

3.3 Potential properties of the superficial layer

3.3.3 Physico-chemical parameters

- ② (1) Brittleness- Ductility
- ③ A property opposite to brittleness is **ductility**- the susceptibility of metals to **permanent plastic deformation without the formation of cracks**.
- ④ Ductility is one of the basic characteristics of the metallic state. Often the term "ductility" is used as a synonym of **plasticity** but it means a **qualitative(定性的), non-measurable characteristic, strongly dependent on structure, processes occurring at the atomic level and on the type of slip**.

(3) Residual stresses

- stresses of the **IIIrd kind**, termed **microstresses**, formed as the result of non-homogeneity of metallic structure, **consisting of grains and grain blocks**.
- Microstresses are formed between separate components of the **microstructure** and act upon various microstructure elements which already are subjected to **different microstresses**. Their **chief source** is different **crystal orientation** and the associated **anisotropy(各向异性)** of elastic and plastic properties of the various crystals.
- **microstresses of the IIIrd kind**, termed **submicrostresses**. They are treated as stresses of the material's crystal lattice, especially in zones with defects.
- In such zones the proper structure is disrupted by the occurrence of own or foreign atoms in improper interstitial and nodal sites **缺陷** or the existence of **voids(空位)**.

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(3) Residual stresses

Generally, with a rise in the **strength of the mechanically strain-hardened material** and in the **strain-hardening parameters** (mainly, the loading force), **residual stresses in the superficial layer increase**.

Their value, depth of penetration and character of distribution may all **be controlled by** treatment operation parameters.

In almost all cases the **formation of compressive stresses in the superficial layer causes a rise of fatigue strength** (with tensile stresses the effect is opposite) and **hardness, wear resistance and corrosion resistance**.

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(3) Residual stresses

In all materials subjected to extraneous effects, there occur **non-uniform volume changes**, both reversible and irreversible, causing the formation of stresses.

Stresses describe the **state of internal forces and moments of forces**, brought about by the interaction, in a given locality, of two parts of the material, **situated on either side of an apparent crosssection**.

After the **removal of external effects**, reversible changes (elastic deformations) undergo atrophy. However, **some irreversible changes (plastic deformation) remain in the material, along with stresses caused by them which are referred to as residual stresses**

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(3) Residual stresses

Residual stresses are characterized by their sign ("-" compressive and "+" tensile), their value, distribution, gradient and depth of penetration.

In the superficial layer there exist three kinds of residual stresses; they are **manifest predominantly as macrostresses**.

Micro and submicrostresses affect the limit of elasticity of the material but have only a small influence on its strength.

Factors causing the formation of residual stresses:

- mechanical,
- thermal,
- structural

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(3) Residual stresses

The value and distribution affect **strength properties**, especially fatigue strength, resistance to dynamic loading and to brittle cracking, as well as tribological properties, especially contact fatigue.

A particularly significant effect of residual stresses on mechanical properties, especially **fatigue**, is revealed in the case of superficial layers **containing technological or structural flaws, surrounded by stress concentrations**.

Residual stresses may be caused by treatment operations or service (e.g. through friction). In the first case, **treatment or technological residual stresses** are formed, while in the latter, **service residual stresses**. Service conditions may cause the relaxation and redistribution of technological residual stresses.

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(3) Residual stresses

Type of the residual stress

According to the classification by N.N. Davidenkov

- stresses of the **Ist kind**, termed **macrostresses (body stresses)**, caused by the **mutual interaction of macroscopic-size zones of the material**. Macro stresses are caused directly by **non-uniform plastic deformation, temperature changes, changes in the material structure or a combination of the above**.

They may be regarded as the result of the total average interaction of micro stresses, assuming homogeneity of the material microstructure, i.e. **isotropic properties(各向同性)**.

These stresses cause changes of dimensions, deformation or cracking of the object or its superficial layer.

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(3) Residual stresses

In the absolute sense, a **given value of residual stresses** when all other parameters are equal **depends heavily on the method of measurement**. Numerical values of residual stresses, obtained by **different measurement methods**, may differ.

