deformation, the percentage of embrittlement can be calculated in relation to the reference values found on the uncoated substrate.

Delayed fracture tests, carried out under different loads, enable us to highlight the incubation phenomenon frequently encountered in hydrogen embrittlement processes. Their main drawback is the large number of test specimens required to obtain a complete fracture load vs. time curve similar to that used to determine fatigue endurance limits. These tests therefore require a relatively long experimentation phase.

- **Porosity control**

The presence of porosities within a deposit can lead to significant corrosion of the substrate by galvanic effect when the coating has a higher corrosion potential than the base metal (more noble than the latter, e.g. Cr or Ni coating on steel). The porosity of this type of deposit can be controlled chemically or electrochemically, but physical control methods are also available.

In the case of coatings that are less noble than the metal substrate, porosity is of lesser importance, as this is a sacrificial protection whose effect will be felt as long as the coating is not completely consumed. In the latter case, however, corrosion resistance is a significant factor, since it enables us to assess the durability of the protective action of the metal substrate.

- **Chemical methods**

Chemical methods for detecting porosity are based on the principle of galvanic etching of the substrate. They generally result in the appearance of colored products and the release of hydrogen at discontinuities.

Chemical methods have the disadvantage of attacking the coating as well as the substrate, making it more difficult to locate defects and increasing their quantity. They cannot be used when the coating is anodic to the substrate.

- **Electrochemical methods**

The principle of electrochemical testing is the same as that of chemical testing, with the action of the reagents being replaced by anodic dissolution of the substrate at pore level. The procedure for electrochemical processes is more complex than for chemical processes, but can be applied to coatings that are nobler than the substrate, as well as to sacrificial coatings.

A first example of the application of these methods is the electrolytic deposition of copper on a chromium coating on a steel substrate: as chromium is passive, copper is deposited only on the uncoated areas where the base metal appears (standard NF EN ISO 12540, solution of 200 g/l SO_4Cu and 20 g/l H_2SO_4 concentrate, 0,3 A/dm^2, 1 min).

A second example is the application of potentiostatic methods to the deposition of copper-nickel-chromium and nickel-chromium on steel substrates. The device uses a potentiostatic set-up with a saturated calomel reference electrode and an electrolyte of the following composition: sodium nitrate 10 g, sodium chloride 1,3 g, nitric acid (d 1,42) 5 mL, water 1 liter. The imposed potential of +0.3 V/ECS dissolves the undercoat and substrate without attacking the chromium film. After electrolysis, red spots appear in the porosities by immersing the samples in a reagent based on acetic acid (2 mL), potassium thiocyanate (3 g) and 30% hydrogen peroxide (3 mL) in 1 liter of water.

The advantage of electrochemical methods is that they can be used to simulate phenomena that may occur if protective coatings are porous, e.g. in the presence of chloride media. These phenomena are as follows:

- generation of pitting by surface initiation on defects, impurities or pores,
- corrosion propagation by galvanic coupling between dissolving anode zone and unaffected coating surface,
- acidification of the medium in the puncture.

Using these methods, it is possible to carry out electrochemical tests under optimum conditions as follows:

- research into the conditions for active dissolution of the substrate (determination of activation pH) in a conventional neutral chloride solution, or one made more severe by acidification,
- plot the i = f (E) curves of the protective coating(s) in the same medium and determine

the optimum etching conditions for the substrate alone,

- carrying out tests at imposed potential under the conditions determined above.

- **Electrochemical impedance spectrometry**

This method provides information on the reactivity of a surface in an electrochemical medium. It involves measuring the response of an electrode to a low-amplitude sinusoidal modulation of potential as a function of frequency. Such a modulation can be superimposed on an imposed anode or cathode potential, or on the equilibrium potential. Alternatively, the current can be modulated and the potential measured. Impedance spectroscopy is the result of impedance measurements presented as a function of modulation frequency. This method is particularly useful for studying the protection of conversion layers, such as chromate layers or anodic oxidation layers, and for characterizing insulating coatings (ceramic or DLC coatings). It enables contributions to be separated:

- the dielectric behavior of the material making up the protective film,
- alteration of the film-substrate interface through corrosion or delamination.

- **Corrosion testing**

It has previously been shown that electrochemical methods are of particular interest when the metal substrate is protected by a more noble coating. In this case, the presence of porosities can lead to significant corrosion of the substrate by galvanic coupling. A few examples demonstrate the positive influence of increasing the thickness of the protective coating on the risk of corrosion.

Corrosion tests are generally of interest for simulating real-life conditions of use for coated parts, with a reduction in duration due to an increase in the severity of the environment. These tests can be carried out regardless of the conditions under which metal substrates are protected, either by sacrificial action or by a more noble material. It should be noted, however, that corrosion tests are for comparative purposes only, and can only be used as a criterion for ranking substrate protection solutions.

- Salt spray tests

These are the most common corrosion tests, and are laid down in standard NF EN ISO 9227. Parts are exposed in an oven to a mist obtained by spraying a 5% ClNa solution in water, at a temperature of 35°C. The relative humidity of the air is 80-90% at 35°C, with prior passage into a chamber where the temperature is maintained at 45°C. The pH of the solution is 7 and the duration of the test is variable. The criterion used is the time after which corrosion pitting appears.

These conditions can be made more severe by acidifying the solution with acetic acid (pH equal to 3.2) or acetic acid plus 0.3 g/l of
Cl_2 Cu, with a pH of 3.2, but at a temperature of 50°C.

- Specific tests

A first type of test, particularly aggressive, is designed to assess the behavior of copper, nickel and chromium coatings for thicknesses in excess of 20 µm. This is the **Corrodkote** test corresponding to standard NF EN ISO 4541, carried out in a solution containing the following in 100 ml of water: 0.07 g copper nitrate, 0.33 g ferric chloride, 2 g ammonium chloride and 60 g kaolin. The parts are covered with this paste-like mixture and placed in an oven at 38°C and 94% humidity for 16 hours. This test is likely to generate pitting and crevice corrosion s which are recorded after the test.

There are other specific types of test that can simulate industrial environment conditions with much greater severity:

- Sulfur dioxide exposure test: samples are placed for 24 hours in a chamber at a temperature of 25°C and exposed to sulfur dioxide vapors produced by the reaction between 200 ml of a 200 g/l sodium thiosulfate solution and 50 ml of a 50% by volume sulfuric acid solution (d = 1.40);

- the **sulfide** test **using thioacetamide** (CH_3 $CSNH_2$), whose effects are comparable to those of hydrogen sulfide, maintained for 48 hours in an atmosphere with 75% humidity using a saturated solution of sodium acetate (NF EN ISO 4538);

- the **nitric acid** test, in which the parts are first subjected for 1 or 2 hours to vapors of 70% concentrated acid poured into the bottom of the chamber, then steamed at 125°C for 30 minutes.

All these tests end with observation of the corrosion facies using a binocular magnifying glass and a scanning microscope, and in some cases identification of the corrosion products. They enable us to establish classifications and selection criteria for optimal protection solutions for metal substrates.

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