Residual stresses in a superficial layer **directly affect the layer's cohesion**, but their action may also be of an **indirect nature - by forcing the migration of atoms with small diameters** through the crystal lattice of the host material. **Less than 弱于 浓度和温度引起的 concentration and heat diffusion**.

However, local stresses may cause migrations of interstitial **空隙** atoms to sites **preferred by geometry or thermodynamics** (vacancy clusters, dislocation lines, grain boundaries and stacking faults).

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(4) Absorption

A **physico-chemical process of permeation** **渗入, 通过** of mass, consisting of the **taking up** of a constituent, usually a gas mixture called **absorbate**, by a liquid or a solid (called **absorbent**) and **uniform dissolution** of the former in the entire mass of the latter.

The effect of absorption is **widely used** in the chemical and related industries in order to **separate** a harmful or a valuable component out of a gas mixture or to combine the gas with an absorbent to **obtain a compound**, an **extraction(萃取) of a substance** dissolved in a liquid, etc.

In surface engineering, absorption of gases by solids is utilized chiefly in order to **saturate the superficial layer by the diffusing element**. The course of absorption is, in this case, dependent on the difference of **chemical potentials in solids and the surrounding environment**.

Absorption also plays an important role in tribology

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(5) Adsorption

is the process of **attraction** of substances (gases, vapors, solids in solution, ions and liquids) and their **collection at the surface** of solids and liquids, at the interface between solid and gas or liquid and gas.

Adsorption is manifest in **changes of concentration** of a substance in the boundary layer between two neighboring phases and depends both on the properties of the adsorbing body (**adsorbent** 吸附剂), as well as the adsorbed body (**adsorbate**).

Greater adsorption is exhibited by bodies with a **developed surface** (e.g., **rough and porous**) than by bodies with smooth surfaces.

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(5) Adsorption

Adsorption at the surface of **crystalline substances** usually **lowers their strength properties**.

Adsorption is **utilized** in processes of **machining**, by the introduction of adsorbable 能吸附的 components to lubricants and coolants;

in **service**, by using lubricants containing adsorbable components for machine lubrication in order to prevent dry friction;

ALSO, in **thermo-chemical processes** and in **plating metal substrates**

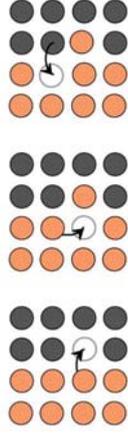
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(7) Diffusion

basic diffusion mechanisms (crystal) :

– **vacancy** - 指以空位为媒介而进行的扩散 occurring mainly in substitution-type solutions, when the displacement of atoms takes place by way of vacancies, i.e. point defects of the lattice, created by the absence of an atom in a lattice node.



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(5) Adsorption (type)

Physical adsorption (also termed: *molecular, surface, specific or physisorption*) consists of densification 凝聚作用 of a substance at the surface of the adsorbent under the influence of intermolecular forces of attraction, so-called **Vander Waals forces**.

Condensation adsorption (also called *capillary*) consists of such a high densification of gases and vapors of the adsorbent that after covering the surface with a monomolecular layer they undergo condensation to the liquid state. **This type of adsorption takes a somewhat longer time than the physical**, it is **partially reversible**. The desorption curve differs from that of adsorption (this is the so-called *adsorption hysteresis*).

Chemical adsorption (*chemisorption*) is also often called **activated adsorption** because it calls for a much higher activation energy than physical adsorption and is of the order of 20 to 80 kJ/mole.

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(6) Solubility 溶解度

The **ability** of a substance in the solid, liquid or gaseous state to **form**, together with other substances, **mixtures** which are **homogeneous** from a physical and chemical point of view.

At a given temperature and under a given pressure, **solubility depends on the state of aggregation of the dissolved substance and of the solvent**.

Physical solubility consists of the formation of interstitial 间隙式 solutions

Chemical solubility means the formation of a special type of chemical compounds.

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(7) Diffusion

Besides basic diffusion mechanisms, in specific conditions, especially in the case where a tendency exists to form intermetallic compounds or specific lattice defects (dislocations), **special mechanisms may occur**

– **reactive diffusion** - consisting of the formation, at phase boundaries in the matrix, as the result of reaction between the guest element and the matrix or precipitations and the formation of new phases with different lattice structures

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(5) Adsorption

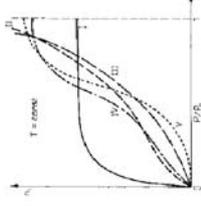
Types of adsorption isotherms of gases and vapors, according to Brunauer;

n_1 - total amount of adsorbed substance 1;

p - pressure; P_0 - pressure of saturated gas.

Type I - typical curve for chemical adsorption, less frequent for physical adsorption;

Types II to V - various curves for physical adsorption; **the most frequent is type II, least frequent - type V**



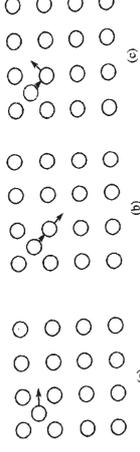
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(7) Diffusion

basic diffusion mechanisms (crystal) :

– **interstitial** - occurring mainly in **interstitial solutions**, when, by means of jumps, atoms smaller than those of the matrix move from one interstitial (interatomic) void to the next. Such voids occur always, even in lattices with closest packing and their size depends on the type of lattice.



Direct interstitial diffusion (a) small lattice deformation, Indirect interstitial diffusion (b), (c) large lattice deformation

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(7) Diffusion

– **dislocation diffusion** (diffusion through dislocations) - occurring in the case of **linear defects** in crystals, which constitute passages of easy diffusion at lower temperatures.

Diffusion is facilitated more by **edge-type** than by **screw-type** dislocations.

Dislocation diffusion plays a significant role in **thermo-mechanical burnishing** 抛光, 抛丸, 抛丸 where plastic deformations raise the density of dislocations. Heating causes them to atrophy 萎缩; 衰退 but aids diffusion (recrystallization, homogenization and recovery occur)

3.3 Potential properties of the superficial layer

3.3.3 Physico-chemical parameters (7) Diffusion

- **grain boundary diffusion** - occurring in **polycrystalline** materials, along surface defects such as **grain boundaries** diffusion along interfaces (surface diffusion)
- occurring with high intensity both across interfaces between the solid phase and gas or liquid, as well as inside multi-phase bodies

3.3 Potential properties of the superficial layer

3.3.3 Physico-chemical parameters (7) Diffusion

- **diffusion along interfaces (surface diffusion)** - occurring with high intensity both across interfaces between the solid phase and gas or liquid, as well as inside multi-phase bodies.

Boundaries between phases are structurally defective areas, thus they constitute **paths of easy diffusion**.

- Effects of diffusion along interphase boundaries **depend on surface tension** between the particular phases; when tension values are close there is a tendency to **form globular phase particles**; when a new phase with a lower surface tension than that of already existent phases is created, due to diffusion, there is a tendency to **penetrate the new phase** along interphase boundaries of the primary phases

3.3 Potential properties of the superficial layer

3.3.3 Physico-chemical parameters (9) Catalysis

The condition for a catalytic reaction of particles at the metal surface is their prior chemisorption.

Metals according to their tendency to chemisorption

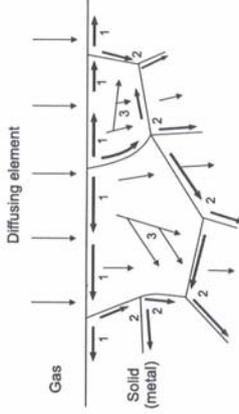
Metals	N ₂	CO ₂	H ₂	CO	C ₂ H ₄	O ₂
Ti, Zr, Hf, V, Nb, Ta, Cr, Mo, W, Fe, Ru, Os, Ni, Co	+	+	+	+	+	+
Rh, Pd, Pt, Ir, Au			+	+	+	+
Al, Cu						+
Li, Na, K						+
Mg, Ag, Zn, Cd, In, Sn, Pb, Bi, Ph, Sb, Bi						+

3.4 Practically usable properties of the superficial layer

- 3.4.2 Tribological properties
- The relation of friction and wear to the superficial layer
 - The **optimized roughness**
- (1) **Roughness**
- (2) **Hardness significantly affects**. Particularly good tribological wear resistance is exhibited by superficial layers obtained by heat and thermo-chemical treatment.
- (3) Residual stresses in the superficial layer affect tribological properties only **slightly**. Usually **compressive stresses increase resistance to abrasive wear**.



3.3 Potential properties of the superficial layer 3.3.3 Physico-chemical parameters (7) Diffusion



1 - easiest diffusion - along surface;
2 - more difficult diffusion - along grain boundaries;
3 - most difficult diffusion - across grains (inside grains)

3.4 Practically usable properties of the superficial layer

3.4.2 Tribological properties

Types of friction

From the point of view of the presence of a lubricant between rubbing surfaces, the following types of kinetic friction may be distinguished

- physically dry friction** - when no other bodies (solid, liquid or gaseous) are present between the rubbing surfaces while the rubbing surfaces themselves are not coated by any adsorbed chemical compounds; in practice, this type of friction occurs extremely seldom in vacuum;
- technically dry friction** - when the rubbing surfaces may be coated with oxides and layers of adsorbed gases or vapors;
- boundary friction** - when the rubbing surfaces of both bodies are separated in the contact zone by the so-called boundary layer, formed by components of the lubricating substance (lubricant)
- fluid friction** - when between the surfaces of rubbing bodies there is a continuous, unbroken layer of liquid or gaseous substance, under pressure which balances out forces of normal load pressure from both bodies to such an extent that surface asperities do not come into mutual contact.
- mixed friction** - which is an intermediate case between dry and fluid friction.

3.5 Structure and type of the coating

The cover of animals' bodies no general terminological specification defining

3.5.1 Definition of coating

- Coating - a layer of material, formed naturally or synthetically or deposited artificially on the surface of a object made of another material, with the aim of obtaining required technical or decorative properties.

Superficial layer < > coating

3.4 Practically usable properties of the superficial layer

3.4.1 Strength properties---material fatigue

Effect of properties of superficial layer on fatigue strength

- the **increase of the hardness**, significantly improve fatigue properties;
- the highest improvement of fatigue strength may be achieved through **an increase in surface smoothness, and the decrease in surface roughness and flaws**

- a lesser degree of improvement of fatigue strength, 40 to 45% on average, is achieved by **changes in the chemical composition** of the superficial layer (diffusion alloying with carbon, nitrogen, chromium boron, etc. or their combinations)

Residual stresses have a **significant effect** on fatigue strength. These stresses *superimpose* themselves (i.e., add algebraically) on those stemming from external loading and **cause either a rise or a drop of the fatigue limit of an object**, depending on whether the net result will be an increase or decrease of the sum total of stresses at concentration sites

Corrosive environments such as moist air, tap water, sea water, and 32 electrolyte solutions all **lower fatigue strength**.

3.4 Practically usable properties of the superficial layer

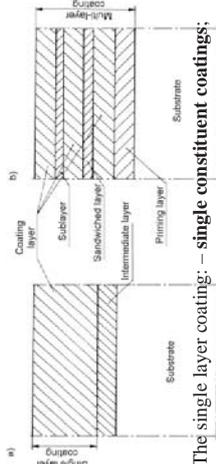
3.4.3 Anti-corrosion properties

The relation of anti-corrosion property to the superficial layer

- (1) The **chemical composition** of the superficial layer has a decisive influence on the extent of corrosion.
- (2) **Surface roughness** significantly affects corrosion resistance. The lower the roughness, the higher the resistance.
- (3) The **structure of the superficial layer** also affects the extent of corrosion
- (4) **Deformation** disturbs the crystalline structure, favor the susceptibility of alloys to corrosion.
- (5) Compressive **residual stresses** do not exhibit a detrimental effect and even slightly improve corrosion resistance of metal alloys. Tensile residual stresses cause a deterioration of corrosion resistance

3.5 Structure and type of the coating

3.5.2 Structure of the coating



The single layer coating: – single constituent coatings;
– multi-component coatings

The multi-layer coating: – multiple coating;
– sandwich coating;
– self-stratifying paint

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3.5 Structure and type of the coating

3.5.3 Types of coatings

Division of coatings by material

1) Metallic coatings

2) Non-metallic coatings

Paints

Varnishes 清漆

Resins

Oils

Cements

Waxes

Lubricants

Metal ceramics

Ceramic materials

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Compounds of substrate metals
Synthetics (plastomers, plastic mixes)
Indiarubbers (latexes)

Rubbers are products of vulcanization 橡胶硫化

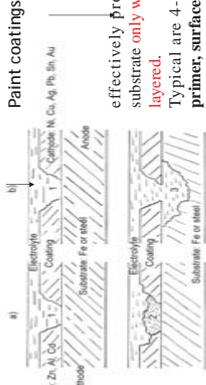
3.5 Structure and type of the coating

3.5.3 Types of coatings

Classification of coatings by application

1) Protective coatings

Anodic coatings and Cathodic coatings



effectively protect the metal substrate **only when they are multi-layered.**

Typical are 4-layered coating: **primer, surfacer, enamel, varnish.**

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3.5 Structure and type of the coating

3.5.3 Types of coatings

Classification of coatings by application

2) Decorative coatings

Decorative coatings, once called ornamental, serve predominantly to give the metal or non-metal object an aesthetic external appearance.

This depends first of all on **color, luster and resistance to tarnishing** 变色.

It is evident that decorative coatings, in many cases, make good protective coatings.

Decorative coatings may be both metallic and non-metallic.

electroplated coatings

paints

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3.5 Structure and type of the coating

3.5.3 Types of coatings

Classification of coatings by application

3) Protective-decorative coatings

Regarding **electrolytic coatings**, the protective-decorative role is fulfilled by nickel, chrome, and copper-nickel-chrome coatings on condition that they are sufficiently thick. It is accepted that their thickness should not be less than 25 µm.

The overwhelming majority of **non-metallic coatings** functions as both protective and decorative, **particularly those of plastic, enamel and paint**

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3.5 Structure and type of the coating

3.5.3 Types of coatings

Classification of coatings by application

4) Technical coatings

Coatings which enhance tribological properties

In the majority of cases, **better tribological properties are exhibited by harder than by softer metal coatings.**

Most frequently, as resistance coatings wear, hard chrome-plated layers of 10 to 30 µm thickness are used. For high sliding velocities and high unit loads, electroplated silver or indium coatings of 500 to 1500 µm, as well as porous chrome coatings, are used.

Among **non-metallic coatings**, very high hardness and excellent tribological properties are exhibited by **nitride, oxide, carbide and boride coatings**, deposited in vacuum by PVD and CVD techniques.

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3.5 Structure and type of the coating

3.5.3 Types of coatings

Classification of coatings by application

4) Technical coatings

Coatings which enhance electrical properties.

These coatings serve first and foremost to enhance electrical conductivity of terminals and are used in electrical and electronics applications.

Since very good electrical conductivity is exhibited by silver, very often silver coatings are deposited on copper, brass and bronze substrates

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3.5 Structure and type of the coating

3.5.3 Types of coatings

Classification of coatings by application

4) Technical coatings

Coatings enhancing solderability of joined surfaces

These are tin and copper coatings, as well as alloys: zinc or zinc-lead, less often cadmium and twin-layered cadmium-tin and copper-tin, deposited on brass and steel components.

Copper coatings of 2.5 to 7 µm, often protected by a layer of varnish against tarnishing, are applied to components immediately before soldering.

The thickness of tin coatings, which insignificantly oxidize and for that reason require the use of fluxes 助焊剂, is 5 to 15 µm.

Alloy coatings composed of **70% tin and 30% zinc** are well suited for soldering and for service in tropical climates.

The best proportion of **tin to lead** in tin-lead coatings is 40/60

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3.5 Structure and type of the coating

3.5.3 Types of coatings

Classification of coatings by application

4) Technical coatings

Coatings protecting against diffusion, particularly of carbon, nitrogen, and other elements in thermochemical treatment operations, are applied as electroplated or in the form of pastes.

They fulfill the role of a blockade 阻挡, stopping the passage of a given element to a given (coated) fragment of the component which is subjected to thermo-chemical treatment.

Electroplated coatings are usually copper or tin, as well as alloys of copper and tin with a thickness of up to 25 µm.

Paste coatings with varied chemical composition may reach thicknesses of over 1 mm

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3.5 Structure and type of the coating

- 3.5.3 Types of coatings
 - Classification of coatings by application
 - 4) Technical coatings
 - Catalytic coatings.
 - These coatings serve to **change the rate of reaction** in the gaseous environment with which it is in contact, as well as to raise or lower the temperature at which the reactions occur.
 - Since a **large area of contact** between the coating and the surrounding gas is required, the real surface should be developed as much as possible.
 - The coating material may be **metallic, metal ceramic and ceramic**

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3.5 Structure and type of the coating

- 3.5.3 Types of coatings
 - Classification of coatings by application
 - 4) Technical coatings
 - Coatings enhancing selected thermophysical properties
- Most often, these coatings are applied in order to enhance resistance to the effect of elevated temperatures, as well as **emissivity and thermal conductivity properties, themselves dependent on temperature**
- Coatings which enhance emissivity may be monolayer, but those which retard or enhance thermal conductivity, as well as heat-resistant coatings, are all multi-layered, most often comprising three layers, in order to **improve adhesion to the substrate and thus to prevent cracking of the external layer** due to excessive residual stresses which rise with a change in temperature.
- Metal ceramic and ceramic coatings are characterized by high emissivity, within the range of 0.6 to 0.95.

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3.5 Structure and type of the coating

- 3.5.3 Types of coatings
 - Classification of coatings by application
 - 4) Technical coatings
 - Ablation(烧蚀) coatings

These constitute one type of coating with special thermophysical properties.

They are most often produced by thermal spraying of ceramic refractory 粉末的绝缘的 materials (the main constituents of which are Al_2O_3 and ZrO_2 , as well as silicides $ZrSiO_4$ and $MoSiO_4$) onto metallic or non-metallic surfaces with good thermal insulation, in order to protect them against the effect of elevated temperatures at which the surface may melt.

Carbon ablation materials

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3.5 Structure and type of the coating

- 3.5.3 Types of coatings
 - Classification of coatings by application

- 4) Technical coatings
 - Ablation(烧蚀) coatings

Under the influence of heat they undergo ablation, thereby protecting the substrate material.

Such coatings are deposited on **gas turbine blades, components of high temperature equipment and, primarily, on short and long range ballistic rocket heads, as well as on external surfaces of space vehicles**. In the latter case, they enable the vehicle to overcome the **heat barrier** during re-entry into the dense layers of the earth's atmosphere.

As an example, at a speed of 6000 km per hour, at an altitude of several kilometers, the temperature of the vehicle surface, due to friction from atmosphere particles, reaches approximately 1600 K.

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3.5 Structure and type of the coating

- 3.5.3 Types of coatings

- Classification of coatings by application

- 4) Technical coatings
 - Optical coatings

These coatings may have different tasks.

Steel and brass elements are coated with electroplated silver, chrome and rhodium, nickel-chrome and copper-nickel-chrome layers to **enhance surface luster**.

Thin multi-layered **anti-reflection** coatings are applied by PVD techniques to surfaces of glass and plastics. These coatings may absorb or reflect selected bands of thermal radiation, especially in the visible range; they may transmit radiation in one direction and they may counteract(抵消) the accumulation of dust, gases, vapours, etc

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